UNITED STATES DEPARTMENT OF THE INTERIOR
Harold L. Ickes, Secretary
GEOLOGICAL SURVEY
W. E. Wrather, Director

Bulletin 928-C

ADSORBENT CLAYS
THEIR DISTRIBUTION, PROPERTIES PRODUCTION, AND USES

BY

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Contributions to economic geology, 1941-42
(Pages 127-221)

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1943

For sale by the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C.
Price 20 cents

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ADSORBENT CLAYS, THEIR DISTRIBUTION, PROPERTIES PRODUCTION, AND USES

By P. G. Nutting

ABSTRACT

Scope of the report.—This bulletin is a summary of present knowledge of the adsorbent or bleaching clays—their distribution, field and laboratory identification, physical and chemical properties, uses, quality, and value. Problems in the drying, treating with acids, and washing are discussed, and methods of testing and rating decolorizing efficiency are described. These include groups of tests for finding the best commercial treatment for any given clay. The methods outlined and conclusions drawn are based on several thousand laboratory tests made in the Geological Survey by the writer.

Character and distribution of the clays.—Adsorbent clays of various types are abundant in the southern half of the United States. They also occur in scattered localities in the northern half of the United States and in Canada, Mexico, Europe, Asia, and Africa. They range in geologic age from Ordovician to Pliocene.

Physical properties.—The color, texture, density, opacity, refractive index, and the slaking and swelling properties of adsorbent clays all have a bearing on their utility. Refractive indices vary with water content and with the removal of bases by acid. Interplanar distances vary stepwise with moisture variation. Water is associated with adsorbent clays in at least four different ways, which are evaluated by vapor pressure and thermal tests. Clays decolorize oils by the selective adsorption of the darker, more basic and less saturated constituents.

Chemical properties.—In composition the adsorbent clays have a silica-alumina ratio ranging from 1:2 to 1:8, but the chemical composition bears no apparent relation to activity or activability. Base-exchange properties are pronounced. All bases are soluble in strong acids, leaving isotropic silica. Activable bentonites attain maximum bleaching efficiency on removal of about half their bases by leaching in strong acid. In dilute acid the various types of adsorbent clays lose bases in ways characteristic of the type. Time of storage affects the bleaching efficiency of some clays.

Uses.—The principal use of adsorbent clays is in decolorizing oils. Special uses are in insecticides and fungicides, fertilizers, water softeners, adsorbent carbon, ceramic materials, drilling muds, molding sands, cements, and as catalysts in cracking and reforming oil products.

INTRODUCTION

PURPOSE OF THE REPORT

The purpose of this report is to assemble and interpret all available information relating to the occurrence, properties, and uses of that class of clays possessing selectively adsorbent properties, which are known also as active or bleaching clays and as decolorizing earths. Because of the intricate and little understood nature of selective adsorption by clays, sections on the physical and chemical properties of adsorptive clays are included to serve as a basis for further study and research. Useful methods of testing and research are given prominence. An adequate explanation of the diverse properties of clays of the montmorillonite and related groups will require much further study.

PRODUCTION OF ADSORBENT CLAYS

Although ordinary clays and soils are among the commonest materials at the surface of the earth, the bleaching clays occur only in limited amounts in a few geographic areas and a few geologic formations. However, the workable deposits of high grade are known to be ample for all prospective needs. This country is not only far the largest producer but is also the largest consumer of both natural and activated adsorbent clays. At least 90 percent of the adsorbent clay is used for decolorizing and stabilizing petroleum lubricants. The remaining 10 percent is used chiefly in the fat and vegetable-oil industries. During the decade 1930-40 the annual production of naturally active clay, or fuller's earth, has ranged from 220,000 to 336,000 tons, or roughly from 100 to 150 acre-feet. Its value has ranged from about $2,000,000 to $4,000,000 or more. The annual production of activated bleaching clay has been 30,000 to 80,000 tons, valued at $2,000,000 to $4,000,000. The bleaching-clay market is as closely allied with the production of petroleum as the petroleum market is with the internal-combustion motor.

EARLY USES

The use of certain clays in removing oil and grease from wool and textiles was known to the ancients. Bentonitic "soap" clays have been used by the Chinese for thousands of years. The use of fine adsorbent clays for purifying oils, fats, and waxes in essentially the modern manner called "contacting" was described in 1868 by Fordred in British patent 2,356. The fine clay was mixed with the hot oil or fused wax for a time and then strained out with the adsorbed darker and less stable constituents of the oil adhering to it.

The discovery of the activation of bentonitic clays by partial leaching in acid is obscure. It may well be as old as chemistry. Ullman[1] states that Smith and Field of London as early as 1873 activated clays for decolorizing purposes. Porter[2] in 1906 described and discussed the decolorizing earths then known, gave chemical and mineralogical compositions, and attempted an interpretation of the known effects of alkali and acid treatments on decolorizing power. Activation by such treatment was a well-known art at least as early as 1915 (Walsh, United States patent 1,132,050). The use of both active and activated clays has steadily expanded with the expanding petroleum and automobile industries.

English fuller's earth has been used on lard, and Florida clay on oils since about 1890. Early in the twentieth century active clay near Macon, Ga., was used in refining cottonseed oil. About 1921 the plants at Quincy, Fla., and Attapulgus, Ga., were developed to a capacity of 10,000 tons per month each, and since that time have supplied most of the market with granulated naturally active clay. Lesser workings are at Ocala, Fla., Creede, Colo., and Olmsted, Ill. Since about 1920 the Standard Oil Co. of California has been activating the bentonite that occurs near Otay, Calif., for its own use, and the Filtrol Co. of Los Angeles has developed the bentonite deposits near Chambers, Ariz., for the open market. In 1936 the Filtrol Co., which was later affiliated with the Attapulgus Clay Co., opened a new plant at Jackson, Miss., for activating the local high-grade bentonite that forms a bed in the Vicksburg group.

NATURALLY ACTIVE VERSUS ACTIVATED CLAYS

The market is about equally divided between the naturally active and activated clays. The naturally adsorbent clays, which are far less expensive ($10 to $20 per ton), give less trouble to use (by percolation, granulated), may be reburned and reused many times, and leave the refined oil stable. The activated clays are incoherent and must be used in powdered form (contact process). They are necessarily much more expensive ($50 to $90 per ton), but they are about four times as powerful as the natural clays. They are not reused. The added cost is due to the acid treatment, not to the raw material. As the major part of the cost of the naturally adsorbent clay is transportation, the nearness of supplies to the refineries is important.

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[1] Ullman, F., Encyclopedia Tech. Chemistry, vol. 5, p. 375, 1914.

[2] Porter, J. T., Properties and tests of fuller's earth: U. S. Geol. Survey Bull. 315, pp. 268–290, 1906.

RECENT ADVANCES IN THE STUDY OF ADSORBENT CLAYS

Twenty years ago the adsorbent clays had been very little studied. Little was known of their nature, or of their action on oils, or of the location and extent of deposits. Promoters of inferior clay deposits, of alleged superior processes of activation, and of synthetic material flourished, owing to the lack of accurate information, and of standards and precise test methods of determining quality. Oil refiners and other prospective customers simply found the amount of a given clay necessary to give the required color to the oil they were refining. Poorer and more distant deposits were being worked when better and nearer ones, though then unknown, were available. In a word, the lusty young industry was in need of rationalization.

The first task was to develop standards (of clay and test oils) and precise methods of testing. Another was to find the precise nature of the bleaching action and thus provide a secure foundation for all other work. Another was to study, classify, and rate all materials possessing bleaching properties, listing those of high value, or of exceptional interest. The study of activation processes involved a wide range of physical and chemical experimentation to find the optimum procedure and to find its limitations. To place the geographic and geologic distribution of adsorbent clays on a firm footing has required the careful testing of thousands of samples from all over the world and careful correlation of results. Although many points may remain obscure, it is felt that most of the more significant problems have been cleared up and that the time is ripe for summarizing for public use the results of the writer's 12 years of work at the Geological Survey.

Several preliminary reports on bleaching clays have been published. Circular 3 of the Geological Survey, 1933 (51 pp., mimeographed). is the most comprehensive. A paper published in the American Association of Petroleum Geologists Bulletin, July 1935, is the best recent summary. It contains references to six earlier papers published in Economic Geology and the Oil and Gas Journal.

From March 1934 to May 1935 an allotment from Public Works Administration funds was available for field work on clays in the Southeastern States and in Texas under the general supervision of G. R. Mansfield. Field parties were under the direction of Harry X. Bay, Philip B. King, M. N. Bramlette, and Arthur C. Munyan, who submitted several thousand samples for testing and rating by the writer and his assistant, L. C. Drake. The outstanding result of this work was the discovery of extensive and very valuable beds of highly activable bentonite in northwest Florida. Close coordination between field and laboratory was vital. Although bentonites may be recognized in the field with some certainty and microscopic study is helpful, it is quite impossible to distinguish between those of high- and low-bleaching power without such laboratory leach and bleach tests as have been developed at the Survey. Geologic reports were made by the leaders of the various field parties to the States concerned. Test results, with an outline sketch of geographic and geologic distribution, are summarized in the following pages.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my deep indebtedness to my colleagues at the Survey, in particular to C. S. Ross, petrologist and specialist in clay minerals, and to Roger C. Wells, chief chemist, for helpful advice and discussion. Geologists L. W. Stephenson, C. W. Cooke, Philip King, E. B. Eckel, and W. H. Monroe, have given valuable advice on the geologic ages of deposits. I am also indebted to all the major clay producers for numerous samples and for permission to visit their plants and mines. Most of all I am indebted to the producers and users, who in great numbers have submitted samples and freely discussed their clays and clay problems with me. Samples from all but one of the 80 deposits listed on pages 140 and 141 have come from parties outside the Survey. This bulletin is the result of an attempt to assemble such information as was shown by conversation and correspondence to be of most interest to all who are studying, locating, and producing bleaching clays.

MISCELLANEOUS ACTIVABLE MATERIALS

A great many materials other than fuller's earths and bentonites will bleach oil if properly prepared but are of little commercial interest because of their low bleaching power, their limited occurrence, or the expense or difficulty of their preparation. They are worth a brief description, however, for the light they throw on the bleaching action.

Ordinary field soil possesses some bleaching action owing to selective adsorption, which may possibly be related to the preparation, storage, and release of plant food. Many quartz oil sands, such as the Tensleep of Wyoming, and tar sands, such as the Alberta, have activated surfaces and are coated naturally with an adsorbed layer, which will not wash off in solvents but may be removed by chromic acid. Modern river silts, ceramic clays, and sea sand have little or no bleaching power. Some soils derived from diabase rank as fairly good bleaching agents. A residual decomposition product from a granite area in Washington, D. C., may be activated to a bleaching power more than half that of a commercial bentonite. The maximum solubility of the bases of this clay in hydrochloric acid was 49 percent.

Some gouge clays and some clays derived from pegmatites test very much like the best bentonites. A gouge clay from Twin Falls, Idaho, and a pink pegmatite clay from southern California, though neither is derived from volcanic ash, behaved like bentonites toward acid and oil, and even their thermal dehydration curves bear a striking resemblance to those characteristic of all bentonites.

Certain olivines and blast-furnace slags are readily attacked by acid and may be made into fairly good bleaching material if the leaching is carried to the proper point. This is difficult, however, on account of the strong tendency to form gelatinous silica, which gives a slimy unworkable mass. Olivine and serpentine rocks that have undergone certain types of weathering are less difficult to leach and give high bleaching power, but these materials when of uniform composition occur in such limited quantities that they are of little practical interest. The hydrous alumino-silicates are in general far more tractable than other silicates. Silica gel is only a poor adsorbing agent in either the synthetic form or in that resulting from overleaching bentonites. Hydrous alumina may have either a high adsorbing power or none at all, depending on details of preparation and of age (crystallization?). The water-softening zeolites, either artificial or natural, are poor bleaching agents at best. Halloysite, bauxite, nontronite, and many similar minerals will activate to a limited extent but are of no practical interest.

Tests on several deeply buried (500–8,000 feet) ash falls from southern oil fields show only slight alteration toward bentonite on grain surfaces. These materials are in a class by themselves as they have fairly well defined leaching and adsorbing characteristics intermediate between those of a fresh ash and a bentonite composed of completely altered ash and yet are different in character from both and from the well-known swelling Wyoming type. One very interesting ash from Colorado was found to be sufficiently converted to a bentonitic clay to be activable, although it retained the gritty feel and thermal dehydration curve of an unaltered ash.

Also in a distinct class are the Ordovician bentonites. These are all characterized by a potash content of about 5 percent and are mineralogically distinct from other normal types of bentonite. The potash is chiefly in the form of either feldspar or biotite. These bentonites are usually very hard and dense, but they slake in water and leach in acid like those of later geologic periods. Though they are widely distributed, their usual occurrence in layers only 2 to 3 feet thick, interbedded with solid limestone, makes their mining expensive. Beds at High Bridge, Ky., in the Avondale quarry near Chattanooga, Tenn., and in Walker County in northwestern Georgia are well-known bentonites of Ordovician age.

Considerable interest has been aroused in glauconite (greensand) as a source of bleaching material on account of its abundance and easy accessibility. Glauconite occurs in beds 5 to 40 feet thick near the surface from New Jersey to Maryland, in Texas, Missouri, Australia, and many other localities. It contains chiefly sand and clay as impurities, most of which are easily separated by screening and washing. Glauconite is readily attacked by acid, the maximum removable soluble material being about 37 percent of its weight. Maximum adsorbing power is attained by removing about 25 percent of soluble material. The addition of salt to the leaching acid appears to give better control over the leaching, as the grains vary considerably in the solubility of their bases. Simply dried and ground, glauconite effectively bleaches cottonseed oil.

Some impure bauxite occurring in Georgia, Alabama, and Arkansas, although inactive and not activable by acid, may be activated to the adsorbing power of fuller's earth by roasting to a temperature of 1,000 to 1,600° F., which would destroy the activity of other active clay. Although more expensive to prepare, this heat-treated bauxite stands reburning for reuse better than fuller's earth.[3]

SYNTHETIC MATERIALS AND SPECIAL TREATMENTS

Many amorphous mixtures called silicates may be prepared by adding sodium-silicate solutions to solutions of different salts or acids. The dilution should be such that the gel solidifies only after at least 5 minutes. The gel is dried, ground, and thoroughly washed in pure or slightly acid water. The bleaching power of these synthetic materials ranges from that of ordinary silica gel up to that of a gel precipitated with chromic-acid solution, which is about equal to a fuller's earth. Aside from their low bleaching power, the cost of preparing such synthetic materials appears to be too great for them to be of commercial interest.

Special treatments for clays, designed to modify the ionic concentrations on their grain surfaces, have been investigated. Such treatments as excessive leaching in pure water, electrodialysis, heating in acid-salt solutions, spraying the dry clay with acid, base exchange before acid-leaching, and bacterial cultures all produce interesting changes in clays. Some of these enhance the bleaching power, but none sufficiently to justify the additional expense from a practical viewpoint. These studies, however, are a fruitful field of scientific investigation, particularly in relation to soils and plant food.

NATURE OF THE ADSORBENT CLAY

All the adsorbent clay of industrial importance is composed chiefly of minerals of the montmorillonite group, namely, montmorillonite, beidellite or saponite. These are hydrous magnesium aluminosilicates. Such clay differs from clay of the kaolin type, which is dominantly kaolinite ($Al_2O_3.2SiO_2.2H_2O$), in containing a higher proportion

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[3] Hubbell, R. H., and Ferguson, R. P., Refiner and National Gasoline Manufacturer, March 1938.

of silica ($Al_2O_3 : SiO_2 = 1:2$ up to $1:5$), a divalent base such as calcium or magnesium, and a lattice structure that swells in the *c* direction with each addition of $6H_2O$.

Chemical composition alone is not sufficient to identify montmorillonite or adsorbent clay. Not only is the composition variable, owing to a rather ready substitution of one base for another, but other minerals have alumina-silica ratios within the range of the montmorillonite group (e.g., pyrophyllite, $Al_2O_3 : 4SiO_2 : H_2O$). Pyrophyllite and kaolinite are characterized by their stability, resistance to acids, and nonhygroscopic nature. Differing from montmorillonite and kaolin is halloysite ($Al_2O_3 : 2SiO_2 : 4H_2O$), which forms one hydrate and is moderately activable by removal of part of its alumina with acid.

The mineralogical characteristics of montmorillonite clay are difficult to establish, because individual crystals are too small to be identified with certainty with a petrographic microscope and because of the wide variation of refractive indices with the ferric-iron content and with the amount of water in the specimen. The lattice dimensions, as shown by X-ray diffraction spectra, are of little service for identification, as the *a* and *b* dimensions in the lattice plane are the same for montmorillonite and several other clay minerals while the *c* dimension varies with the moisture content and with the presence of slight impurities in the clay. The structure and physical properties of adsorbent clay are discussed later.

The moisture content of adsorbent clay at different temperatures and in atmospheres of different humidities appears sufficient to identify it as such almost as well as an oil-bleaching test, except that the moisture test does not exclude the inactive and almost inactivable swelling bentonites. A number of weight-temperature and vapor pressure curves are given and discussed later. In brief, the thermal dehydration curve of montmorillonite clay shows a decided slope in the temperature range from 150° to 450° C., which is identified with adsorbed H_2O or H and OH ions, followed by a more abrupt drop in the range 450° to 650° C., which is identified as structural H and OH within each lattice sheet. The normal $1H_2O$ structural water amounts to about 5 percent and is shown at about 400° C. for most montmorillonite clay. Removal of the adsorbed water permits the selective adsorption of the darker constituents of an oil that is bleaching, but removal of the intralattice water by heating above 600° C. destroys the crystal itself. Likewise the removal of all soluble bases by long leaching in hot acid destroys the crystal lattice, leaving only isotropic silica gel, highly adsorptive for water but of low adsorbing power for oils.

SUBCLASSES OF MONTMORILLONITE CLAYS

The commercial value and industrial use of adsorbent clay depend on its properties and behavior toward water, acids, oils, and other substances. The behavior varies widely, so that it is necessary to subdivide the group into at least five classes adapted to different uses and processes. Little is yet known of the underlying causes of these differences in behavior, but such classes are clearly recognized by industry. These subclasses are as follows:

I. Inactive and nearly inactivable montmorillonite clay of the bentonite type. Some of these, occurring abundantly in the region north and west of the Black Hills, swell greatly and gel freely in water and are valued for drilling muds, for waterproofing earthen dams and reservoirs, as carriers of insecticides, and as additions to molding sands.

II. Inactive but highly activable clays, chiefly very pure bentonite such as occurs in the Vicksburg group of Oligocene age in central Mississippi and in the Oligocene of northeastern Arizona. The highest-grade activated clay is prepared from clay of this class.

III. Active and highly activable clays. These occur in extensive deposits in northwest Florida; Brooks County, Ga.; Jasper County, Tex.; and Morden, Manitoba. English fuller's earth is in this class. It and the Texas clays have been extensively used as naturally active clays, but none have yet been activated commercially.

IV. Active clays little affected in activity by acid treatment. The well-known Porters Creek clay, which is mined at Olmstead, Ill., and extends in a thick belt southward to Alabama, is typical of this class. Its thermal dehydration curve suggests that it may be an altered and reworked bentonite mixed with silt.

V. Active clays whose activity is lowered by acid leaching. The well-known fuller's earth of northern and central Florida is a typical example. Its origin is uncertain, but material having similar properties may be produced from bentonite by long treatment with dilute acid, and many deposits grade off into activable clay of type II at the bottom or to one side.

Material belonging to classes III, IV, and V is called fuller's earth; it may be used after no other treatment than drying and grinding. These clays commonly dry into hard masses, are readily granulated, and do not disintegrate in water. The swelling property of some class I bentonites is probably due to saturation with sodium, because other clays and soils may be given the same swelling property by soaking in soda solution. The Ordovician bentonite, high in insoluble potash, belongs to class III. The composition of the clay from Marianna of class III corresponds closely to beidellite, but by no means do all clays of that class have that composition.

The characteristic properties of clays of classes I, IV, and V are very persistent, but those of classes II and III change rapidly on room drying. The swelling bentonite is extremely resistant to weathering, stream washings and redepositions, retaining its original swelling property and apparently never altering to another class. Clays of classes II and III lose as much as 30 percent of their activity on merely air-drying for a month and must be tested within a few hours of the first drying. They may be kept almost unaltered in a water-saturated atmosphere. Such clays also age rapidly after treatment, but age least in cool dry air. Class IV and V clays on the other hand age little if any and are therefore useful reference standards.

NATURE OF THE ADSORBING ACTION

The decolorizing action of adsorbent clays on oils is not a filtering or straining action but a selective adsorption, such as occurs in dyeing fabrics. The dye leaves the solution and adheres to the textile fibers and will not wash off. In a similar manner the darker constituents of oil are preferentially adsorbed on active clay, leaving behind the colorless constituents. The adsorbed coating, except the loosely held outer portion, cannot be washed off by even the most powerful solvents.

Many oil and tar sands of pure quartz are known in which the grains are naturally covered with a black tarry coating, the inner portion of which is removable only by combustion. Coatings on some sands of this kind, such as the Tensleep of Wyoming, were found by the writer to be 0.75 micron (0.00003 inch) thick. The removal of this coating by chromic acid showed the underlying quartz surfaces to be etched like ground glass. Soaking these clean grains in the original crude oil over night restored a coating 0.69 micron thick, not removable by washing with naphtha. Here there is no straining action, for there are almost no pores.

It was found by the writer [4] that pieces of quartz crystal, sea sand, and other minerals could be activated (made selectively adsorbing) by abrasion, fine grinding, or by etching with alkali or hydrofluoric acid so as to leave open bonds on removal of adsorbed H and OH by heating. When bentonites are activated by partial acid leaching, the removal of some of the cations from lattice faces must leave similar open bonds having like adsorbing properties, but with a far greater specific surface than is feasible with etched quartz grains. Clay grains in which the less accessible cations are left beneath the surface adsorb much more powerfully than those from which all cations have been removed, leaving pure silica. In active but not further activable fuller's earths, effective cations seem to have been replaced by hydrogen, so that further acid treatment does not increase their number. The adsorbing powers of fuller's earth, completely acid-leached bentonite (silica), synthetic silica gel, and of water-softening zeolites are all nearly the same.

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[4] Nutting, P. G., Chemical activation of quartz surfaces, Science, new ser., vol. 72, p. 243, Sept. 5, 1930.

GENERAL OCCURRENCE AND CHARACTER OF DEPOSITS

Both the naturally active and the activable types of clays are found widely distributed over the earth and through an extensive range of geologic formations. Europe is represented by worked deposits in England, Bavaria, Rumania, Sicily, the Faeroe Islands, Poland, and Russia. In Asia, deposits in India, China, and Japan are well known.

In North America, adsorbent clay is found from Mexico to northern Alberta and from South Carolina to Utah and California. Extensive beds of such clay occur at many places in the southern half of the United States, and some are known in the Black Hills and in North Dakota. The well-known deposits of bentonite in Wyoming and Montana, however, do not consist of active or activable clay.

Apparently all the significant deposits of adsorbent clay were formed from volcanic ash deposited either directly in water or transported and redeposited. The thickness of the deposits, in places as much as 60 feet, is greater than is reasonable to expect from any single ash fall far from the source. The occurrence of others in scattered thick, lenticular beds suggests deposition in lakes. The bottoms of several thick beds are highly bentonitic, whereas the upper parts are fuller's earth.

In the West and Southwest many adsorbent clay deposits occur in what are probably ancient lake basins. Some are of small extent but thick, such as the deposit at Westcliffe, Colo., which is 30 feet thick; others are extensive but thin, such as that northeast of Chambers, Ariz., which is about 30 inches thick but covers several thousand square miles.

In the Southeast, bleaching clay deposits occur in the Coastal Plain in a belt that extends along the edge of the Piedmont Plateau through Columbia, Macon, and Montgomery. This belt is known to have been covered by the ocean. Just east of Macon, Ga., the extensive 20-foot bed of active clay in the Twiggs clay member of the Barnwell formation of Eocene age, worked by the General Reduction Co. of Macon, is underlain by a thick bed of sand, and this is underlain by another bed of active clay that rests on the Ocala limestone. The bottom of the lower bed, 100 feet down, is an excellent activable clay, only slightly inferior to the best known. The base of the upper clay bed is also decidedly activable.

The extensive 12- to 15-foot beds of white active clay mined in Decatur County, in the southwest corner of Georgia, by the Attapulgus Clay Co. and in the adjacent Gadsden County, Fla., by the Floridin Co., appear to be parts of the Hawthorn formation of Miocene age, which is much younger than the Barnwell. The long series of beds of active and highly activable class III clay in northwest Florida, extending west from Marianna, includes both Hawthorn and other deposits.

In the Mississippi embayment, which extends from the Gulf to southern Illinois, activable bentonitic clays of several ages occur. The oldest is in a series of small isolated irregular beds of Upper Cretaceous age. One bed in the Coffee sand in northeastern Mississippi, 5 miles southeast of Booneville, has been worked for some years. Similar small deposits were found by H. X. Bay and A. C. Munyan in deposits of Upper Cretaceous age at different points between Booneville, Miss., and Montgomery, Ala.

A single but rather large deposit of fairly high-grade activable bentonitic clay was found in the base of the Prairie Bluff chalk of Upper Cretaceous age 4 miles northeast of Pontotoc, Miss., in 1935 by Tennessee Valley Authority geologists. Another was found northeast of Amory in the older Eutaw or the Tuscaloosa formation. These Upper Cretaceous bentonites have not been found to the north in Tennessee or Kentucky.

The Porters Creek clay (Eocene, of Midway age), which is 60 to 100 feet thick, crops out in a narrow belt that runs from southeastern Missouri through southern Illinois, western Kentucky and Tennessee, and northeastern Mississippi to central Alabama. It is a low-grade active clay or fuller's earth throughout its entire length and thickness. It is mostly light to dark gray, with locally a purplish cast. Some possibly contemporary samples from central Georgia are black with organic matter. It is commercially worked at Olmsted, Ill., and Murray, Ky. Similar clays appear in southeastern Missouri, central Arkansas, and southeastern Texas. It is perhaps best and thickest (85 feet) at Pinson Hill, in western Tennessee. It may be a much reworked bentonite mixed with about an equal amount of inert silt, accumulated on an old shore line. Its adsorbent power is very little enhanced or depressed by acid treatment.

In the Tallahatta formation of the Claiborne group (Eocene) there is a large deposit of fairly good fuller's earth (class V) at Whites Bluff, on the Tombigbee River, near Cunningham, Ala. This is light gray, nearly white, and occurs in alternate layers of hard and soft clay to a total depth of about 100 feet. On drying it becomes very hard, and it does not slake or even soften in water.

The best activable bentonite known occurs in the Oligocene Vicksburg. The thickest beds (5 feet) of high-grade material are in Smith County, Miss. In Jasper County the beds are 2 to 3 feet thick and in northern Wayne County 25 feet thick, and are mostly silty and weathered. In Alabama few promising exposures of the bentonitic beds of the Vicksburg group are known. Near Cordele, Ga., there are extensive 20-foot beds, but they are of inferior quality. In Mississippi this bentonite is uniformly a waxy yellowish gray. Near Marianna and Cordele it is either green or reddish brown, locally variegated like "marble" cake. The bentonite of Hawthorn age near Tallahassee is similar in appearance.

In Jasper County, Tex., along the northern border, there is a series of beds of green bentonite, very similar in occurrence and properties to the bentonite in the Vicksburg group to the east. Previously mined and sold untreated as "Nacogdoches" fuller's earth, it was recently found by the writer to be highly activable, and its development as such is in prospect.

The ancient Ordovician bentonite of east-central Kentucky and the surrounding area is of considerable interest, because it closely resembles much younger bentonite in bleaching power and in thermal dehydration, though high in potassium and giving different X-ray spectra. It is described more fully below.

Similar but far less activable clay occurs near Evensville, Pikeville, and Chattanooga, Tenn., and in northwestern Georgia. These last mentioned are in thick, steeply tilted beds, whereas those at High Bridge, Ky., are horizontal. Attempts have been made to use the clay in northwestern Georgia to purify the water supply of Atlanta but with indifferent success.

The Southwest has not yet been systematically explored for adsorbent clays by Survey geologists, but several hundred samples from that area have been tested at the Survey by the writer, and at least half a dozen clay beds are being worked. Results of the tests are listed under separate states below. The most important appear to be the fuller's earths of southeastern Missouri; the fuller's earths of central Arkansas and the bentonites of southwestern Arkansas; the bentonites of western Oklahoma, New Mexico, Colorado, Utah, and Arizona; the fuller's earth of Creede, Colo., and Olancha, Calif.; and the bentonites of Nevada and Otay, Calif.

DISTRIBUTION BY AREAS

In the following pages the occurrence and character of the clays is discussed by areas, and the results of the bleaching power of the more important adsorbent clays is given. The results tabulated below are selected from tests of more than 4,000 samples covering 10 years of study. They show the range of bleaching power to be expected. Nearly all are definite and repeatable, so that such a test may help to identify a clay. There appears to be a definite maximum of adsorbent power, which is approached but not exceeded by the better activable clays. In the naturally active clays such a maximum is less in evidence, as natural activation has proceeded to various stages.

Test standards must be chosen from among active clays, some of which change by less than a measurable amount during storage for 5 years. The activable bentonites, even when kept over water in a closed vessel, change gradually in water content, physical and chemical properties, and bleaching power over a period of years. A satisfactory reference standard is commercial 30–60 mesh Floridin reground to 150 mesh and stored room dry in bottles.

The numerical bleach ratings are fully explained in the section on the testing and rating of clays. (See pp. 204–208.) In brief, a black neutral crude testing oil is percolated through a layer of clay (150-mesh that has just been dried at 160° C. for 1 hour) in a tube having a permeable bottom. The test oil emerges first water white, then green, yellow, red, and finally black (end of bleaching). The four numbers are the ratios of the volume of oil bleached to these colors to the volume of clay.

Bleaching tests of more important adsorbent clays

	Class	Bleach rating[1]							
		Untreated				Acid treated			
Haddonfield, N. J	II	0.6	0.7	0.7	0.7	1.9	3.0	3.1	3.1
Sewell, N. J., glauconite	III	.8	.9	.9	.9	1.6	2.2	2.7	3.0
Kaylor, Md., glauconite	III	1.2	1.4	1.5	1.7	1.9	2.3	2.5	2.9
Aiken, S. C	IV	1.0	1.2	1.3	1.5	.9	1.1	1.2	1.4
Aiken, S. C. serpentine	II	.3	.3	.3	.3	1.0	1.6	2.2	2.7
Dry Branch, Ga	IV	.9	1.2	1.3	1.6	.8	1.1	1.4	1.8
Cedar Grove, Ga	III	.6	.7	.8	.8	1.5	2.2	2.4	2.5
Base, Twiggs-Barnwell	III	.7	.9	1.0	1.1	1.4	2.1	2.6	2.7
Irwinton, Ga	III	.6	.8	.9	1.0	1.5	2.1	2.5	2.9
Vienna, Ga	III	1.0	1.2	1.3	1.5	1.6	2.1	2.8	3.4
Cordele, Ga	III	.6	.8	.7	.7	1.3	1.5	1.7	2.0
Attapulgus, Ga	V	.9	1.1	1.3	1.5	.6	1.0	1.2	1.5
Attapulgus, Ga	II	.2	.3	.3	.3	.8	1.3	1.6	2.2
Beachton-Meridan	III	1.2	1.4	1.5	1.7	1.4	2.1	2.9	3.6
Brooks Co., Ga	III	1.1	1.2	1.2	1.3	1.1	2.3	2.8	3.5
"Floridin," average	V	1.0	1.3	1.5	1.7	.6	.8	1.0	1.3
"Floridin," selected	V	1.3	1.8	2.1	2.3	.6	.9	1.2	1.6
Ocala, Fla	V	1.0	1.4	1.5	1.7	.7	.9	1.0	1.1
Ocala, Fla	III	.9	1.0	1.1	1.2	1.3	2.1	2.4	2.6
Cottondale, Fla	III	1.1	1.3	1.4	1.5	1.2	2.0	2.9	3.8
Marianna, Fla	III	1.3	1.4	1.5	1.6	1.8	2.9	3.6	4.0
Montgomery, Ala	II	.2	.3	.3	.4	1.5	2.4	3.0	3.5
Tuskegee, Ala	II	.3	.4	.4	.4	1.6	2.2	2.5	2.9
Choctaw Co., Ala	II	.4	.5	.5	.5	1.1	1.8	2.3	2.9
Whites Bluff, Ala	V	.9	1.1	1.2	1.3	.6	.7	.8	1.0
Smithville, Miss	II	.4	.5	.5	.5	2.0	2.8	3.0	3.3
Booneville, Miss	II	.3	.4	.4	.4	1.4	2.0	2.5	2.9
Aberdeen, Miss	II	.2	.3	.3	.4	1.4	2.0	2.2	2.4
Pontotoc, Miss	II	.5	.6	.6	.6	1.5	2.4	2.9	3.5
Polkville, Miss	II	.2	.3	.3	.3	1.3	2.3	3.0	4.1
Lemon, Miss	II	.2	.3	.3	.3	1.6	2.4	3.0	3.9
Ripley, Miss	V	1.1	1.4	1.1	1.9	.6	.9	1.0	1.2
Amory, Miss	II	.3	.4	.4	.4	1.8	2.8	3.2	3.5
Walnut, Miss	III	.5	.6	.8	.9	1.1	1.7	2.0	2.4
Pinson, Tenn	IV	.7	.9	1.1	1.2	.8	.9	1.0	1.1
Murray, Ky	IV	.6	.8	.9	1.1	.6	.8	.9	1.1
High Bridge, Ky	III	.8	.9	.9	1.0	1.2	1.9	2.2	2.9
Olmstead, Ill	IV	.6	.8	.9	1.1	.7	.8	.9	1.0
Goose Lake, Ill	III	.9	1.0	1.0	1.1	1.0	1.6	1.9	2.0
Clark Co., Ark	III	.8	.9	.9	.9	1.6	2.6	2.7	2.7

[1] The numbers in the four columns are the ratios of the volume of oil bleached to water white, green yellow, and red to the volume of clay bleaching it.

Bleaching tests of more important adsorbent clays—Continued

	Class	Bleach rating							
		Untreated				Acid treated			
Pike Co., Ark	II	0.3	0.4	0.4	0.4	1.9	2.5	3.0	3.9
Woodward, Okla	II	.4	.5	.5	.5	1.6	2.1	2.4	3.0
Riverside, Tex	IV	.6	.8	.9	1.1	.7	.9	1.1	1.3
Lena, Tex	II	.5	.6	.6	.6	1.0	1.4	1.5	1.6
Mackay, Tex	IV	.9	1.2	1.4	1.7	.8	1.2	1.5	1.9
San Antonio, Tex	II	.3	.4	.4	.5	1.2	1.7	2.0	2.4
Whitewright, Tex	II	.3	.4	.4	.4	1.1	1.5	1.9	2.7
Chatfield, Tex	II	.4	.5	.5	.5	1.4	1.9	2.4	2.8
Corsicana, Tex	II	.4	.5	.5	.5	1.4	1.9	2.5	2.9
Browndell, Tex	III	.9	1.0	1.0	1.1	1.6	2.2	2.7	3.3
Rockland, Tex., Bennett & Clark clay pit	III	1.0	1.1	1.2	1.3	1.2	2.0	2.3	2.6
Rockland, Tex., Max B. Miller clay pit	IV	1.1	1.6	1.7	1.9	.6	1.1	1.3	1.6
Santa Cruz, N. Mex	II	.3	.4	.4	.4	.9	1.5	2.4	3.0
Hachita, N. Mex	III	.8	.9	.9	.9	1.1	1.8	2.5	3.1
Hatch, N. Mex	II	.4	.5	.5	.5	1.7	2.8	3.0	3.2
Creede, Colo	IV	1.0	1.2	1.3	1.5	1.1	1.6	1.9	2.2
Westcliffe, Colo	II	.4	.5	.5	.5	1.3	2.1	2.6	3.2
Box Elder, Utah	II	.6	.6	.6	.6	1.3	2.1	2.5	3.1
Chito, Ariz	II	.4	.5	.5	.5	1.5	2.4	2.9	3.5
Otay, Calif	II	.4	.5	.5	.5	1.0	1.9	2.6	3.3
Olancha, Calif., "Calearth"	III	1.3	1.6	1.8	2.0	1.9	2.4	2.6	2.9
Muroc, Calif	IV	.7	.8	.9	1.0	.7	.9	1.1	1.3
Wyoming swelling	I	.3	.4	.4	.4	1.0	1.2	1.4	1.7
Rapid City, S. Dak	III	1.0	1.1	1.1	1.1	1.2	1.8	2.6	3.4
Fairburn, S. Dak	III	.6	.8	.9	1.0	1.3	1.9	2.5	3.2
Mountain, N. Dak	III	.6	.7	.8	.8	1.6	2.4	3.0	3.5
South St. Paul, Minn	III	1.2	1.5	1.6	1.8	1.3	2.0	2.4	2.8
Morden, Manitoba	III	1.2	1.5	1.6	1.8	1.1	1.6	2.1	3.2
Edson, Alberta	III	.8	1.1	1.2	1.4	1.7	2.7	3.0	3.5
Milk River, Alberta	II	.3	.4	.4	.4	1.5	2.7	3.2	3.6
Saskatchewan	II	.4	.5	.6	.6	1.8	2.4	3.0	3.6
Princeton, B. C	IV	1.0	1.2	1.3	1.5	.8	1.1	1.3	1.5
Veracruz, Mexico, pink	II	.4	.5	.5	.5	1.6	2.5	3.1	3.7
English "XL"	III	1.1	1.2	1.3	1.4	1.6	2.6	3.1	3.5
Faeroe Islands, clay rock	II	.4	.5	.5	.5	1.4	2.2	2.5	2.7
Bavaria, "Tonsil"	II	.4	.5	.5	.5	2.1	2.4	2.8	3.4

New Jersey and Maryland.—Glauconite occurs in extensive beds of Cretaceous and Eocene age that have been worked at Sewell, N. J., and in Maryland at the head of tidewater on the Patuxent River. Dried and ground, glauconite bleaches cottonseed oil as well as does good fuller's earth, bulk for bulk, but as it is considerably heavier it is of interest only where distances are short or where water transportation is available. Similar considerations apply to acid-treated glauconite. By volume test, glauconite activates nearly as well as the best activated bentonite. Tests of the glauconite at Sewell run 0.8 to 0.9 raw and 1.6, 2.2, 2.7, 3.0 acid treated. The Maryland glauconite tests 1.2, 1.4, 1.5, 1.7 raw and 1.9, 2.3, 2.5, 2.9 treated.

In 1936 L. W. Stephenson discovered a broken 6-inch bed of very pure bentonite 3 miles southwest of Haddonfield, N. J. This bed is Upper Cretaceous in age. A covering of 10 feet of sand protected it from drying and excessive weathering. It tested 0.6 to 0.7 raw and 1.9, 3.0, 3.1, 3.1 acid treated.

A dark bluish-gray clay (Arundel formation?) mined near Baltimore, testing 0.8 to 0.9 raw and but slightly activable, has been found useful as a binder in an asphalt-water-clay emulsion prepared as an adhesive. For this purpose it probably serves as well as would the more active commercial adsorbent clays.

Virginia and North Carolina.—No promising adsorbent clays have yet been found in Virginia, and their existence is very doubtful. About 40 samples from the region between Raleigh and the coast have been found to be low-grade active clays. Of these perhaps 5 have sufficient bleaching power to warrant drying and grinding for local uses, such as the re-refining of crankcase oil.

South Carolina.—The Barnwell formation, which contains the active clay mined near Macon, Ga., extends northeastward to southern South Carolina. Just northeast of Aiken, S. C., is a 5-foot bed of active clay in the Barnwell which tests practically the same as that near Macon. This is the only known deposit of possible commercial interest in South Carolina. Its extent was determined by 78 samples taken by H. X. Bay and tested by the writer in 1934. Of scientific interest are a small waterfall near Aiken, the lip of which is fuller's earth with marked resistance to erosion, and a 3-foot bed of green decomposed ferromagnesian rock (olivine?) on the Cooper farm, 1 mile northeast of Salley, Aiken County. The middle of this tests 0.3 to 0.3 raw and 1.0, 1.6, 2.2, 2.7 acid treated. It is nearly as activable as a bentonite and has a good color spread.

Georgia.—The adsorbent clays of east-central, Georgia, Twiggs County, and of southwestern Georgia, Decatur, Grady, and Thomas Counties, have long been known and extensively operated. Of recent interest is the extent of these high-grade fuller's earths toward the east. Activable bentonite of Ordovician age has been found in the extreme northwestern part of the State and of Eocene age at the bottom of the Twiggs clay member of the Barnwell formation in Twiggs County. Activable bentonites of Oligocene age occur around Vienna in west-central Georgia and similar bentonite of Miocene age along the southern border of the State. About 400 samples were tested in 1934.

Of 48 samples of Ordovician bentonite taken by H. X. Bay in Dade, Walker, and Chattooga Counties, only 1 even approached the lower limit (1.4 to 2.9) of commercial interest. This was from the Atkins and Hobbs property half a mile north of Cedar Grove, Walker County, and tested 0.6 to 0.8 untreated and 1.5, 2.2, 2.4, 2.5 after acid treatment. The low green and red separation indicates weathering. The various beds dipped 30° to 40°. The boring tool used could not penetrate the very hard unweathered portions of the bentonite, and there is a bare possibility that bentonite of commercial grade lies at greater depths but within working distance of the surface.

A great many samples of the active clay from the Twiggs clay member of the Barnwell taken in Twiggs, Wilkinson, Washington, and Burke Counties show that there is a practically unlimited quantity of this well-known bleaching clay available in thick (15-foot) and nearly continuous beds equal in quality to but none of them better than that mined by the General Reduction Co. near Dry Branch. As the market is already well supplied, this means that huge reserves of this type of clay are available when needed.

The active clay of the upper part of the bed in the Barnwell is but slightly affected by acid treatment. Clay samples from near the top are generally slightly lowered in adsorbing power by that treatment, and those from near the base are slightly enhanced. The lower 8-foot clay bed of the Twiggs clay member of the Barnwell formation, which is 100 feet below the upper beds, rests directly on the Ocala limestone and is all activable—slightly at the top and to 1.4, 2.1, 2.6, 2.7, at the base, which is the bleaching power of a fairly pure bentonitic clay only slightly leached or weathered. The sample tested was taken by auger on the J. C. Miller property, 1.5 miles west of Fitzpatrick Station, Twiggs County. Two miles east of Irwinton, on a cut of the Balls Ferry road, three samples of an 8-foot exposure all tested 0.6 to 1.0 raw and 1.5, 2.1, 2.5, 2.9 acid treated. This is up to the lower commercial limit of activable clay and may well be of interest.

No good active or activable clays were found in the older formations (Upper Cretaceous and Eocene) to the southwest of Macon, and it is doubtful whether any of commercial value exist, although attempts have been made to mine and market them in several locations.

The Oligocene enters Georgia in a belt at the southwest corner of the State and extends, partly under cover, to the Savannah River. Between Americus and Vienna the exposure is broad. Many samples from this locality were found to be activable, but only one was sufficiently so to be of commercial interest. This was from a 9-foot bed with a 3-foot outcrop on State highway 90, 4.6 miles northwest of Vienna, and tested 1.0 to 1.5 raw and 1.6, 2.1, 2.8, 3.4 treated. These clays, which are tentatively referred to the Flint River formation, of Oligocene age, are normally strongly colored either dark green or dark red-brown, and most of them are mottled with these colors. They are of class III adsorbent clays, active and further activable.

On the property of Law & Co., 2.5 miles east of Cordele, is an extensive 24-foot bed of active and further activable clay, possibly a bentonitic clay, mottled gray and brown above and clear dark gray below. A dozen auger samples from three holes showed fairly uniform characteristics, 0.6 to 0.7 raw and 1.3, 1.5, 1.6, 2.0 acid treated. This bed is not of commercial interest as either a fuller's earth or as an activable clay, but it is of considerable geologic interest. It extends at least 16 miles south and southeast of Cordele.

Near the west half of the Georgia-Florida border are many clay beds in the Hawthorn formation; a few are highly activable, others are naturally active, and a few are both. In the belt centering on the line through Attapulgus, Cairo, and Ochlocknee are large quantities of excellent active clay in extensive beds 7 to 18 feet thick protected by a light overburden. It is usually yellowish but sometimes greenish gray. In a few places thin beds of green and brown somewhat activable clay occur above the active clay.

Just south of this fuller's earth belt is a similar belt of activable clay centering on a line though Marianna and Tallahassee and extending on to southern Brooks County, Ga. Of possible commercial interest are a bed 1.4 miles north of the Georgia-Florida line, on the Bleachton-Meridian highway, testing 1.2 to 1.7 raw and 1.4, 2.1, 2.9, 3.6 treated, and a deposit on the property of C. E. Clanton, in the southeast corner of Brooks County, 8 feet thick but not very extensive, testing 1.1 to 1.3 raw and 1.1, 2.3, 2.8, 3.5 treated.

Near Attapulgus, 10 feet above the fuller's earth bed being mined in 1935, is a 3-foot bed of greenish-gray soft clay, which tests 0.2 to 0.3 raw and 0.8, 1.3, 1.6, 2.2 treated, suggesting that it is possibly a silt-bentonite mixture in which the bentonite is but little weathered. This forms part of the Hawthorn formation of Miocene age.

Florida.—Active clays in extensive deposits are known and worked near Quincy, Gadsden County, by the Floridin Co. and the Fuller's Earth Co., and 15 miles northwest of Ocala, Marion County, by the Superior Earth Co. In both locations the supply in sight is ample for all prospective needs. The Floridin Co. has mined out at least a dozen 40-acre tracts over a region 10 miles across. Clay similar in quality to that being mined near Ocala was found by H. X. Bay to extend northward from the present mine for at least 15 miles into Alachua County.

The bentonitic clays of northwestern Florida, recently shown by the writer to be highly activable, are less broken down by weathering than those in Georgia but more so than those of Mississippi. Some large deposits are too far gone to be worth working, but many of the largest are in prime condition. Under Marianna and Tallahassee the clay is of excellent quality but only about 3 feet thick. On State Highway No. 20, 1.7 miles south of Cottondale, H. X. Bay found a bed more than 9 feet thick, which throughout gave the high test 1.3, 1.5, 1.6, 1.8 raw and 1.6, 2.6, 3.2, 3.9 acid treated, which is first class both as a fuller's earth and as an activable clay. At the junction of United States Highway No. 90 and Florida Highway No. 6, on the northwest edge of Marianna, is a 14-foot bed, which tests on an average 1.1, 1.3, 1.4, 1.6 raw and 1.2, 2.2, 2.7, 3.4 acid treated, and is fairly uniform throughout. This is well within the range of commercial interest but less activable than the best. At a distance of 1.5

miles southwest of Marianna, on the Kynesville road, a 12-foot deposit similar in quality to the above occurs. A mile south of Alford, a 6-foot bed of similar clay is exposed in the railroad cut.

At Campbellton, northwest of Marianna, activable clay is found, but it is of low grade. The thickest deposit of first-class clay found by A. C. Munyan was 4 miles west of Cottondale, 200 yards south of United States Highway No. 90. From a depth of 14 to 41 feet all tests were good, averaging 1.1 to 1.5 raw and 1.2, 2.0, 2.9, 3.8 treated. The eastermost deposit was 1 to 5 miles north of Monticello, where a 6-foot bed was found to be active (0.6 to 1.1) and activable (1.2 to 2.5), but this is of no commercial interest. A similar bentonitic clay, was found 5 miles southeast of Tallahassee on United States Highway No. 19.

Exploratory work has merely proved the existence of high-grade active and further activable clay over a curved belt at least 100 miles long by 30 miles wide. Owing to the enormous tonnage easily available, the high quality, and the favorable location with respect to other sources of activable clay and to markets, this series of deposits will doubtless become commercially important. However, no start has yet been made toward development, and it is evident that extensive detailed mapping must be done before a mining and treating plant can be properly located. The wide extent of the deposits should make difficult their monopoly by a single firm.

Alabama.—Few bleaching clays of interest have been found in Alabama, and these are mostly of the active type. The only samples of activable clay of high grade were from a 30-inch bed in the Eutaw formation of Cretaceous age of limited extent exposed in a cliff in the outskirts of Montgomery, testing 0.2 to 0.4 raw and 1.5, 2.4, 3.0, 3.5 treated, and from a 3-foot bed of possibly the same clay 5.5 miles south of Tuskegee, testing 0.3 to 0.4 raw and 1.6, 2.2, 2.5, 2.9 treated. A number of samples of lower-grade activable clay were found by Bay in the Eocene Lisbon formation in Choctaw County in 6- to 13-foot beds, tests of which averaged 0.4 to 0.5 raw and 1.1, 1.8, 2.3, 2.9 treated. The tests indicate a mixture of inert silt with a high-grade bentonitic material.

The large deposit of active clay in White's Bluff, on the Tombigbee River, near Cunningham in Clarke County, has long been known but never used until recently. The clay occurs in the Tallahatta formation of the Claiborne group of Eocene age. Its bleaching power is nearly the same as that of the well-known Quincy-Attapulgus fuller's earth of Hawthorn age. It occurs in alternating hard and soft layers. Twenty-eight samples of it showed but little variation in decolorizing efficiency through its 100-foot depth.

What appears to be Oligocene Vicksburg bentonite occurs in beds 250 to 300 feet above sea level in the hills near Cunningham. This has the appearance and properties of the bentonite in the Vicksburg group of Smith County, Miss. It contains abundant shards of volcanic glass, some of which are not completely altered to montmorillonite.

Mississippi.—Activable clays of high grade and of three widely different geologic ages occur in Mississippi. In the northeast corner, 5 miles southeast of Booneville, is a small bed in the Coffee sand of the Upper Cretaceous, which has been worked by the Williams brothers for years at the rate of about a carload a week. This is dried and shipped in peanut size to those oil refiners who activate their own clay. The deposit is small and isolated. Several other similar deposits of the same age were found by Bay to the southeast. From their relative positions these were thought to represent four different ash falls. The tests run 0.3 to 0.4 raw and 1.4, 2.0, 2.5, 2.9 leached, which is considered the lower limit for activable clays of commercial interest at present.

The oldest Upper Cretaceous bentonitic clay yet discovered is in the upper part of the Tuscaloosa formation, at the Cox place, east of Smithville, Monroe County. This tests 0.4 to 0.5 raw and 2.0, 2.8, 3.0, 3.3 treated, which is rather high grade. The low color separation (2.8 to 3.3) indicates weathering and the possibility of higher quality deeper in the bed. Near Amory, Miss., is a 16-foot bed in the older (Tuscaloosa?) Upper Cretaceous, a bentonitic clay that tests 0.3 to 0.4 untreated and 1.8, 2.8, 3.2, 3.4 acid treated and is therefore well within the range of commercial interest. A green clay in the Tombigbee sand member of the Eutaw formation of Upper Cretaceous age occurring near Aberdeen was considered by geologists to be an unusually pure bentonite. This was extensively prospected in 1934, and about a score of samples were tested by the writer; all showed only about half the activability of the best clay. It is now being worked by the American Colloid Co.

At the base of the Prairie Bluff chalk (Upper Cretaceous), 4.5 miles northeast of Pontotoc, is a 5-foot bed of good activable clay estimated to contain at least 3 million tons, which was found by F. F. Mellon, then of the Tennessee Valley Authority staff. The writer's tests of two samples run 0.5 to 0.6 raw and 1.5, 2.4, 2.9, 3.5 treated, which is well within the range of commercial interest.

The Porters Creek clay of the Midway group (Eocene) extends in a broad thick belt across northeastern Mississippi. In Tennessee, Kentucky, and Illinois the Porters Creek clay varies little in bleaching power; in Mississippi it exhibits a wide variation. A sample collected by H. X. Bay 2.3 miles north of Ripley, Tippah County, on State Highway 15, tested 1.1, 1.4, 1.6, 1.9 raw and 0.6, 0.9, 1.0, 1.2 acid-treated; this is an excellent fuller's earth. At the opposite extreme is a sample from a mile west of Walnut, Tippah County, on State Highway 2, which tested like a bentonite, 0.5, 0.6, 0.8, 0.9 raw and 1.1, 1.7, 2.2, 2.4 treated, just under the Booneville limit. The only use of the Porters Creek clay as an adsorbent appears to be that of furnishing a cheap low-grade fuller's earth for nearby refineries.

The bentonite in the Vicksburg group in the northwestern part of Smith County has the highest activability known. It occurs in six or more areas, isolated but near each other, which are underlain by beds 3 to 5 feet in thickness. It has the brown color and waxy texture of a laundry soap. It was discovered 2 miles north of Lemon in 1931 by Dr. A. C. Trowbridge while he was seeking a location for a gas well. A sample sent to the Survey was found to be a true bentonite of high purity and very highly activable. In 1933–34 it was mapped in detail by H. X. Bay and Urban Hughes for the Eastman, Gardner Lumber Co. Production was begun in 1936 at the James farm, near Polkville. This clay is treated in the new Filtrol plant at Jackson.

Even after detailed mapping the production of this clay is not easy The terrain is much dissected by ravines, the deposits are only 3 to 5 feet thick, the overburden is considerable, and the dip is 30 to 60 feet per mile. Joint cracks are numerous and are filled with red and weathered material of inferior grade, which is not readily separated. The clay itself is either light or dark yellowish brown, but both kinds are of equal activability. The lighter colored bentonite consists almost entirely of shard relicts. The clay is fairly tough chemically, and its acid treatment therefore is more easily controlled than that of the tender bentonite of Chito, Ariz., which heretofore has been largely used. If mined at the anticipated rate of 100 tons a day, the deposit should last for a generation. To the southeast, from Bay Springs to Heidelberg, the beds are only 2 to 3 feet thick but are of good quality, whereas in Wayne County they thicken to 25 to 30 feet but are of poor quality. A typical test of the best clay of the Vicksburg group runs 0.2 to 0.3 raw and 2.1, 3.0, 3.6, 4.1 treated.

Tennessee.—In Tennessee the clays of possible commercial importance on account of their adsorbent power are the active clays of the Porters Creek clay of the Midway group of Eocene age that cross the State from north to south near its western end. The green Ordovician (?) bentonites from near Evensville and Pikeville, in the eastern part of the State, though attractive in appearance, are but slightly active or activable.

Two sections of the Porters Creek clay were obtained by M. N. Bramlette of the Geological Survey, samples being taken every 5 feet for 85 feet, (1) at Pinson Hill, on the Walter Lester farm, three-fourths of a mile northeast of Pinson, Madison County, and (2) from a hill 3 miles northeast of Huntington, Carrol County. These showed remarkable uniformity in adsorbing power, the tests averaging about 0.7, 0.9, 1.1, 1.2 for either treated or untreated clay. Treatment with acid slightly enhanced the adsorbing power of some samples and depressed that of others.

Illinois.—Adsorbent clays thus far exploited in Illinois are confined to the southern tip of the State. The Porters Creek clay at Olmsted is 60 feet thick and is similar in appearance and properties to that farther south. Samples taken at intervals on the worked mine face showed an average test of 0.6, 0.8, 0.9, 1.1, with little deviation and no effect of acid treatment, except at the base of the deposit, where an acid-treated sample tested 0.8, 1.3, 1.5, 1.7, as though it were somewhat more bentonitic. The clay at Olmsted dries into a hard mass and granulates well. It has been mined for years and used for decolorizing oil in the nearby refineries of the Sinclair Co. and the Standard Oil Co. of Indiana, partly in granular form for percolation and partly powdered for contact bleaching. A little is used in molding sand.

The old bed of Goose Lake, near Joliet, mined for fire clay by the Illinois Clay Products Co., contains a bed of high-iron beidellite clay testing 0.9 to 1.0 raw and 1.0, 1.6, 1.9, 2.0 acid-treated. As an active clay this is better than most Porters Creek clay and nearly as good as Floridin, but acid treatment would not pay. It is a good example of an active clay that is probably not of bentonitic origin.

Missouri.—In the early Eocene formations in southeastern Missouri are a number of thick and extensive beds of Porters Creek clay as active as that east of the Mississippi river but somewhat softer and lighter in color. Owing to their location and quality and the abundance of more active clays nearer markets, it is doubtful whether these deposits will be developed.

Arkansas.—The above statements regarding the clays of southeastern Missouri apply to those of northeastern Arkansas that are of similar age. Near the center of the State in Saline and Grant Counties, both active and activable clays are abundant, but they are of low grade. From the sector south and southwest of Little Rock about 40 samples were submitted by R. V. West and G. C. Branner, State geologist. Of these the best, which was from Clark County, tested 0.8 to 0.9 raw and 1.6, 2.6, 2.7, 2.7 treated. A very dark red sample of bentonite (Cretaceous) from Pike County tested 0.3 to 0.5 raw and 1.9, 2.5, 3.0, 3.9 acid-treated. This is a high-grade activable clay, but the deposit is said to be small.

Near Nashville, at the southwest corner of the State, is an abundance of greenish-gray altered coarse-grained volcanic ash, which activates but to only about half the decolorizing power of the best bentonites. There appears to be little chance of finding a good bentonite in this locality.

Arkansas has decided possibilities as a producer of adsorbent clay and is near Oklahoma and Texas refineries, but it has never been systematically prospected.

Louisiana.—No commercially important deposits of bleaching clay of either the active or activable type have yet been found in Louisiana. Formations in the northwest quarter of the State are middle Eocene; those in the remainder are chiefly Pliocene and Recent. A white volcanic ash occurs near Monroe. Near Good Pine, 15 miles north of Jena, the ash is of petrographic interest in that the grains of tuff are just about half altered to clay. A belt of "volcanic ash" in the Citronelle formation (Pliocene) extends from Bogalusa, La., to Woodville, Miss. These clays commonly are marbled bluish brown and greenish gray near the surface and clear greenish gray below, like that near Cordele, Ga. Of 80 samples submitted by C. K. Moresi, State geologist, a few were highly activable. These samples were from test holes 20 to 74 feet deep along lower Bogue Lusa Creek. The deeper tests showed clay of similar nature down to at least 74 feet. Although the petrographic microscope does not clearly show evidence of volcanic origin in these clays, their thermal dehydration curves closely resemble those of pure montmorillonite.

Oklahoma.—Little is known of the geology of the adsorbent clays of this State. The 5-foot bed of impure pink bentonite near Woodward has been known and worked for years. This tests 0.4 to 0.5 untreated and 1.6, 2.1, 2.4, 3.0 treated. A few chalky-white samples having brown seams, submitted by Max B. Miller and tested by the writer, were found to be active clays, testing 1.1, 1.5, 1.7, 2.0 untreated and 0.8, 1.1, 1.2, 1.4 leached. These tests indicate the possibility that worth-while beds of both kinds of adsorbent clays might be found by systematic prospecting for them.

Texas.—Clays of both active and activable types but of low grade are abundant near the inner border of the Coastal Plain in Texas. About 200 samples collected by P. B. King, of the Geological Survey, and tested by the writer, were from a belt running from San Antonio to Gonzales and thence to Riverside, Walker County. Many of these were from pits previously worked. Included were samples from the mines now being worked by the Texas Co., 3 miles southeast of Riverside and between West Point and Muldoon in Fayette County, and by the Continental Oil Co., a mile west of Riverside.

The fuller's earths near Riverside, (Miocene(?)Catahoula) test uniformly 0.6, 0.8, 0 9, 1.1 untreated, like Porters Creek clay; they do not activate. The Fayette County deposit of Jackson age varies widely in quality with depth. A sample prepared by the Texas Co. for shipment to their treating plant tested 0.6 to 0.6 untreated and 1.0, 1.4, 1.5, 1.7 after activation, only half the bleaching power of the best activable clays. The best active clays found by King, testing 0.9, 1.2, 1.4, 1.7 untreated, were from the Upper Cretaceous 8 miles west of San Antonio, 1 mile northeast of the Mackey School, on the east bank of Huebner Creek. Another of Jackson age, testing the same, was from the pit of the Earthern Products Co., 6 miles south of Gonzales, 1.5 miles east of Yoakum road. Though called a bentonite by the producers, this clay does not activate appreciably.

The most activable clay found by King was from a 13-foot bed of soft yellowish-gray clay in the upper part of the Taylor marl, exposed in a railway cut in the eastern part of the city of San Antonio between the overpasses of Jim and Carson Streets. At the top, and at depths of 4 and 11 feet this tested 0.3 to 0.5 untreated and 1.2, 1.7, 2.0, 2.4 treated, just under the commercial range in activable clays.

A bentonite was found in the Austin chalk (Cretaceous) by L. W. Stephenson, of the Geological Survey, in 1935, 0.7 mile northwest of Whitewright, Grayson County, northeastern Texas. It tested 0.3 to 0.4 raw and 1.1, 1.5, 1.9, 2.7 treated, just under the limit of commerical interest as an adsorbent clay. This is a dark-gray waxy bentonite containing fine specks of biotite. The test indicates an impure montmorillonite, as the color separation is good. Three more samples of Upper Cretaceous bentonite were submitted by Mr. Stephenson in 1936. The youngest was from a locality 1.6 miles northeast of Chatfield, Navarro County, in the upper part of the Nacatoch sand of the Navarro group and tested 0.4 to 0.5 raw and 1.4, 1.9, 2.4, 2.8 treated. Two others were from 4 miles west by north of Corsicana, Navarro County, in the Nelandville marl of the Navarro group, testing the same as the Chatfield sample. All these test practically the same as the Upper Cretaceous bentonites of Mississippi and are similar in appearance and texture.

Along the northern border of Jasper County, near the contact of outcrops of Oligocene and Miocene age, is a series of deposits of greenish gray clay assigned to the Miocene Catahoula, which have the highest adsorbent power of any yet found in Texas. A sample submitted by W. G. Hugly, geologist of the Houston Oil Co., in July 1936 gave a high test both as an active and as an activable clay. This was from an extensive 22-foot bed near Browndell, Jasper County, 15 miles north of Jasper, on the Houston & Texas Central R. R., section 171 and S. C. Ferris survey. Although mapped as Miocene Catahoula this bentonite has properties similar to that from the Oligocene Vicksburg of Mississippi. This bed has been worked as a fuller's earth by Bennett and Clark, who dried and ground it in their plant at Nacogdoches; hence its name "Nacogdoches clay." Like the bentonite at Marianna, it is almost as active without acid treatment as the fuller's earth of Quincy and Attapulgus, yet it was found to activate as well as the clay from Chambers, Ariz. It tests 0.9 to 1.1 raw and 1.6, 2.2, 2.7, 3.3 acid treated (20 percent loss in weight). This bentonite is of considerable commercial as well as geologic interest. On the Houston Oil Co.'s property in Jasper County, 4 miles northwest of Rockland, Tyler County, is the Bennett-Clark clay pit (S. W. Blount survey, abstract 73). A sample from a shipment of this clay tested 1.0, 1.1, 1.2, 1.3 raw and 1.2, 2.0, 2.3, 2.6 treated. About 3,500 feet west of the Bennett-Clark pit is the "Milwhite," or Max B Miller pit, on the Harrelson tract of the J. C. Everett survey. A shipping sample of this tested as high-grade normal fuller's earth, 1.1, 1.6, 1.7, 1.9 raw and 0.6, 1.1, 1.3, 1.5 treated. If these three neighboring beds were derived from the same ash fall, they exhibit an interesting series of alterations; if not, their geologic sequence should be established.

Aside from the belt and isolated deposits just mentioned, Texas has not been searched for bleaching clays. Bentonites are said to occur near Lubbock, in the Panhandle, but no samples have come to the Survey. The clays of the San Antonio-Gonzales region, despite their fine appearance, all run high in lime, which seems to make them useless as a first-class adsorbent clay. The beds of most probable interest are the Upper Cretaceous and those in which active and activable clays have been found elsewhere.

New Mexico.—In New Mexico there is an abundance of both kinds of absorbent clay, particularly of the highly activable type. Several of these clays are being produced, but freight charges are an important item in their economic development.

In the north half of New Mexico the Rio Grande Valley appears to have contained a series of ash-collecting lake beds as it now contains much activable bentonite. One sample from near Santa Cruz analyzed very pure montmorillonite and tested 0.3 to 0.4 raw and 0.9, 1.5, 2.4, 3.0 treated, but it is too easily acted on by acids to be of commercial interest, as underleaching or overleaching would be difficult to avoid.

Near Santa Rita, Hachita, and Deming and at other places in the southwest corner of New Mexico are at least a dozen deposits of good adsorbent clay. A sample from near Hachita tested 0.8 to 0.9 raw and 1.1, 1.8, 2.5, 3.1 treated, a class III clay. Near Hatch is a large deposit, the property of the Bentonite Co. of Pittsburgh of massive waxy greenish-gray and dark reddish-brown montmorillonite clay testing 0.4 to 0.5 untreated and 1.7, 2.8, 3.0, 3.2 after acid treatment.

Colorado.—Near Creede, Colo., is a large deposit of active but not much further activable bentonitic clay of the class IV type that has been mined for years by the Peerless Clay Co. This tests 1.0, 1.2, 1.3, 1.5 raw and 1.1, 1.6, 1.9, 2.2 treated and has found favor as a bleaching clay for cottonseed oil on account of its low oil retention. Near Gunnison occurs a white bentonite closely resembling that at Chito, Ariz. Near Westcliffe and Silver Cliff are several large deep deposits of excellent activable bentonite. Near Westcliffe is a bed of pinkish mottled bentonite said to be 30 feet deep and to cover at least a square mile, which tests 0.4 to 0.5 raw and 1.3, 2.1, 2.6, 3.2 treated. Other favorable localities not yet explored are just north of San Luis; between Kiowa and Castle Rock; southeast of Hot Sulphur Springs; and in the Oligocene of Weld and Logan counties.

Utah.—The deposit of active and slightly activable clay near Aurora, Sevier County, has long been known and was mined for a time. Selected beds test a little better than Floridin fuller's earth, but the dip is steep and the deposit is laminated and comprises beds of different bleaching power. A sample of creamy white bentonite from Box Elder County, submitted by William Peterson in 1935, tested 0.6 to 0.6 raw and 1.3, 2.1, 2.5, 3.1 treated. This was said to be from a large deposit in the extreme northwest corner of the State.

Nevada.—The adsorbent clay of Ash Meadows, about 35 miles south of Beatty, has been known and worked at times for years. The best beds at this time are composed of excellent fuller's earth, but this has never had a firm position in the strongly competitive market for active clays. A bed of white bentonite that occurs at Mason Springs, in the Pahrump Valley, near the southwest corner of Clark County, checks closely in appearance and adsorbent power with that from Chito, Ariz. Little is known of the clay resources of the rest of the State.

Arizona.—The extensive deposits of highly activable bentonite extending for 30 miles along the Puerco Valley from Navajo to Allentown have long been the source of nearly all American activated clays. The bed is level, 2 to 6 feet thick, and was found by E. B. Eckel, of the Geological Survey, to extend 40 miles northward to Ganado. For the most part it is covered by Tertiary sands and must be mined, but near Chito the overburden is soft. The lake bottom on which the ash was deposited must have been very flat, and it has been little dissected since being drained. The alteration from tuff to bentonite is incomplete at the north end, near Navajo at the southwest corner, and perhaps elsewhere. Near Chambers the clay is pink, at the Chito-Sanders mine it is snow white with black specks of manganese oxide, and near Allentown on the east it is dark gray. It has long been used by the Indians for scouring wool. Its activability is fairly uniform and high, though slightly inferior to the clays of the Vicksburg group in Mississippi. The ease with which it is attacked by acid makes it difficult to treat without overleaching or underleaching. A typical sample from Chito tested 0.4 to 0.5 raw and 1.5, 2.4, 2.9, 3.5 treated.

California.—Although many deposits of adsorbent clay of both kinds have been found in California, none are entirely satisfactory as to quality, volume, and availability. Perhaps the best known and most used is the Otay deposit of gray activable bentonite just southeast of San Diego. This is thick, 30 to 60 feet at least, and extensive, but the quality of most of the bed is not high. About a carload a month of selected clay is treated and used by the Standard Oil Co. of California at their El Segundo refinery. The best clay appears to be at about the middle of the exposure; of this some lumps are quite translucent. Boring might reveal clays of higher grade in greater volume, but does not appear promising, Tests by the writer average about 0.4 to 0.5 raw and 1.0, 1.9, 2.6, 3.3 treated, for the selected material. Samples of the Oxnard, Hector, San Pedro, Kettleman Marker, and "Inyo Ash" activable clays tested considerably lower.

Active clays occur in many places. Near Tehachapi a deposit has been mined by the Filtrol Co. for some years; it tests slightly above standard Floridin but is marketed only in powdered form. Though an inactivable fuller's earth, this clay shows abundant shard relicts, like a bentonite. In the Coso-Olancha region, just south of Owens Lake, are many deposits of active clay composed of beds widely different in bleaching power. One of the best, "Calearth," tested 1.3, 1.6, 1.8, 2.0 and was decidedly greenish. The Muroc clay gave tests of 0.7, 0.8, 0.9, 1.0, between Porters Creek and Floridin in bleaching power. From Canoas and Tar Canyons, west of the Kettleman Hills, M. N. Bramlette collected a number of samples of the bentonite correlated with the bentonite marker bed in the Kettleman Hills subsurface section. This appears to be of type III but is impure, testing 0.4 to 0.5 raw and 0.6, 0.8, 1.2, 1.5 treated. The well-known bentonite occurring just northeast of Ventura has not yet been tested as an adsorbent clay at the Geological Survey.

Altogether, southern California appears to be a rather promising field for systematic prospecting and testing. What has already been found indicates that the State is sufficiently supplied for at least its own needs.

Wyoming and South Dakota.—The swelling type of bentonite is abundant in the Upper Cretaceous north and west of the Black Hills. A partly dry lump placed in water swells slowly to about 50 times its volume in a day or two, remaining in hydrosol form indefinitely without disintegration. This property makes it a useful binder in drilling muds, molding sands, rubber filler, putty, insecticide and fungicide support, animal dips, and the like. It is not an active adsorbent clay and is but slightly activable, testing 0.3 to 0.4 dried and ground and 1.0, 1.2, 1.4, 1.7 at the best acid treatment (17–21 percent removed).

Two samples of class III clays from the Black Hills have been tested. A greenish-gray sample from F. A. Bald, Rapid City, S. Dak. tested 1.0 to 1.1 raw and 1.2, 1.8, 2.6, 3.4 acid treated. A waxy chocolate-brown bentonite from W. T. Gorsuch, Fairburn, S. Dak., tested 0.6, 0.8, 0.9, 1.0 raw and 1.3, 1.9, 2.5, 3.2 acid treated.

North Dakota.—A single sample from North Dakota tests also as a class III adsorbent clay. This was from the Upper Cretaceous area near the northeast corner of the State and tests 0.6 to 0.8 raw and 1.6, 2.4, 3.0, 3.5 treated. It is similar in properties and probably in age to a sample from Morden, Manitoba, 50 miles north.

Minnesota.—In east-central Minnesota an excellent type III clay occurs. It is greenish gray and forms a thick bed just above the St. Peter sandstone. It is preferred to the imported English fuller's earth for bleaching lard. It tests 1.2, 1.5, 1.6, 1.8 untreated and activates to 1.3, 2.0, 2.4, 2.8. Its relations to the St. Peter are not known.

Montana.—In Montana beds of bentonite 2 to 30 inches thick are not uncommon, but none of the dozen samples tested by the writer which were sent by A. C. Munyan from the Fort Belknap region and by J. T. Pardee from the southwest corner of the State, were of the swelling variety. All slaked in water without swelling but showed the same low bleaching power as the Wyoming swelling variety.

Canada.—A number of samples from a locality between Morden and Thornhill, in southern Manitoba, are distinctly of the activable type of bentonite. A white sample submitted by Hugh Spence from a thin bed between beds of black shale, tested 1.2, 1.5, 1.6, 1.8 raw and 1.1, 1.6, 2.1, 3.2 acid treated. A pinkish-white bentonite, said to be from near Edson in northern Alberta, tested 0.8, 1.1, 1.2, 1.4 raw and 1.7, 2.7, 3.0, 3.5 treated, which placed it as a good grade of class III bentonite. Near Princeton, British Columbia, is a bed of green bentonite of class IV, which tests as a good fuller's earth, 1.0, 1.2, 1.3, 1.5 raw and 0.8, 1.1, 1.3, 1.5 treated. Near Milk River, Alberta, is a waxy dark-green bentonite of class III, testing 0.3 to 0.4 raw and 1.9, 3.1, 3.6, 3.8 acid treated. Four samples of friable, nearly white bentonite from southern Saskatchewan, submitted by Prof. W. G. Worcester, of Saskatoon, test 0.4 to 0.6 raw and about 1.8, 2.4, 3.0, 3.6 treated. Two of these are composed almost entirely of shard relicts but very lightly consolidated.

Mexico.—Although bentonites are known to be abundant in Mexico, few samples have come to the Geological Survey. A sample from near Tatitila, State of Veracruz, secured through W. F. Foshag, tested 0.4 to 0.5 raw and 1.6, 2.5, 3.1, 3.7 treated; it is therefore a high-grade clay of the activable type. This clay is a waxy pinkish white and dries to an ivory texture. Acid removed no iron or magnesium, only aluminum and calcium in the ratio 7:3. White bentonites are not uncommon, but this is the first one the writer has tested that contained neither iron nor magnesium in acid-soluble form.

England.—The English fuller's earth has been well known and widely used for at least half a century. It has been shown to be a true bentonite, containing shard structures and consisting chiefly of montmorillonite. It has recently been shown to be further highly activable (type III). The writer has tested only the greenish-gray "XL" brand and the yellowish gray from Surrey. The greenish earth behaves in acid like a normal bentonite, and the test shows 1.1, 1.2, 1.3, 1.4 raw and 1.6, 2.6, 3.1, 3.5 treated. The variety from Surrey is somewhat less active, but is preferred for biological work, such as collecting vitamins from yeast.

Faeroe Islands.—A mottled dark green clay from a 20-inch bed under coal and on basalt, submitted by A. Gernow, of Copenhagen, tested 0.4 to 0.5 raw and 1.4, 2.2, 2.5, 2.7 treated. A petrographic examination by C. S. Ross showed granules of montmorillonite in a groundmass of halloysite. A few particles appeared to be tuff, but whether the mass was once ash or lava is not clear. It is of unusual practical interest in that it slakes in coarse hard 5 millimeter grains and may be acid treated without further disintegration.

Germany.—There appears to be an ample supply of high-grade activable bentonite in Germany but a dearth of fuller's earth comparable to the Floridin clay. Bentonite is produced in the region of Landshut and Mainberg, in lower Bavaria, by the Sirius Werke A. G. and sold under the trade name "Tonsil." It tests 0.4 to 0.5 raw and 2.1, 2.4, 2.8, 3.4 treated. Another preparation, "Priemsil," tests the same.

Other countries.—Russia, Rumania, and Italy are said to be well supplied with both types of adsorbent clay, but no samples have yet been studied by the writer. It is of interest that rough tests on small samples of montmorillonite and halloysite from their type localities showed both to be poor adsorbent clays. Neither would have market value as such. Argentina is said to have ample supplies of both the swelling and the activable forms of bentonite for her own use in drilling muds and as bleaching clays. Japan also is well supplied with both types of adsorbent clays, which have been studied by Japanese chemists. A sample of Japanese "acid clay" sent to the writer in 1931 by Prof. Yoshio Tanaka tested like the Georgia-Florida fuller's earths.

A comprehensive study of the decolorizing earths of North Africa has been made by Frey, Yovanovitch, and Burghelle.[5] Twelve samples of Miocene montmorillonite clay from the area between Camp Berteaux, eastern Morocco, and Biskra in Algeria were analyzed and compared with Bavarian earth, to which all were inferior. The

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[5] Frey, Robert, Yovanovitch, Branko, and Burghelle, Jean, Morocco Service des Mines, Mém. 38, 1936, 65 pp.

petrographic study indicated that these clays originated not from volcanic ash but from magmas that have been suddenly cooled.

DISTRIBUTION BY GEOLOGIC AGES

The geologic ages of adsorbent clay deposits are of practical interest, because, if the age of one is known, likely places of finding additional deposits of the same age may sometimes be located with the aid of a geologic map. Conversely, the deposits may be helpful in geologic mapping as horizon markers and as indicators of ancient volcanic activity, earlier climatic conditions, and former sedimentation basins. An urgent present need is for greater knowledge of the conditions under which the five different classes of montmorillonite clays are formed and of the composition of their parent tuffs.

Ordovician.—At least two Ordovician deposits, each 2 to 5 feet thick, separated by about 10 feet of limestone, occur in east-central Kentucky. Bentonite high in potassium has been recognized in a belt about 300 miles wide extending from northern Alabama and Georgia into Canada.

Mississippian.—Bentonite of Mississippian age is reported in Nova Scotia.

Permian (?).—Bentonite has been found in western Oklahoma and the Texas Panhandle. Its age is not established; it is possibly much younger than Permian. Permian bentonite is well known in the New Mexico salt beds.

Upper Cretaceous.—At least six Upper Cretaceous formations contain adsorbent clays. Named from oldest to youngest they are the Austin chalk, in northeastern Texas, and the Tuscaloosa formation in Mississippi and South Carolina; the Tombigbee sand member of the Eutaw formation, at Aberdeen, Miss.; the Coffee sand, at Booneville, Miss.; the Neylandville marl, at Corsicana, Tex.; the Nacatoch sand, at Chatfield, Tex.; and the Prairie Bluff chalk, near Pontotoc, Miss.

Eocene.—Clays of Eocene age are found in at least four and probably five formations: Porters Creek Clay of the Midway group, an enormous but impure deposit; Lisbon formation of the Claiborne group, in Choctaw County, Ala. (activable); Tallahatta formation of the Claiborne group, in Clarke County, Ala. (active clay); and two thick, well-separated deposits in the Twiggs clay member of the Barnwell formation, in central Georgia (active clay above, activable clay at base).

Oligocene.—One extensive and very pure deposit of Oligocene age occurs in the Vicksburg group in Mississippi and one in the Flint River formation of Georgia. They are probably the same.

Miocene.—At least one and perhaps several deposits of Miocene age occur in the Hawthorn formation of the Alum Bluff group, in southwest Georgia and northwestern and central Florida, in thick partly isolated beds. There is at least one in the Catahoula sandstone in Texas of probable Miocene age.

Pliocene.—Numerous late Tertiary (Miocene and Pliocene) lake beds of the Southwest contain extensive deposits of very pure bentonite, but, although there are many excellent exposures, much remains to be determined as to their age and correlation.

PHYSICAL PROPERTIES OF ADSORBENT CLAYS

FIELD AND LABORATORY IDENTIFICATION

Among the physical properties of adsorbent clay of general practical or scientific interest are those relating to its identification in field or laboratory, its testing and rating, and its behavior toward water and oils. Means of identification include such properties as texture, density, color, transparency, optical properties, and the property of slaking or swelling in water. The behavior toward water includes the relation between water content and humidity and temperature. Finally the behavior toward oils, fats, and waxes includes the whole gamut of selective adsorption of the hydrocarbons, a property that is the function of adsorbent clay in decolorizing, deodorizing, catalyzing, and stabilizing these substances.

TEXTURE AND COLOR

Although montmorillonite clay can be identified with certainty only by laboratory tests, a good guess may be made in the field. A clay belonging to any of the five classes of montmorillonite clays if fresh from the ground, will usually have a greasy, soapy texture and will cut with a knife like a cake of fresh laundry soap and without any gritty feeling. A shaving will be decidedly translucent like soap. This extra translucency may often be detected even in a partly dry lump at its thin edges in a good light. A sedimentary clay by contrast is opaque to the eye and gritty to the knife, finger nail, or teeth. The translucency and waxy texture are more marked in the higher grade activable bentonites of Mississippi and swelling bentonites of Wyoming than in fuller's earth and impure bentonite clays.

Color is of little significance in distinguishing adsorbent clays from ceramic and sedimentary clays but may be very useful in tracing continuities. Adsorbent clays range in color from coal black to pure white. Tan gray is common, as are gray green and deep red. Much of the Porters Creek clay is a purplish gray. A single bed in Arizona ranges in 40 miles from pink to snow white to tan to dark gray. A marble-cake effect in deep red and light green is characteristic of many beds in southwestern Georgia. Some active clay of the Clayton formation of Midway age in central Georgia is black with organic matter but becomes tan gray after oxidation of the organic matter with chromic acid.

SLAKING

Slaking and swelling tests cannot be made on samples immediately after they have been taken from the ground, but they may be made on partly dried lumps and are best made on a sample that has been air-dried a week or more. Swelling bentonites are of no interest as bleaching clays. An active but not further activable clay (fuller's earth) will neither slake nor swell in either a wet or thoroughly dry condition.

When an activable bentonite, after partial drying, is slaked in water, it always leaves chip-shaped granules, some of which are large enough, 0.1 to 1 millimeter, to be seen with the naked eye. These may be collected and washed on a sieve. Viewed in water under low magnification, they are seen to be transparent at thin edges. The quantity of granules larger than 150 mesh, 0.1 millimeter, may range between 10 and 90 percent of the whole, but in thousands of samples the writer has yet to find an activable bentonite in which these granules are entirely absent. They are as highly activable as any constituent of the clay. They are useful in judging a clay and comparing one clay with another. If the granules are large and abundant, they may be separated by screening and used for special purposes where highly active clays are desired for bleaching by percolation or for use as vapor-phase catalysts.

DENSITY

Density is a reliable rough criterion for adsorbent clays, as they are noticeably lighter than the kaolins and sedimentary clays, size and moisture content being the same. Even fresh moist lumps are noticeably light for their size. Lightest of all are the active clays. For a room-dry lump of high-grade Florida fuller's earth the writer obtained a density of 1.061 with mean grain density 2.251 (compare kaolin, 2.6), voids being 53 percent. This is nearly light enough to float on water. These same grains, after removal of all but structural water by heating to 160° C., showed a mean density of 2.50. In impure active clay and activable bentonite the lightness is hardly noticeable, especially when they are moist.

REFRACTIVE INDICES

Interesting relations between water content and the refractive indices of clays have been obtained by Mehmel.[6] The loss of the

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[6] Mehmel, M., Water contents of kaolinite, halloysite, and montmorillonite: Chemie der Erde, vol. 11, pp. 1–16, 1937.

lattice water in kaolinite by heating to 600° C. drops the index from 1.566 to 1.530. That of halloysite rises from 1.532 to 1.548 on losing the first $2H_2O$, then drops to 1.537 after heating to 600° C. With montmorillonite, the first dehydration up to 200° raised the index from 1.492 to 1.560. Further heating to 400° raised the index only to 1.565; heating to 600° lowered it to 1.529, just below that of kaolinite and halloysite that have been heated to a like temperature. Similar alterations of refractive indices on acid-leaching are considered in the following pages.

The petrographic microscope affords useful supplementary data. The kaolins may be distinguished from the montmorillonite-beidellite group, but the five classes of adsorbent clays show few characteristic differences. The minerals of the kaolin group—kaolinite, dickite, nacrite, and halloysite—have higher indices of refraction (1.55 to 1.57) with low birefringence (0.006), whereas montmorillonite has a low mean index (1.49 to 1.51) with higher birefringence (0.021), and beidellite (class III) has higher indices (1.52 to 1.55) and birefringence (0.031).

In thin section, a moderate magnification easily reveals the texture characteristic of bentonites derived from glassy volcanic shards, if any are present, but the absence of shards is no proof that a clay was not once a bentonite, as the shard structure may have disintegrated. However, as bleaching properties are not confined to clays definitely derived from volcanic ash, the name bentonite is reserved for clays in which such a derivation is evident to some degree. Shard structures may be found in all five classes of bentonite, but neither they nor the montmorillonite forming the shards afford any optical evidence as to the class in which a bleaching clay belongs.

X-RAY PATTERNS

X-ray diffraction patterns (powder photographs) show minor differences between the kaolins and bentonite but none between the different classes of adsorbent clays. X-ray work has shown one very significant feature of montmorillonites. The separation of the lattice planes varies enormously with the water content of the clay, as though the planes were pushed apart by the water. As partial dehydration vitally affects the bleaching power of an active clay, X-ray studies may throw light on the nature of the bleaching action.

CLAY-WATER RELATIONS

No clay as it comes from the ground, wet, will decolorize oil. An active absorbent clay approaches its full bleaching power only after drying to at least 160° C. (320° F.) either in air or in the oil to be decolorized. Heating to 500° C. or higher destroys the bleaching power of an active clay almost completely, along with its hydrophilic nature; that is, only low-temperature water is readily reversible. These considerations indicate the potential value of a careful study of the relations between clay and water.

Water is associated with clays and soils in at least three different ways, distinguishable to some extent by the effects of temperature and humidity upon them.

Lattice water.—The essential or lattice water, which is, strictly speaking, not water at all but H and OH ions built into the unit cells of the crystal lattice as integral parts of it, is most firmly held. These ions may be driven off in pairs as H_2O by heating to a high temperature, usually 500° to 700° C. The expulsion of lattice water is accompanied by swelling in hydrophyllite and vermiculite and probably montmorillonite.

Lattice water lost on heating may be restored only very slowly, if at all, by soaking the material in water—a matter of years with most clay materials at room temperature—though it is said to be restored to dehydrated kaolin in an autoclave in a few hours. When adsorbent clay is deprived of lattice water the bases become nearly insoluble in acid, and the bleaching power is destroyed.

Adsorbed water.—Adsorbed water is of at least three kinds, possibly five. The first inner layer of water molecules or of H and OH ions in contact with an active surface is retained by forces comparable to those of chemical valences. A study of adsorption on silica surfaces (see fig. 8) indicates that the energy of association remains high and with a steep gradient until the adsorbed layer is about 100 molecules deep, then slopes off much more gently to a depth of at least 700 molecular diameters. This outer layer appears to be what varies with humidity, and it is completely removed at zero humidity in a desicator. The inner firmly adsorbed layer, 100 molecules deep, is removed only by heating—the last of it only by heating nearly to temperatures that will drive off lattice water. Silica gel appears to retain some water up to above 900° C.

Pyrophyllite, the kaolins, and many hydrated chemical salts show little or no water adsorption of any kind. Their thermal dehydration curves are flat out to the temperature at which lattice water is expelled, and at all low and moderate humidities at ordinary temperatures they do not adsorb, that is, they are not hygroscopic. Similarly with oil and bleaching clay, in used clay the firmly adsorbed inner coating cannot be washed off with solvents as can the outer layer.

A third kind of adsorbed water is the so-called osmotic water retained on grain surfaces by ions that are themselves adsorbed in accordance with the Donnan equilibrium. The literature on the subject bearing on soils is extensive.[7] Adsorbent clays, however, of both the active and activable types, seem to have few adsorbed ions other than hydrogen and hydroxyl. The Donnan theory applicable to water solutions might be modified to apply to the adsorption of oil on clay but with no probable results commensurate with the labor involved.

It is readily seen that the adsorption of water must run parallel with the bleaching action. The bleaching clay must be a powerful adsorber of water and have high adsorption capacity, so that, when deprived of that water, it will powerfully adsorb the open and multiply the bonded and polar constituents from oil. Many minerals, such as kaolin and pyrophyllite, do not bleach oil, because they do not markedly adsorb either water or oils. Chemical composition is of no consequence, except as it may influence the adsorption of polar molecules of a single kind; in other words, the thermal dehydration curve must have a pronounced slope before the shoulder indicating loss of lattice water is reached. The dehydration curves of the hydrous oxides of aluminum and iron have such a slope, but it is short and their bleaching power is low. Silica gel is a powerful adsorbent for water, but its capacity is low, about 4 percent, and its bleaching power is also low.

The close correlation between bleaching power and water driven off in the range 50° to 200° C. was pointed out in Circular 3.[7a] However, at that time the cause of the further drop in weight at the 500° shoulder (not producing but destroying bleaching power) was unknown. Recent work on pyrophyllite has shown this shoulder to be due to lattice water similar to that in montmorillonite, and the close correlation between bleaching power and loss of adsorbed water is made evident. This holds up to temperatures at which the lattice structure breaks down. If lattice water escapes (water of hydration is given off) before all the adsorbed water is removed, careful work is required to distinguish between lattice and adsorbed water. Shoulders due to hydrates stand out above the normal smooth dehydration curves due to adsorbed water. The curves for the fuller's earths and hydrous oxides are conspicuous examples, as shown later.

Free-pore or capillary water.—A third class of water in clay, free-pore or capillary water, may exist when grains are coarse and the structure loose, but in the purer montmorillonite clays carrying a substantial overburden there seems to be little if any free water. The 50 to 60 percent of water carried by such clays in place appears to be practically all either adsorbed water or water of hydration, and its loss on drying alters the properties of the clay.

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[7] Anderegg, T. O., and Lutz, R. P., Soil Sci., December 1927, p. 403. Mattson, Sante, idem, April 1932, p. 301.

[7a] Nutting, The bleaching clays: U. S. Geol. Survey Circ. 3, p. 40, 1933. [Mimeographed.]

ADSORBED AND LATTICE WATER

The adsorption of pure water on a clean surface free from pores is shown in figure 8. In the paper in which this figure first appeared,[8] data on heat of wetting per gram of silica were reduced to energies of association as a function of thickness. Parks' constant, 0.0105 cal./cm.^{2}, for the total heat of wetting of a surface was used to compute the specific surface, in this case 25,000 cm.^{2} per gram. The two markedly different slopes of the pressure gradient curve are clearly shown with the transition at 4–5$\times 10^{-6}$ cm., which is roughly 100 times the diameter of a water molecule (4×10^{-8} cm.). The inner portion of the adsorbed film of water is seen to be very strongly held with a pressure known to be many thousand atmospheres and is probably ionic (H and OH). The outer portion is only loosely held and would evaporate in dry air.

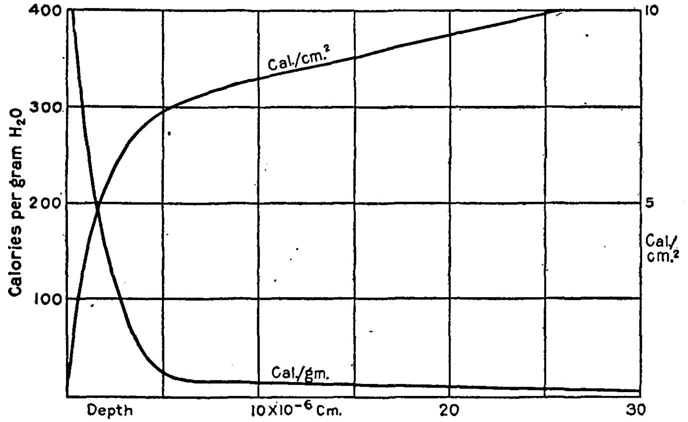

FIGURE 8.—Heat of wetting and adsorption potential in the film of water adsorbed on silica.

These determinations relate to finely powdered silica. Silica containing different amounts of water, found by weighing, was immersed in water and the heat generated measured. From this heat and the computed specific surface the writer has computed thicknesses of water film, adsorption potentials, and the corresponding cohesive pressure as given in the following table.

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[8] Nutting, P. G., The adsorptive force of silica for water: Jour. Phys. Chem., vol. 31, pp. 531-534, April 1927.

Adsorption of water on silica

Thickness of film (centimeters)	Heat of wetting (calories per square centimeter)	Adsorption potential (calories per gram)	Cohesive pressure (atmospheres)
0.0×10^{-6}	(?)	420	17, 410
.5	1. 8	353	14, 630
1.0	3. 1	274	11, 360
1.5	4. 4	205	8, 500
2.0	5. 3	157	6, 510
2.5	6. 0	120	4, 970
3.0	6. 45	88	3, 650
4.0	7. 04	44. 5	1, 845
5.0	7. 32	22. 0	912
7.5	7. 72	16. 5	684
10.0	8. 18	15. 1	626
15.0	8. 82	12. 1	502
20.0	9. 42	11. 5	477
25.0	9. 94	8. 7	361
30.0	10. 28	5. 6	232

The adsorption potentials shade off to nothing for thick films, as they are obtained by an immersion method. In air they would be higher by the surface energy of water (32.8 callories per gram at 25° C.).

On account of the difficulty in making accurate observations of small quantities of heat and the small differences upon which some of the calculations rest, it seemed advisable to check these fundamental data by other simpler and more direct methods.

Clear crystalline quartz was ground to pass a 300-mesh sieve, left over night to come to equilibrium with air moisture, and then weighed at intervals of 24 hours in a crucible suspended from a balance at furnace temperatures of 29° to 800° C. Adsorption potentials (energies of association of water with the quartz) are calculated from the slope of the weight-temperature curve in terms of energy in calories per gram of water, $q=\frac{R}{M}\frac{d \log C}{d\ (1/T)}$, in which $R=1.986$ (the gas constant), M is molecular weight ($=18.00$), C is water concentration (in any units since $d \log C=dc/c$ is of zero dimensions), and T absolute temperature. There is less uncertainty in these energies than in film thicknesses computed from weight of water (5.1 milligram per gram of quartz at 25°) and specific surface (about 560 $cm.^2$ per gram) from direct measurements of grains. Weights are corrected for the variable buoyancy of air at different temperatures. It is significant that powdered quartz loses its power of adsorption after being heated to 800° C., that is, such miscellaneous valence bonds as are left open by fracture close themselves on heating, as do those of active and activated clays.

The results obtained are given in figure 9 and the following table. The weight-temperature curve for powdered Pyrex glass is added for comparison. The shoulder on the latter is apparently caused by a compound that is stable up to about 260° C.

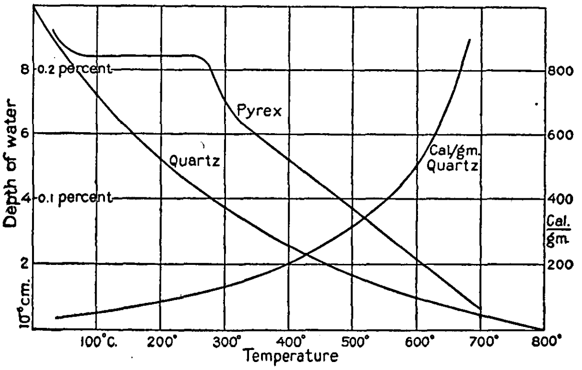

FIGURE 9.—Adsorbed water and adsorption potentials for powdered quartz and weight-temperature curve for powdered Pyrex glass.

Adsorption potentials and film thicknesses for powdered quartz

Thickness of film (centimeters)	Temper ture (°C.)	Adsorption potential (calories per gram)	Thickness of film (centimeters)	Tempera- ture (°C.)	Adsorption potential (calories per gram)
9×10^{-6}	30	34	5×10^{-6}	211	88
8	65	40	4	278	118
7	107	53	3	359	168
6	155	67	2	460	260
			1	600	450

These adsorption potentials are of the same order of magnitude as those above found from the heat of wetting of silica. Considering the uncertainty in the area of surface exposed, the base weight for anhydrous quartz (the weight is still decreasing at 800° C.), and the possibility of sintering, the agreement is surprisingly close. The slope of the straight portion of the curve for glass (350° to 700°) indicates an energy of association of 69.6 calories per gram of water. The mean slope of the weight-temperature curve for silica gel from 160° to 700° gives 66.7 cal./gram, nearly the same as for glass, although the amount adsorbed is 15 times as great.

ADSORPTION AND HYDRATION OF MONTMORILLONITE

Water in the montmorillonite group of minerals is associated in several different ways, instead of the single one discussed above for plain quartz surfaces. Conspicuous among these are water built into the lattice sheets, water adsorbed on the surfaces of lattice sheets, and water of hydration. Capillary and osmotic water probably occur only in negligible amounts, except at low temperatures.

The weight-temperature curve is given in figure 10 for the purest known montmorillonite, that is, bentonite containing no foreign material, such as other clay material, silt, or unaltered glass, not reworked or redeposited and not further altered by weathering, leaching, or oxidation. Curve A of figure 10 is a composite of three almost identical curves, two of bentonites of practically the same composition from the Vicksburg formation ($RO:R_2O_3:SiO_2=0.82:1:4.5$) and one of a Bavarian bentonite that differs but slightly in composition. The constant vapor pressure was 14.7 millimeters, or 62 percent relative humidity. The percentage of water relative to the weight of clay at 800° C. as base is as follows:

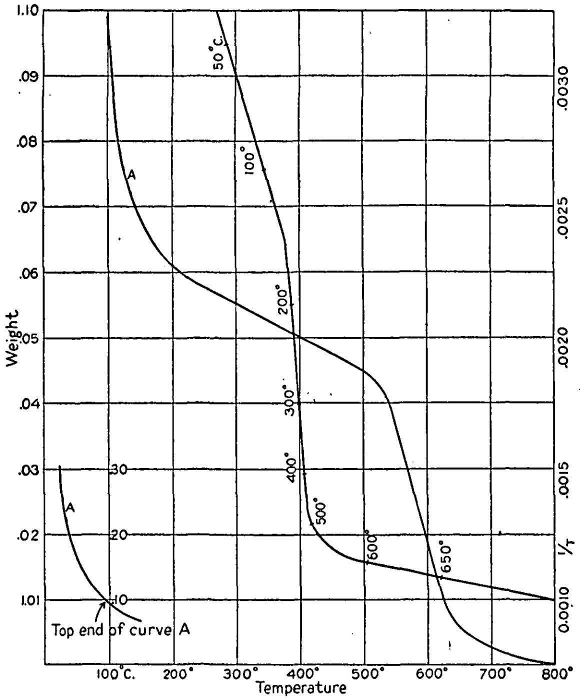

FIGURE 10.—Weight-temperature and log C(1/T) curves for normal bentonite.

Temperature (° C.)	25	50	75	100	150	200	300	400
Water (percent)	30.5	16.4	12.4	9.90	6.81	6.08	5.51	5.00
Temperature (° C.)	500	525	550	600	625	650	700	------
Water (percent)	4.49	4.30	3.70	1.90	1.00	.58	.25	------

The drop in the weight-temperature curve from 500° to 800° C. is ascribed to loss of structural or lattice water, the straight line portion from 200° to 500° C. is thought to characterize interlattice adsorbed water, and the low-temperature drop of 25° to 150° C., probably indicates the breakdown of one or more hydrates stable only at low temperatures and high humidities. The interlattice adsorption is evidently different in nature from that on a quartz surface, indicated in figure 9. This linear relation between weight and temperature is characteristic of all the montmorillonite group of clays but has yet to be explained, though vital to the theory of selective adsorption.

The plot of log concentration of water as a function of reciprocal absolute temperature breaks up into three straight lines. At low temperatures, 50° to 150° C., the slope indicates an energy of association of water with the clay of 136.8 calories per gram. From 150° to 480° C. it is 37.2 calories per gram (adsorbed water), though the lattice water is apparently retained with an energy of about 2,000 calories per gram. The rounding off of the curve between 480° and 590° C. indicates that lattice water begins to escape before all the adsorbed water has left the clay.

The two energy lines for hydrate and adsorbed water intersect quite sharply at 153° C. and 6.7 percent water, indicating very little overlap in these two kinds of thermal dehydration. The two energy lines for adsorbed and lattice water, if produced, intersect at a point indicating 480° C. and 4.6 percent water, which may be interpreted as the point at which lattice water begins to escape. Calculated according to composition, $1H_2O$ for these bentonites is 4.36 percent.

Further evidence as to the nature of the energy of interlattice (adsorbed) water is furnished by X-ray studies by W. Bilke and others on the relation between swelling and water content in montmorillonite which is discussed later. The point at issue is the interpretation of the linear decrease in adsorption potential with increase in water content, in terms of structure.

VAPOR PRESSURE OF WATER IN CLAYS

Bentonites in the ground contain 50 to 60 percent by weight of water, which is about $30H_2O$ in molar proportion to Al_2O_3. Lumps of bentonite in equilibrium with a water-saturated atmosphere, over water in a closed vessel, contain about 45 percent of water, or $19H_2O$. When room-dry they contain 20 to 25 percent of water, or $1+6H_2O$. In a very dry atmosphere, over P_2O_5 or concentrated H_2SO_4, the water content is 8 to 12 percent, of which about 4.5 percent is lattice water, 2 percent is adsorbed water, and the remainder is water of hydration. As shown by Bradley, Grim, and Clark,[9] bentonites take up and give off water in blocks of $6H_2O$ per unit cell, their X-ray analyses showing corresponding discontinuities in the separation of the lattice planes. In normal bentonite, $1H_2O$ (4.36 percent) is structural water. The various hydrates then contain $(1+3\ n)H_2O$, the lowest being stable at room temperature and 60 percent humidity and containing 23.3 percent of water. These hydrates are being further investigated by vapor pressure and rate of drying methods.

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[9] Bradley, W. F., Grim, R. E., and Clark, G. L., A study of the behavior of montmorillonite upon wetting: Zeitschr. Kristallographie, vol. 97, pp. 216–222, 1937.

A block and a powder of the same room-dry clay placed in a saturated atmosphere take up the same amount of water, about 45 percent, in about the same time, showing that the surface effect is slight. Equilibrium is approached in 1 or 2 months, the half way point in as many days.

Clay muds belong to an interesting class of substances, wet gelatine being a familiar example, which will lose water even in a saturated atmosphere. Powdered glass will not. A bentonite mud so thin as to settle out, leaving as much as 2 millimeters of clear water above it, will gradually lose water, crack, and shrink, ending of course with the water content (42 to 45 percent) of a lump in a water-saturated atmosphere. A highly activable bentonite, a swelling almost inactivable bentonite, and an ordinary lake mud show no essential difference in this behavior. All these shrink at least 40 percent after starting to crack. The formation of hydrates stable only at low temperatures suggests itself. The matter appears to be well worth further study.

The moisture content of a number of materials brought to equilibrium with air of various humidities are given in the following table and in figure 11. These data are selected from Circular 3.[10] Other data showed that the effect of apparent grain size, aging, and of a gentle preliminary heat treatment is so small as to be negligible, but the effect of impurities in the hydrous oxides is large. Heating to 800° C. increases the water-holding power of raw serpentine but greatly decreases that of the bentonites. We are here interested chiefly in energies of association.

Moisture content of clays at different humidities

[Percent by weight, grams of water per 100 grams of clay at zero humidity]

Relative humidity (percent)	A	B	C	D	E	F	G	H	I	K	−RT log H (calories per gram)
5	1.5	3.0	2.6	2.0	3.7	2.2	2.25	2.2	4.0	2.8	98.8
10	2.5	4.8	4.0	3.5	6.0	3.5	4.15	3.7	7.5	5.0	75.9
20	4.0	6.9	6.0	6.0	9.1	5.5	6.90	5.8	12.8	8.2	53.1
30	5.4	8.3	8.2	8.2	12.2	7.1	8.45	7.3	15.8	11.1	39.7
40	7.5	10.5	10.7	10.9	15.5	8.7	9.35	8.4	17.4	13.8	30.2
50	9.8	14.3	13.1	14.6	18.8	10.2	10.2	9.6	19.3	19.2	22.9
60	14.5	19.3	14.9	18.9	21.9	11.7	11.5	11.8	21.8	28.6	16.8
70	28.4	24.8	16.2	24.3	25.1	13.3	13.7	15.0	25.0	38.3	11.8
80	57.3	29.6	16.9	27.8	28.3	16.3	17.9	20.7	29.1	46.4	7.36
90	61.9	32.5	17.2	29.5	33.6	22.4	28.6	31.3	34.6	53.1	3.47
95	62.8	33.5	17.3	30.1	38.5	31.4	38.5	40.8	41.1	56.2	1.69
800° C	------	------	------	−8.3	------	−19.9	−10.9	−6.7	−9.5	−10.2	---------

A. Pure silica gel (SiO_2), prepared by the writer, 100 mesh.
B. Alumina (Al_2O_3), prepared by the writer, 100 mesh.
C. Iron oxide (Fe_2O_3), prepared by the writer, 150 mesh.
D. Acid-leached serpentine, white, 150 mesh.
E. White otaylite (bentonite) from California, 150 mesh.
F. Permutite, Folin preparation, 100 mesh.
G. Fuller's earth from Quincy, Fla., Floridin Co., 150 mesh.
H. Fuller's earth from Macon, Ga., General Reduction Co., 150 mesh.
I. Bentonite from Chambers, Ariz., Filtrol Co., raw, 150 mesh.
K. Bentonite, same as I, activated.

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[10] Nutting, P. G., The bleaching clays: U. S. Geol. Survey Circ. 3, 51 pp., 1933. [mimeographed.]

In the last column is given the work or energy necessary to bring water vapor at the partial pressure of the first column to its saturation pressure, that is, the external work done by the clay. R is 1.98. T=26+273=299. RT log H is calories per mole; divided by 18 it is calories per gram. The work of condensation from saturated vapor to liquid water is an additional RT cal./mole, so that the total is RT (1+log H), but we are concerned here only with the effect of adsorption. Relative humidity, H, multiplied by 25.1 gives vapor pressure in millimeter Hg.

The graphs of clay moisture versus vapor pressure (fig. 11), show some characteristics worth noting. None of these clays or hydrous oxides strictly obey Henry's law (concentration of water proportional to pressure); although the curve for the Otay clay (E) is very straight between 10 and 80 percent humidity. Hence water is not held in simple solution in these materials.

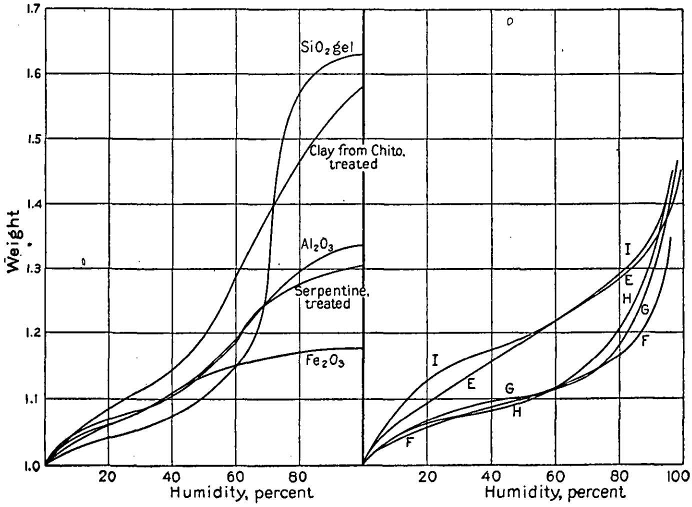

FIGURE 11.—Weight of various adsorbent materials at different humidities and constant temperature (26° C.).

E, White otaylite (bentonite) from California.
F, Permutite.
G, Fuller's earth from Quincy, Fla.
H, Fuller's earth from Macon, Ga.
I, Bentonite from Chambers, Ariz., raw.

All the clays and hydrous oxides take on water with great avidity at low vapor pressures, followed by a lower rate at 40 to 50 percent humidity (room conditions). At the highest vapor pressures, 80 to 100 percent humidity, approaching saturation, the simple oxides appear to form definite hydrates. SiO_2 is $SiO_2.2H_2O$ at 84 percent humidity ($SiO_2.2H_2O$: SiO_2=1.60); Al_2O_3 is approaching $Al_2O_3.2H_2O$ (ratio 1.35); and Fe_2O_3 at 17.3 percent humidity is very close to

$2Fe_2.O_3.3H_2O$ (ratio 1.17). The residue from acid-leached serpentine is nearly pure silica and approaches $SiO_2.H_2O$ very closely. The silica in partly leached (activated) Chambers bentonite is near $SiO_2.2H_2O$ at high humidities, but its curve resembles that of raw bentonite (I).

On the other hand, the clays and the synthetic "zeolite" permutite (F) are extremely sensitive to humidity changes in the higher range. The curves all shoot up with no indication (at 26° C.) of a hydrate shoulder, unless this be at 50 to 60 percent water content and with supersaturation. Their behavior in the middle range of humidities, 40 to 70 percent, indicates two distinct classes of clays. The two bentonites E and I contain twice as much hygroscopic water in this range as the two fuller's earths G and H and the "zeolite" F.

A relation between the amount of water in a clay and the energy of its association with the clay is of interest. From the preceding table and figure 11 it is readily found that for silica gel the energy change is 20 calories per gram for a water change from 2 to 3 percent, 0.2 calories per gram for 1 percent change in concentration at 45 percent, and again large and about 2 calories per gram near saturation (energy of hydration). For the clays, similar energy rates are obtained, except that they do not increase again approaching saturation. No strictly linear relations appear in any of the graphs.

As the water-clay relation is in a sense a solution, plotting log concentration of water against log H (or energy RT log H) is suggested. Such graphs are straight lines from low concentrations up to above 20 percent water. In this range therefore $\log H = a + b \log C$, where a/b is the value of $-\log C$ when $H = 1$ (saturation) and $b = d \log H : d \log C$, the slope of the line. Since $H = p/P$, $p = KC^b$, which is identical with the empirical Freundlich relation between adsorption and the density of the adsorbed gaseous or dissolved material. The constant b is close to 1.5 for each of the clays and hydrous oxides listed. It is of course independent of the units in which either pressure or concentration is measured.

The slope of the $\log H - \log C$ line (H=humidity, C=concentration) gives the energy of association of the loosely adsorbed water. That energy is constant at low humidities but indicates hydrate formation as saturation is approached.

Four typical logarithmic curves are reproduced in figure 12. They show the initial straight portion, followed by a dip and then a rise for the untreated bentonite and the fuller's earth but the opposite sequence for the acid-leached bentonite and silica gel. Writing E for the external energy of adsorption, $E = RT \log H = RT (\log p - \log P)$. But $\log H = a + b \log C$ for any straight portion of such curves and therefore $d \log p = b\, d \log C$ is the relation between vapor pressure and concentration of water in a moist clay under isothermal conditions, T and P not varying.

For the initial straight portions of each of these four curves (low vapor pressures), $d \log c : d \log H = 0.757$, corresponding to an energy of association of about 25 calories per gram of water. This must therefore be the work done in pushing apart the lattice sheets. If the lattice sheets are pushed apart bodily without internal change in those sheets and with but negligible compression of water the pressure involved is simply $25 \times 42 \times 10^6 = 105 \times 10^6$ dynes/cm.^{2} $= 106$ atmospheres. This is less than one-twentieth of the internal cohesion pressure in pure water and somewhat less than the force holding the inner layer of water adsorbed on an external surface.

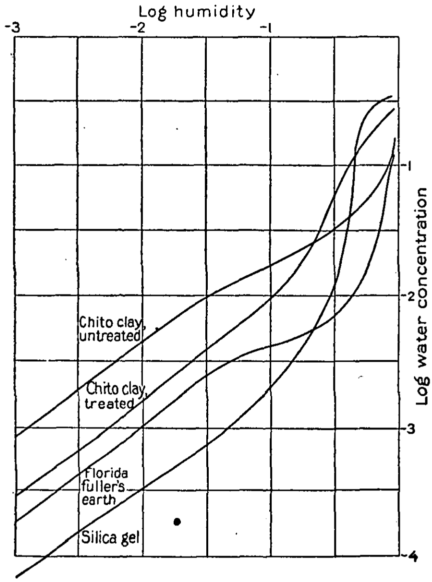

FIGURE 12.—Energy of hygroscopic water.

THERMAL ANALYSIS OF CLAYS

Clay and many other minerals, weighed at 50° intervals (time being allowed to attain constant weight) from room temperature to 800° C., show a weight decrease whose irregularities are characteristic and repeatable with considerable accuracy. The preferred method is to place a gram or two of 150-mesh (0.1 mm.) clay in a platinum crucible suspended by a fine platinum wire from one arm of a balance in a vertical furnace below the balance. Furnace temperatures are regulated by a rheostat and measured by a thermocouple. Weight varies with room humidity only below about 170° C. The correction for weighing in hot air of lower buoyancy is about 2 mg./gm. at 800° C.

Weight-temperature curves for a few clays and related minerals are given in figure 13. In the first group are:

Dickite in fine transparent crystals, from Pennsylvania.
Kaolinite, typical.
Diaspore, from Rolla, Mo.
Goethite, from marcasite, going to hematite, 250° to 310° C.
Gibbsite, synthetic, very pure $(\times \frac{1}{4})$. Curve shows absence of $Al_2O_3.2H_2O$.
Ferric oxide, amorphous, pure. Note absence of hydrate shoulders.

In the second group are:

Serpentine asbestos, $Fe<0.3$ percent. If impure, the curves are lower and more rounded.

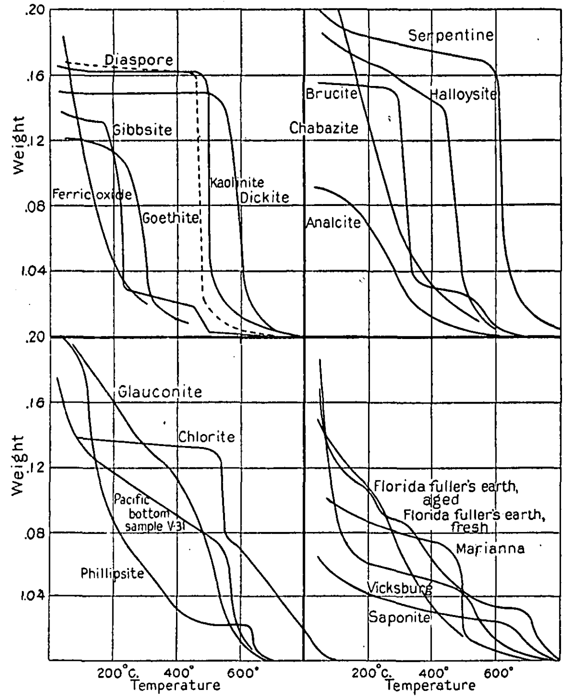

FIGURE 13.—Weight of various clays and related minerals at different temperatures and constant humidity.

Halloysite, mean of five samples, curves almost identical.
Brucite, pure, from Nevada $(\times \frac{1}{3})$.
Chabazite, pure, crystalline. Shoulders absent as in permutite, allophane, and amorphous hydrous oxides.
Analcite, pure crystalline material.

In the third group are:

Chlorite, green, from Danville, Va. Note odd shoulder and slope.
Glauconite, from New Jersey $(\times 3)$.
Phillipsite, white, crystalline.
Pacific bottom sample, T. W. Vaughan, 31. Curve unlike glauconite or phillipsite but very like a bentonite.

The fourth group shows curves for different montmorillonite clays:

Florida fuller's earth, fresh from the ground.
Florida fuller's earth, room-dried for several years.
Beidellite type from Marianna, Fla.
Bentonite from Mississippi, Vicksburg group, typical of most pure bentonites.
Saponite, magnesian bentonitic clay, low but stable hydrate.

The curve for fresh fuller's earth exhibits the four shoulders associated with well-hydrated montmorillonite at low temperatures, near 220°, near 320°, and in the region of 500° to 700° C. The last, owing to lattice water, is the most persistent, yielding only to prolonged weathering, drying, or leaching with acid. The two middle shoulders are much more easily affected. The hydrate stable only at low temperatures and high humidities has been established for only a few clays but may be found to be characteristic of all.

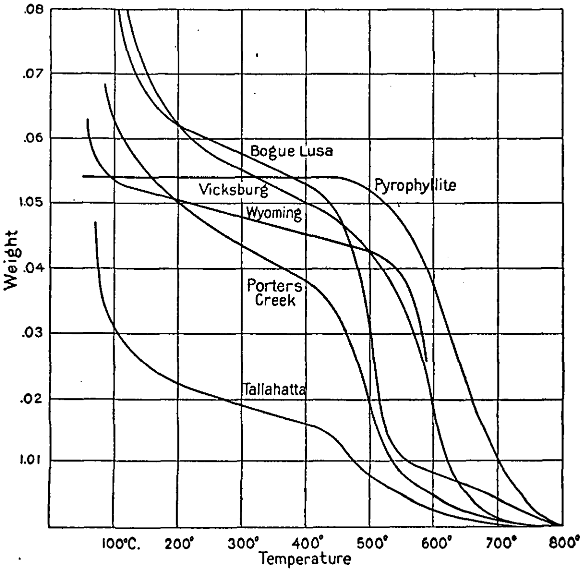

FIGURE 14.—Weight of various clays and of pyrophyllite at different temperatures and constant humidity.

The typical pure bentonite of the Vicksburg group, from Mississippi, is representative of all those that are normal. Many of these curves are given in Circular 3. Essentially different are the fuller's earths, the beidellites, and the highly magnesian bentonites. The montmorillonite from Montmorillon, France, a similar mineral from Santa Cruz, N. Mex., and an active clay from Tehachapi, Calif., however, exhibit an additional small shoulder at 740° C. Bentonites that are high in magnesium are usually less hydrous but more stable than the normal ones; some are the reverse. Few have been studied.

Thermal curves for several types of bentonitic clay are shown in figure 14, and the curve for pyrophyllite, which is similar in composition but different in structure, is added for comparison. The curve marked Vicksburg is for the purest montmorillonite bentonite known. The curve for the swelling Wyoming bentonite, which is high in sodium, is similar but lower. That for a typical Bogue Lusa clay is higher but breaks at a lower temperature. The curves for Porters Creek and Tallahatta show the effects of admixed impurities and of oxidation.

Figure 15 shows some of the significant variants of the thermal dehydration curves thus far determined. The curves in the upper left corner are for normal Otay bentonite and for the nodules washed out of the same clay, dried and ground. The nodules retain less water below the shoulder and more at 600° C., indicating that they are the most stable portion of the clay. Only lattice water is present in either clay at that temperature.

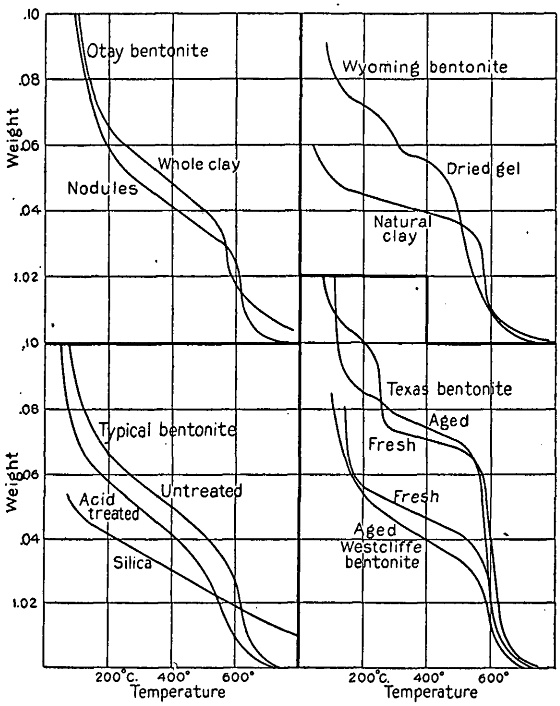

FIGURE 15.—Thermal dehydration curves for coarse and fine constituents and for acid-leached, dry-aged, and moist-aged adsorbent clays.

The curves in the upper right corner are for the swelling Wyoming bentonite. The lump clay gives the lower curve. The upper curve is for material obtained by evaporating the thin water suspension that had been standing over the clay for some months. The 220° and 300° hydrates are marked, but the chief shoulder at 580° is missing from the curve for the dried gel, as though lattice water were absent.

The curves for bentonite in the lower left corner are typical for raw and acid-activated material. The partial removal of bases by acid drops the whole curve toward the silica gel curve, except at the high-temperature end. Some lattice water has been removed. Two bentonites submitted by W. P. Kelley, which had had part of their bases substituted by hydrogen by electrodialysis after very fine grinding, showed precisely the same shift downward and to the left from the original raw clays, as would be expected if acid treatment is essentially a substitution of hydrogen for other bases.

The two pairs of curves in the lower right corner indicate the effects to be expected of different kinds of aging. The upper two represent a Whitewright Texas Upper Cretaceous bentonite fresh from the ground and the same after 10 months as a room-dry powder. The effect on the 220° hydrate is marked. At 400° the aged clay holds more water than that first dried. The reverse is true for Westcliffe bentonite, the lower pair, fresh and aged moist for 18 months. The high temperature effect is also reversed, the moist aged sample being less stable at 600° than the fresh.

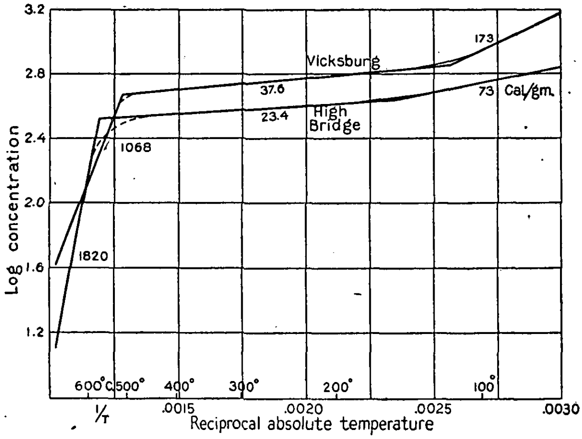

FIGURE 16.—Energy of association of water with clay.

In figure 16 are plotted log water against 1/T for the Oligocene bentonite of the Vicksburg group and for the Ordovician bentonites of High Bridge, Ky. The water is referred to the weight of clay at 800° C. as a unit, but, as d log $C = dC/C$, any other unit would serve as well. $T = °C + 273$. Each curve breaks up into three straight lines, the slope of which indicates the energy of association of water with clay. That energy is lowest for the middle range, 150° to 500° C., and is lower for the Ordovician than for the Oligocene bentonite, except at temperatures above 500° C. This indicates that lattice water is more firmly held by the older clay and osmotic and adsorbed water by the younger.

The above weight-temperature relations may be viewed in the light of the well-known facts of bleaching versus temperature of drying. The writer's standard temperature of drying (160° C.) preceding a cold oil-bleaching test is just sufficient to remove "free" and osmotic water and bring the clay to the middle straight portion of the dehydration curve now thought to represent interlattice adsorption. Tests with heated oil indicate that bleaching power continues to increase at higher temperatures up to at least 370° C.; hence the capacity of clay for selectively adsorbing oil increases steadily with the removal of adsorbed water.

On the other hand, an active clay heated to redness (above 500° C.) in air loses nearly all its adsorbing power. What it would do if heated in oil with all oxygen excluded is not yet known. A lump of activable room-dry bentonite dropped in a furnace at 1,000° C. puffs up like popcorn and is thereafter not only inactive but inactivable and insoluble in acid, with probably complete destruction of the lattice structure.

ADSORBENT CLAYS AND OILS

The value of an adsorbent clay lies in its ability to select and retain certain minor constituents from a mass of oil, melted fat, or wax. Commonly these minor constituents are such as cause color, odor, or taste and are classed roughly as unsaturated hydrocarbons. Olefins are removed from paraffins and napthenes from aromatics, but with sidechains and radicals frequently present in wide variety and number the matter is by no means simple. Gasoline obtained by cracking is deprived of its color and antiknock properties by passing through active clay.

As removal of all free and at least part of the absorbed water from an active clay is necessary to put it in commission, and as removal of H and OH ions would leave open bonds, the writer was led to the open-bond theory of selective adsorption as a summary of the evidence and a fundamental working hypothesis. The free bonds on the clay surfaces unite with the free or easily broken bonds of the passing oil, constituting selective adsorption. With moist clay in hot oil there appears to occur a simple base exchange.

Gasoline and benzine are among the liquids easiest to free from color and other impurities with active clay. Lubricating oils, cottonseed oil, and palm and linseed oils are intermediate. Rosin oil, burned crankcase oil, and petroleum containing several percent of sulfur bleach very little without a preliminary treatment. Lard, oxidized and polymerized by long use in doughnut machines, is very difficult to bleach. An ether or an ester added to a mineral oil does not greatly affect its bleaching, but an alcohol inhibits bleaching. Chlorine compounds like $C_2H_2Cl_4$, $C_6H_3Cl_3$, or CCl_4 considerably enhance bleaching. In other words, free acid, H and OH, mercaptans, sulfonates, etc., inhibit bleaching action, although chlorine appears to assist. The water normally present in cold mineral oil (about 0.02 percent) is too little to decrease the bleaching action greatly.

Many activated clays and a few untreated ones will crack water-white gasoline, neutral laxative oil, or fused paraffin, becoming dark red or black in a few minutes by adsorbing the cracked portions and leaving the oil, or paraffin water white as before. The Georgia-Florida fuller's earths do not do this, but many of the class III beidellite bentonites, which are naturally active, are effective cracking agents. It is reasonable that a highly active surface should be able to break up a long hydrocarbon chain, but why cracking and bleaching powers do not run parallel is yet to be explained. As cracking is a waste of both oil and clay, a maximum of bleaching with a minimum of cracking is desirable.

The stability of a bleached oil is a matter of moment in many instances. Oils treated with the milder fuller's earths possess satisfactory stability, but those treated with activated bentonites tend to age rapidly, probably on account of an excess of disrupted and unpaired radicals resulting from the powerful adsorption.

The amount of oil retained by a spent clay after washing with naptha and blowing with steam or hot air is of special importance when valuable oils are being decolorized. The retention of a clay appears to depend on factors not yet worked out. Of the two clays now most in favor for bleaching cottonseed oil, one is hard and dense whereas the other is extremely light and fluffy.

One essential difference in the action of clay on oil is to be kept in mind in considering the relative merits of the contact and the percolation methods of bleaching. The percolation method is essentially a counter-current method, in which the oil advancing into the fresh clay is that which has been most bleached. In the contact method clay grains are brought at once into contact with the blackest oil, and the coat first adsorbed is that most easily adsorbed. If the same amounts of clay and oil that will give a water-white product by the percolation method are used in the contact method (mixing and straining), only a deep-red product is obtained; i. e., the efficiency is about half. On the other hand, a clay having a high cracking tendency would be wasteful of oil in the percolation method.

The writer is indebted to Herbert L. King, Jr., director of testing and research of the Attapulgus Clay Co., for the data, later published,[11] given in figure 17, which shows relative bleaching powers at different temperatures. This investigation was made by a percolation method, the apparatus being enclosed in a tank held at a fixed known temperature. The test oil was topped crude oil. The unit of bleaching power was that of Attapulgus clay at 200° C. The bleaching power of the

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[11] Funsten, S. R., Oil and Gas Jour., June 3, 1937, p. 57.

activated clays shows large increases at the higher temperatures whereas that of the fuller's earth is but little affected. The behavior of the acid-sprayed fuller's earth (beidellite?) is intermediate between the two types.

The implication of these curves is that firmly adsorbed water ions are driven off even up to the highest operating temperature (700° F.), whereas high temperature has but a slight effect on the bleaching power of the fuller's earth. The thermal dehydration curves (fig. 14) show that the fuller's earths lose even more water than the activated bentonites in the range 150° to 450° C. The inference then is that the water lost by the fuller's earths in that range is largely hydrate water rather than adsorbed water, whereas with the activated bentonites it is all adsorbed water. Evidently the black oil aggregates are too large to enter lattice pores left by the escape of H and OH ions. In the change from bentonite to fuller's earth (both dominantly montmorillonite) additional low-temperature hydrates are provided for, but the pyrophyllite lattice is stable up to about 500° C.

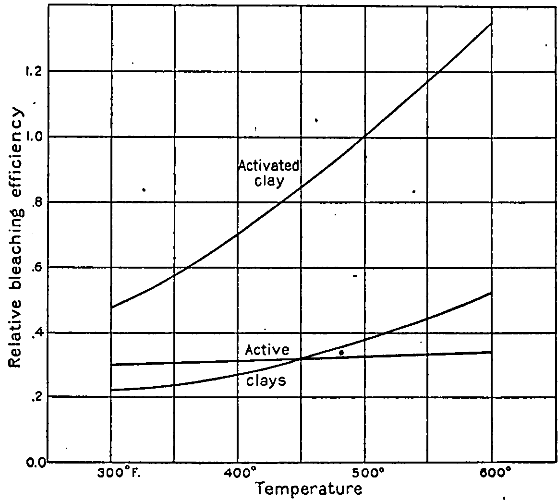

FIGURE 17.—Relative bleaching power of various clays at different temperatures, with Attapulgus clay at 200° C. as unit. Cylinder stock bleached to definite shade of red.

CHEMICAL PROPERTIES OF ADSORBENT CLAYS

COMPOSITION AND STRUCTURE

The correlation of adsorbing power with either chemical or mineral composition, with molecular structure, or with thermal dehydration is not complete, and any general relation that may be formulated is subject to numerous exceptions. A clay that is dominantly montmorillonite-beidellite is quite likely to be active and/or activable, but the swelling bentonites are exceptions, as are also most montmorillonites not derived from volcanic ash or tuff. Limiting the montmorillonites to those that have been derived from ash and do not swell in water excludes the well-known Georgia-Flordia active clays. On the other hand, glauconite, some serpentine, olivine, and hydrous alumina activate.

The lattice structure shown by X-rays shows no better correlation with adsorbing power. In the lattice, $a=5.19$ and $b=8.98\times10^{-8}$ cm., very nearly, for at least 15 different minerals, including the kaolins, micas, talc, halloysite and pyrophyllite, which do not activate at all. Montmorillonite is outstanding only in the large variation of the c dimension with the water content of the clay. Both the weight-temperature curve and the c spacing of a clay (see figs. 10, 18) indicate regions of concentration of water in clay in which adsorption is dominant. Montmorillonite differs from pyrophyllite in having extra variable lattice layers of water.

A few selected chemical analyses of adsorbent clays are given in the following table. They include type material of each of the five classes, Ordovician bentonites from High Bridge and theoretical beidellite and montmorillonite, the last with MgO:CaO=2:1.

Chemical analyses of typical montmorillonite clays

	1	2	3	4	5	6	7	8
SiO_2	59.57	50.20	55.40	64.46	51.28	53.12	50.87	50.73
Al_2O_3	19.67	16.19	23.68	12.95	10.56	18.72	28.78	17.22
Fe_2O_3	2.91	4.13	3.76	2.38	6.73	1.12	--------	--------
MgO	2.46	4.12	1.09	2.36	10.40	6.92	--------	4.54
CaO	.66	2.18	.05	3.17	1.44	1.40	--------	3.16
K_2O	.29	.16	1.73	2.55	Trace	5.72	--------	--------
Na_2O	2.09	.17	.02		Trace	Trace	--------	--------
TiO_2	Trace	.20	.78	.21	Trace	--------	--------	--------
H_2O^-	7.49	15.58	5.50	6.31	7.86	6.56	20.35	24.35
H_2O^+	4.73	7.57	8.00	5.42	12.42	5.48		
	99.87	100.50	100.01	99.81	100.69	99.04	100.00	100.00

1. Swelling bentonite from Thornton, Wyo. Mines of the American Colloid. Analysis supplied by that company.
2. Bentonite of Vicksburg group, Smith County, Miss. R. E. Stevens, analyst.
3. Beidellite from near Marianna, Fla. J. G. Fairchild, analyst.
4. Active clay from near Creede, Colo., Peerless Clay Co. Analysis supplied by the company.
5. Attapulgus, Ga., fuller's earth. Attapulgus Clay Co. Producer's analysis.
6. High Bridge, Ky., Ordovician bentonite, lower bed. E. V. Shannon, analyst.
7. Beidellite corresponding to $Al_2O_3.3SiO_2.4H_2O$.
8. Montmorillonite as $(Mg, Ca)O.Al_2O_3.5SiO_2.8H_2O$, MgO:CaO=2:1.

Analyses of different samples from the same bed show considerable variations. The excess of free silica is uncertain, in sample 4 it was reported to be 7.26, and the base-weight moisture is extremely variable with room humidity; hence such analyses are of value only in showing general character and mole ratios. The clay of the Vicksburg group and the Attapulgus clay, 2 and 5, conform rather closely to montmorillonite. The clay from near Marianna, 3, checks fairly well with beidellite; all others are high in SiO_2. The sample from Creede, 4, is low, and the sample from Wyoming, 1, is high in sesquioxides. the bentonite from High Bridge, Ky., 6, which has the properties (leaching, bleaching, and dehydration curves) of a typical activable bentonite, such as the Vicksburg, would be montmorillonite in composition but for the K_2O.

Reducing to molar proportions and taking $R_2O_3=1$, the molar composition of a number of the better-known montmorillonite clays is given in the following table:

Molar composition of montmorillonite clays

[$R_2O_3=1$]

	SiO_2	(Ca, Mg)O	(K, Na)$_2$O	H_2O	
				25° C.	110° C.
Wyoming swelling bentonite	4.75	0.35	0.13	3.21	1.24
Smith Co., Miss. (Vicksburg group)	4.53	.78	.02	6.96	2.27
High Bridge, Ky. (Ordovician)	4.43	1.04	.32	4.81	1.60
Suifu, China, "soap clay"	5.10	1.41	.31	4.41	1.44
Chito, Ariz., white bentonite	5.43	1.16	.06	8.37	2.44
Santa Cruz, N. Mex., "montmorillonite"	5.65	1.26	.06	7.97	2.49
Otay, Calif., "otaylite"	4.87	1.27	----------	7.52	2.79
Westcliffe, Colo., pink bentonite	6.02	.98	.06	7.71	2.57
Atzcapozalco, Mexico, bentonite	4.35	.58	----------	6.41	1.81
Chihuahua, Mexico, beidellite	3.43	.39	----------	4.99	1.52
Tatitila, Veracruz, Mexico	4.65	1.06	----------	6.60	2.22
Marianna, Fla., beidellite	3.61	.11	.08	2.93	1.74
Beidell, Colo., beidellite	3.11	.28	.06	4.32	1.75
Wagon Wheel Gap, Colo	1.91	.04	----------	3.75	2.35
Attapulgus, Ga., fuller's earth	5.86	1.77	----------	7.71	3.70
Santa Monica Mountains, Calif., tuff	7.44	.31	.25	4.67	3.03
Same (?), altered to bentonite	4.08	.45	.05	5.72	2.05
Ganado, Ariz., tuff	7.55	.59	.37	5.27	2.61
Same (?), altered to bentonite	4.86	.87	.03	7.02	2.26
Original montmorillonite, France	4.16	.18	.10	7.17	1.79
Greenwood Springs, Miss. (Upper Cretaceous)	3.75	.36	----------	----------	3.09
Creede, Colo., fuller's earth	7.56	.85	.23	4.59	2.12
Montmorillonite, theoretical	4.00	----------	----------	8.00	1.00
Pyrophyllite, theoretical	4.00	----------	----------	1.00	1.00
Halloysite, theoretical	2.00	----------	----------	4.00	2.00

The SiO_2:R_2O_3 ratios range from 2 to 7, with all intermediate gradations in the beidellite-montmorillonite series of clays. The (K, Na)$_2$O is small in molar proportion. In the high-potash clays it occurs chiefly as potash feldspar and biotite. The (Ca, Mg)O appears to be essential to most montmorillonites. The two tuffs lose nearly all their alkali and much silica in changing to bentonites by crystallization and hydration.

According to recent theories of crystal structure, (Mg, Ca)O may be an essential constituent in montmorillonite in either of two ways; it may form an occasional lattice sheet $Mg_3O_4(OH)_2$, substituting for (Al, Fe)$_2$O$_4$(OH)$_2$, or 3Mg may substitute occasionally for 2Al in a sheet. Computing the ratios of the groups $3MgO:Al_2O_3:4SiO_2$ from the above table, the writer finds these to be nearly simple—2:8:4 for the clay of the Vicksburg group, 2:5:7 for the Chito and Santa Cruz, 1:3:5 for the Westcliffe, and 1:9:10 for the Wyoming clay, with very little left over. In any event the ratios $3MgO+Al_2O_3:4SiO_2$ are very close to 1:1 for these five clays.

The accepted theory of montmorillonite lattice structure requires one H_2O for each R_2O_3 in the lattice plus an indefinite amount of interlattice water, probably chiefly adsorbed. The lattice H_2O checks well with the thermal dehydration curves. Subtracting unity from the H_2O above 110° of the above table gives the interplanar water ranging from 0.52 for Chihuahua to 1.79 for Otay and averaging about 1.00. The Wyoming bentonite is exceptionally low, 0.24 in interlattice water. It may be stated that all the highly activable bentonites as a class are high in interlattice water, but they cannot be graded relative to each other on that basis alone. The same may be said of the slope of the dehydration curve (gm./° C) between 160° and 500° C. and of the energy (cal./gm.) of association.

LATTICE SPACINGS

Of the three lattice spacings, *a*, *b*, and *c*, determined by Pauling[12] for the types of minerals here considered, *a* and *b* in the lattice plane were found to be almost the same ($a=5.2$, $b=9.0$ angstrom units) for all, but the *c* spacing, normal to the lattice planes, differs for different minerals and varies with moisture content in many hydrous minerals. Pauling's data are summarized and ably discussed by Marshall,[13] who points out that the partial substitution of 3 Mg for 2Al or 2Fe and of Al+H for Si render the silica: sesquioxide ratio meaningless. Bilke[14] has carefully determined the *c* spacing of bentonite containing a varied amount of water. Bilke's excellent data permit a more detailed interpretation of interplanar adsorption.

The following table gives Bilke's data, which are plotted in figure 18. The added columns permit comparison with the writer's results on weight-humidity given in the section on physical properties. (See pp. 162–175.)

c Spacing and moisture in montmorillonite clay

[Data of Bilke]

P (millimeters)	H (percent)	Water in clay (grams)		*c* (centimeters)
		Ignited	Treated with P_2O_5	
0.0	0.0	10.0	1.0	11.2×10^{-8}
.4	2.3	13.9	3.5	12.1
2.4	13.7	19.5	8.6	13.4
4.9	28.0	24.2	13.0	14.6
8.7	49.7	20.5	17.7	15.1
12.0	68.6	36.3	24.0	15.3
14.5	82.8	41.8	29.0	15.4
16.7	95.4	59.0	44.5	17.8
17.5	100.0	(360)		20.7

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[12] Pauling, Linus, *The structure of the micas and related minerals*: Nat. Acad. Sci. Proc., vol. 16, No. 2, p. 123, 1930; The structure of the chlorites, idem, vol. 16, No. 9, p. 578, 1930.

[13] Marshall, C. E., The chemical constitution as related to the physical properties of the clays: Ceramic Soc. Trans., vol. 35, pp. 401–411, 1936.

[14] Hofman, U., and Bilke, W., Kolloid-Zeitschr. Band 77, Heft 2, pp. 238–251, November 1936.

Column P is pressure of water vapor with which clay is brought to equilibrium, which is reduced to relative humidity H in the second column. Water content of clay is in grams per 100 grams of water-free (ignited) clay in the third column and in grams per 100 grams of clay over P_2O_5 in the fourth. The final column is the observed *c* spacing, in angstrom units, or 10^{-8} cm.

The initial four points lie on a straight line, indicating an expansion normal to lattice planes proportional to water content up to about 20 percent total water. The middle part of the curve is nearly horizontal and is followed by a steep final part. The slope of the initial straight line part is 1.2×10^{-8} cm. for each 5 percent H_2O. In $Al_2O_3.4SiO_2.H_2O$ the H_2O is 5 percent. The diameter of a water molecule is usually taken as 4×10^{-8} cm. Expansion is proportional to the water taken in until it reaches about one molecular diameter, then practically ceases. It is as though the water molecules were pushing against an elastic pressure with a force proportional to the number of water molecules until the expansion is equal to a single layer of molecules, after which it remains constant over a range of water concentrations, then increases again.

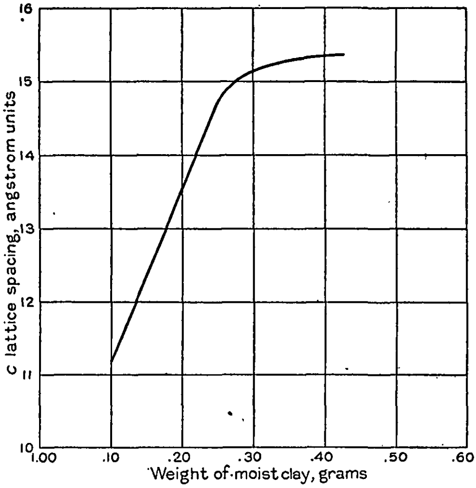

FIGURE 18.—Relation of moisture content and spacing between lattice planes in montmorillonite.

Bilke's relations between lattice expansion and water content are of course directly comparable with the energies of association in clays shown in figure 12 where that energy was found to be constant (about 50 cal./gm.) over a range of low concentrations, low in the middle portion, and then to rise to a high value at high concentrations. This simply indicates expansion proportional to pressure (about 2,400 atmospheres), which is to be expected. After lattice expansion has been studied in the range from 5 to 10 percent moisture (100°–500°

C.), more can be said of the forces and distances concerned in valence adsorption, which is of such vital importance in the bleaching action.

Recent X-ray work on the swelling Wyoming bentonite by Bradley, Grim, and Clark [15] indicates hydration by steps of $6H_2O$ per unit cell, the whole series of five observed hydrates running 2, 8, 14, 20, and 26 molecules of H_2O. The first step is 2.8, the others 3.0×10^{-8} cm. in thickness. With pure, homogenous material, these hydrates should be observable also as steps in vapor-pressure curves such as those of figure 11.

The relation between water content and lattice spacing characteristic of the bentonites holds over a wide range of chemical compositions. The alumina:silica ratio may vary from 1:8 to 1:2 with the same bentonite structure, although part of this variation may be accounted for by substitutions. With further variation, toward silica-free bases or (with acid) toward base-free silica, that structure appears not to persist.

ALTERATION BY NATURAL PROCESSES

All bentonites are believed to have originated as volcanic ash on the evidence of the shard structure (lune-shaped and Y-shaped fragments of glass bubbles or pumicelike grains) that they contain, which could have had no other source. Both active and activable types of adsorbent clays are known that are not bentonites, but these are similar to the bentonites in chemical composition. The parent ash from which bentonites have been derived was probably no higher in silica than andesite. Exposure of ash of favorable composition to water tends to alter its compostion to that of montmorillonite by removal of the excess alkali and silica. Beds of tuff only locally altered to bentonite occur in Arizona and southern California. Bentonite commonly shows more of some bases, MgO for example, than the parent tuff sampled nearby.

Two pairs of analyses are given below of the partly altered tuff and the derived bentonite. One is from the extensive deposit just north of the Puerco River, in northeastern Arizona, and the other is from the north flank of the Santa Monica Mountains, Los Angeles County, Calif. The first was collected by E. B. Eckel and analyzed by J. G. Fairchild and the second was collected by M. N. Bramlette and analyzed by Charles Milton, all of the Survey staff.

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[15] Bradley, W. F., Grim, R. E., and Clark, G. L., A study of the behavior of montmorillonite upon wetting: Zeitschr. Kristallographie, vol. 97, pp. 216–222, 1937.

Alteration of tuff

	Puerco Valley, Ariz.				Santa Monica Mountains, Calif.			
	Analyses		Computed on basis of Al_2O_3 as constant		Analyses		Computed on basis of Al_2O_3 as constant	
	Tuff	Bentonite	Bentonite	Ratio of constituents in bentonite and parent tuff	Tuff	Bentonite	Bentonite	Ratio of constituents in bentonite and parent tuff
SiO_2	63.74	51.10	41.45	0.65	65.66	50.03	38.08	0.58
Al_2O_3	12.72	15.68	12.72	1.00	12.71	16.70	12.71	1.00
Fe_2O_3	2.53	3.38	2.74	1.08	3.54	6.30	4.79	1.35
MgO	2.01	4.52	3.67	1.83	.71	2.78	2.12	2.98
CaO	1.67	2.06	1.67	1.00	1.44	1.20	.91	.63
Na_2O	1.14	.23	.19	.17	1.10	.26	.20	.18
K_2O	3.19	.15	.12	.04	1.72	.60	.46	.27
H_2O-	6.73	15.02	12.18	1.81	4.34	13.53	10.30	2.37
H_2O+	6.60	7.14	5.79	.88	8.03	7.52	5.72	.71
TiO_2	.31	.41	.32	1.00	.40	.65	.50	1.25
	100.64	99.68	80.85	----------	99.66	99.57	75.79	----------

The chemical analyses of the samples from each locality represent the partly altered parent tuff and the bentonite formed locally in the same deposit. As alumina is no doubt the most static element, it may serve as a datum to which other elements may be referred. The third column is computed from the second to show relative changes. On this basis, the tuff from the vicinity of the Puerco River shows a loss of 19 percent and the tuff from the Santa Monica Mountains a loss of 24 percent in total weight in altering to bentonite. The last column shows the change in each constituent relative to alumina.

One striking feature of the alteration is the nearly complete loss of the alkalies Na_2O and K_2O, together with 4 to 8 times as much SiO_2. Why the K_2O practically disappeared in the formation of the Eocene and Cretaceous bentonites but is present as feldspar or biotite in the Ordovician remains to be explained. Iron increased a little and MgO considerably relative to alumina in both cases. Both may have been added from percolating water solutions. Taking the MgO as fixed leads to improbably large losses for other constituents. The large increase in low-temperature water is to be expected when montmorillonite is formed. Similar alterations of an Arkansas trachyte to bentonite, with a large increase in MgO, were noted by Ross.[16] It is thought Mg from salt water displaced the Na and K of the tuff or trachyte and the alkalies on leaving took with them some silica.

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[16] Ross, C. S., Miser, H. D., and Stephenson, L. W., Water-laid volcanic rocks of early Upper Cretaceous age in southwestern Arkansas, southeastern Oklahoma, and northeastern Texas: U. S. Geol. Survey Prof. Paper 154, p. 186, 1929.

BASE EXCHANGE

Base exchange of sodium for calcium takes place quickly and completely with the bentonites from Chito, Ariz., Vicksburg, Miss., and Otay, Calif., when the dry clay, ground to 150 mesh, is shaken in a concentrated solution of sodium chloride for 10 minutes. At most, only a trace of magnesium is exchanged. The same test with Florida active clay shows only half the acid-soluble calcium exchanged, with little effect on the bleaching power. On the other hand, the Nevada (Ash Meadows) bentonite showed very little sodium-calcium exchange, perhaps because the calcium was present as carbonate. The Olancha, Calif., active clay exchanges about 90 percent of its calcium for sodium, the Wyoming swelling bentonite practically none. Such simple base-exchange tests may perhaps be useful in identifying adsorbent clays.

SLAKING

Another test of possible usefulness is the slaking of a room-dry lump of clay in dilute acid and alkali solutions. The following table indicates the slaking behavior of a number of well-known adsorbent clays in 1:4 hydrochloric acid, pure water, 1:2 ammonium hydroxide, and 0.3 N potassium hydroxide. Although some of the bentonites slake in all the solutions and none of the active clays slake in any of them, the behavior of other bentonites is varied and difficult to interpret without further investigation. An Amory, Miss., bentonite from the Eutaw formation (Upper Cretaceous) swelled greatly (at least 15 times) when fresh and only partly dry but slaked without swelling after room-drying for 3 days.

Slaking in acid and alkaline solutions

[S, slaking; NS, nonslaking]

Bleaching clays	Hydrochloric acid	Water	Ammonium hydroxide	Potassium hydroxide
Bentonites:				
Chito, Ariz.; Las Cruces, N. Mex.; Westcliffe, Colo	S	S	S	S
Otay, Calif.; High Bridge, Ky. (Ordovician)	S	S	S	NS
Vicksburg and Booneville, Miss	NS	S	NS	NS
Wyoming swelling	NS	S	S	NS
Fuller's earths: Florida, Death Valley, Calif.; Creede, Colo	NS	NS	NS	NS

One may inquire why eruptive magmas, intermediate between latite and andesite in composition and exposed to water, have not gone to montmorillonite and hence to adsorbent clays. They have been altered to montmorillonite beyond question, but attack, by water accompanied by oxidation and leaching, has spread irregularly from seams and cracks, and the result is residual soil. Contrast such conditions with those that lead to bentonite, where ash is sized by air elutriation, each grain falls nearly the same distance through water, and the homogeneous sediment is protected from other changes during the slow processes of hydration and crystallization. Samples of decomposed rock, capable of rather high activation, are not difficult to find in any crystalline area, but are of little interest as to either quality or quantity. Even where separated and collected by suitable sedimentation, such material is usually weathered to low-grade adsorbent clay or to soil.

The deposits of activable clay occurring in northern Africa, referred to on page 155, are thought to have originated from a rock formed by a magma quickly chilled on being forced up into water, as they contain embedded fragments of andesite. Samples of Atlantic bottom mud, examined at the Survey, contain similar fragments.

Bentonite, after removal from the stable environment in which it was formed or after loss of protective overburden, undergoes rapid changes in several of its properties. Least affected are bentonites of classes I and V. The swelling Wyoming bentonite still swells and does not activate even after much washing, drying, and reworking in stream beds. The fuller's earths (Georgia-Florida, Creede, Porters Creek, Tallahatta) gain slightly in adsorbing power on storage in air of variable humidity and room temperature, but lose as much as 30 percent of their adsorbing power (by oxidation) on heating to 160° C. for 2 weeks in air in an oven. All the activable clays rapidly lose activability on drying, as much as 30 percent the first month. A sample of Chambers bentonite went completely to an inactivable fuller's earth after 2 years in the laboratory with the humidity ranging from 20 to 80 percent, the moisture content of the clay varying about 20 percent. As activable bentonite alters to fuller's earth, which is not further activable, on slow treatment with weak or dilute acids, fuller's earth may have been formed in this way through the action of natural waters containing various plant acids.

Weathering, the combined action of water, air, sunlight, bacteria, and humus, is sufficient to alter any activable clay to soil in a fairly short time. All intermediate grades, corresponding apparently to different degrees of weathering, are found in abundance. In the New Jersey Cretaceous beds a 6-inch bed of bentonite in sand, leached without exposure for a long time, has been left almost unaltered, percolating waters being already charged with dissolved silica from the sand. It is not unusual to find the bottom of a fuller's earth bed either unaltered bentonite or clay hardened by redeposited silica.

DERIVATION OF ADSORBENT CLAYS

There is good field evidence that clays of classes III, IV, and V (naturally active) are derived from clays of class II (inactive but highly activable). Laboratory research confirms this evidence and suggests a sufficient creative agent in extremely dilute acid-water solutions. There is neither field nor laboratory evidence for the alteration of class I clay to any clay of the other four classes, and as to details of the alteration of one type of clay to another we have little definite knowledge. The highest activation is obtained by treating either class II or class III bentonite with strong acid ,whereby little or no silica and only about half the soluble bases are removed. Class III might be derived from class II by removal of part of the silica along with part of the bases; class IV may be similarly derived from class II by removal of silica and bases in such proportion that they retain their original ratios and by later rehydration. The Quincy-Attapulgus and other fuller's earths are montmorillonite, as shown by their composition, X-ray and optical structure, and even solubility in acid, but they are not further activable. We cannot yet explain the inactivability of the fuller's earths or of the swelling bentonites, but X-ray studies indicate that the explanation is to be looked for in an altered montmorillonite structure.

ACID SOLUBILITY AND ACTIVATION

Strong acids rapidly remove bases from bentonites and fuller's earths, leaving the silica practically intact, as at least 5 liters of water are required for each gram of silica dissolved. From 2 to 4 hours of digestion in hot 20 percent HCl or H_2SO_4 leaves pure, optically isotropic SiO_2. In the table following are given two analyses of acid-treated bentonite from Arizona, one after removal of about 15 percent of bases by light acid treatment and the other removal of 34 percent out of a possible 40 percent by severe acid treatment. Analyses of the first group were supplied by the Filtrol Co.; analyses of the second group by J. G. Fairchild, of the Geological Survey.

Solubility of acid-treated bentonite

	Untreated clay	Light treatment	Silica constant	Relative change	Severe treatment	Silica constant	Relative change
SiO_2	51.10	59.30	51.10	1.00	77.19	51.10	1.00
Al_2O_3	15.68	9.53	8.21	.52	4.56	3.02	.19
Fe_2O_3	3.38	1.70	1.46	.43	.72	.48	.14
MgO	4.52	3.20	2.76	.61	.94	.62	.14
CaO	2.06	1.13	.97	.47	--------	--------	--------
Na_2O	.23	--------	--------	--------	.08	.05	.22
K_2O	.15	--------	--------	--------	.11	.07	.47
H_2O-	15.02	15.10	13.01	.87	9.34	6.18	.41
H_2O+	7.14	8.79	7.57	1.06	7.10	4.70	.66
	99.28	98.75	85.08	--------	100.94	66.22	--------

In the lighter treatment, Fe_2O_3 and CaO were most soluble in acid and Al_2O_3 and MgO were least soluble. (See fig. 19.) The data on the alkalies are incomplete. Lattice and adsorbed water were almost unchanged, but the loosely held water was lowered. In the severe acid treatment the CaO completely disappeared; next come MgO and Fe_2O_3 (0.14), then Al_2O_3, Na_2O, and finally K_2O (0.47), the most resistant of the bases. Even the lattice water was reduced by a third, indicating that severe leaching breaks down the crystal lattice along with the Al_2O_3, which is supposed to hold the lattice water. An intermediate leaching of about 25 percent removal of soluble material gives the best activation of this clay. At about this stage the lattice begins to be attacked.

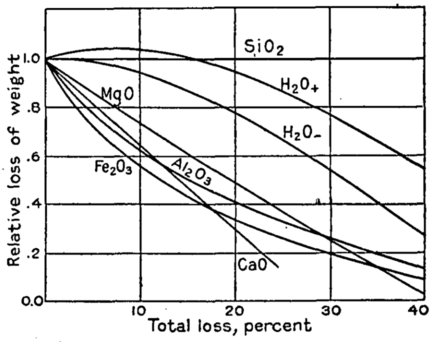

FIGURE 19.—Relative loss of bases on acid treatment.

The refractive indices of an activable clay vary significantly with the degree of activation; for example, the parent tuff of the bentonite from Arizona is isotropic, with the index 1.51, whereas the bentonite derived from it has (at 6.8 percent H_2O) the three indices 1.527, 1.548, and 1.550. When the clay is attacked by acid these indices drop, as shown in figure 20, ending in isotropic silica with an index of 1.451 at room humidity (20 percent H_2O). These indices were determined by J. J. Glass on material prepared by the author. Indices may be quickly determined on a small sample, and the petrographic

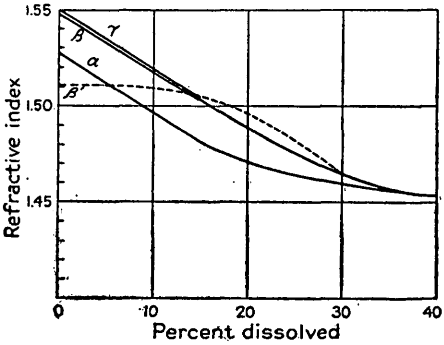

FIGURE 20.—Relation between refractive indices and base removal. α, β, γ, Bentonite from Arizona; β, parent tuff from which this bentonite was derived.

microscope may afford a means of plant control of the degree of activation.

EXPERIMENTS ON SOLUBILITY OF ADSORBENT CLAYS

In an extended study made by the writer[17] of the solubility of different adsorbent clays in acid and alkaline solutions of different concentrations, a number of points bearing on activation were brought to light. There are four variables, concentration of acid, ratio of acid to clay, time, and the temperature of digestion, so that several series of tests were necessary to cover the ground.

In the first series, the time of digestion and concentration of acid were varied in steps of 0.5 to 5 hours and 0.3 to 9 normal hydrochloric acid, using 3.5 grams of clay to 100 cubic centimeters of acid solution and a fixed temperature of 94° C. The effects determined were loss of weight of clay and bleaching power of the product. The losses are shown in figures 21 and 22 as percentages of weight of clay lost, plotted against time of treatment, 0.5, 1, 2, 3.5, and 5 hours, for each of the six concentrations 0.3, 0.6, 1.2, 3, 6, and 9 normal hydrochloric acid for bentonite from Sanders, Ariz., and fuller's earth from Quincy, Fla.

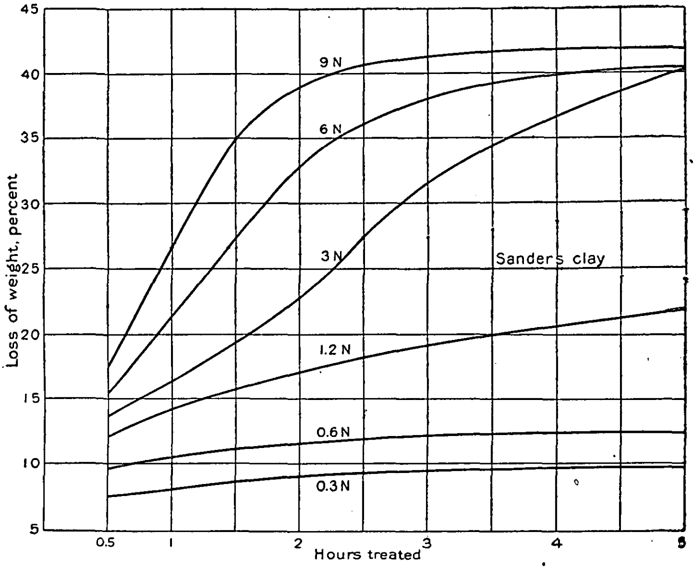

FIGURE 21.—Relations of weight loss of Sanders clay to time and to concentration of acid.

The bentonite is attacked far less than the fuller's earth by the dilute acids and approaches equilibrium with them in about 3 hours, but the fuller's earth is not even approaching equilibrium in a 5-hour digestion. The curves for the fuller's earth are nearly parallel, indi-

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[17] Nutting, P. G., A study of bleach clay solubility: Franklin Inst. Jour., vol. 224, no. 3, pp. 339–362, 1937.

cating that the effects produced by all strengths of acid are roughly similar. On the other hand, stronger acids (3 to 9 normal or 10 to 30 percent) evidently played a different role from the dilute acids in acting on bentonite. The bentonite from Westcliffe, Colo., gave a group of curves similar to those for the clay from Sanders. The curves for the beidellite from Marianna, Fla., are intermediate in character between the two types.

Figure 23 shows relations of bleaching power to loss in weight for each of the six acid concentrations used on the clay from Sanders. The inception of the bleaching action is very well indicated, starting at about 12 percent off. A 2-hour heating in 20 percent acid is standard commercial practice in treating plants. From these curves there is seen to be little choice between 10, 20, or 30 percent acid for this clay. The longer treatment in the 10 percent acid is more readily controlled but more expensive. Leaching to 20 percent loss in weight gives the best water-white color for cottonseed or linseed oil, and to 30 percent gives a red color for lubricants.

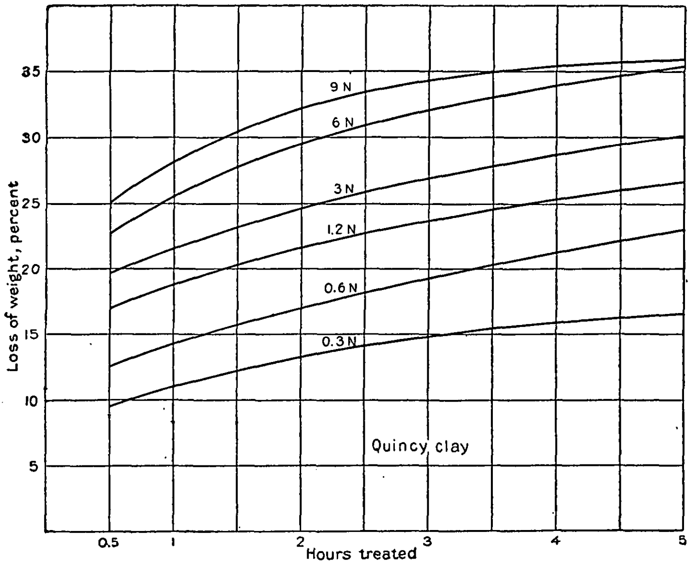


FIGURE 22.—Relations of weight loss of Quincy clay to time and to concentration of acid.

From the two sets of curves for the bentonite from Sanders it is evident that this clay could never be activated in 1 percent (0.3 normal) acid; in fact, 2 percent acid, removing a maximum of 12.5 percent, activates it just to the bleaching power of good (Georgia-Florida) fuller's earth but can do no more. With stronger acids, however, this (12.5 percent weight loss) is so quickly passed that the clay is at no time in the inactivable condition, though having the bleaching power of fuller's earth. That this time element is a considerable factor in the reorganization of an activable bentonite into an inactivable fuller's earth is shown by the age curve for activable clays treated with dilute acid. (See figs. 27 and 28.)

The behavior of bentonite from Westcliffe, Colo., is similar to that of the clay from Sanders, the critical acid concentration being 2 percent

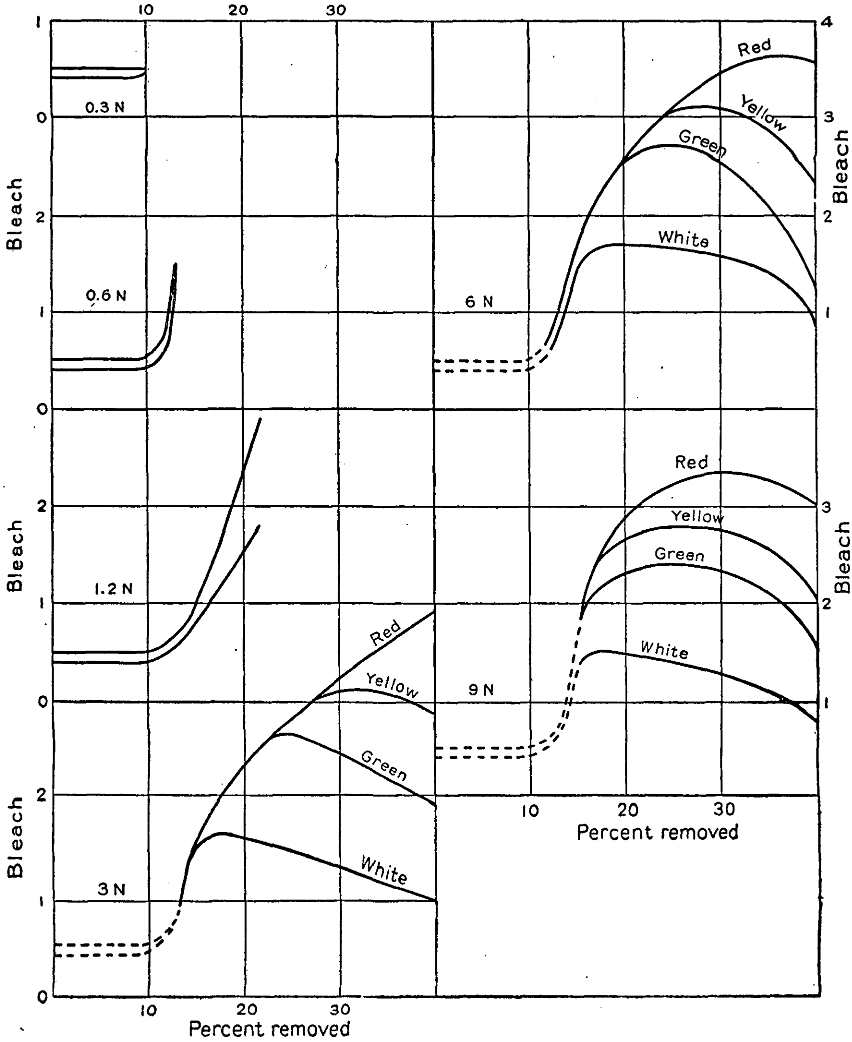


FIGURE 23.—Bleaching power of Sanders clay after various acid treatments.

(0.6 normal) as before but the critical equilibrium being 10.0 percent instead of 12.5; in fact, all the class II bentonites tried showed these same properties. For the class III beidellite (clay from Marianna) there are indications of properties intermediate between class II clays and fuller's earths, an equilibrium with 15 percent loss of weight, attained with 4 percent (1.2 normal) acid, being fairly well defined.

The fuller's earths have no maxima of solubility other than the ultimate solubility in an excess of strong acid.

The effect of acid on adsorbing power of active clay is of interest, as is shown by the color curves in figure 24 for the fuller's earth from Quincy, Fla. The curves for water white and green are little affected by leaching away as much as 15 percent, but with a removal of 25 percent of the soluble material these curves have dropped to a lower level. On the other hand, the yellow and red color curves drop to 10 percent, rise to a maximum at 22.5 percent, drop to a minimum at 24 percent, than rise toward the maximum with leaching away of 36 percent of the soluble material.

It is well known that strong acids remove little silica from bentonite. On the other hand, pure water removes silica chiefly, but very little of it per liter. At some intermediate concentration of acid, therefore, the solubility of silica may be a maximum. The silica left after acid treatment of bentonite is highly soluble in pure water and that of any active adsorbent clay fairly high. This evidence indicates that when the bases of the clay dissolve in acid the silica dissolves in water, provided it has been freed from the bases and there is sufficient water present to keep the silica below saturation (300 parts per million).

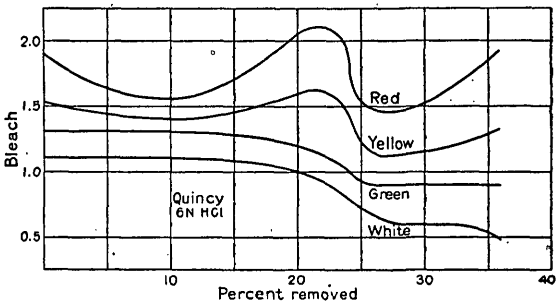


FIGURE 24.—Bleaching power of fuller's earth from Quincy, Fla., after acid treatment.

To obtain data on this point two series of experiments were made, one with water constant and acid variable, the other with acid constant and water variable, the amount of clay, time of digestion (24 hours) and temperature (97°–99° C.) being constant for each series. In the acid-variable series a fixed amount of clay, usually 8 grams, was put in a liter of water, then hydrochloric acid was added to bring the concentration to 0, 0.03, 0.06, 0.12, 0.3, 0.6, and 1.2 normal, the whole digested 24 hours, filtered hot, evaporated to solid, and the silica determined both as a fraction of the solids and as parts per million in solution.

In figure 25 the silica dissolved is plotted against acid concentration for the Wyoming clay, clays from Sanders, Ariz.; Santa Cruz, N. Mex.; Westcliffe, Colo.; and Marianna and Quincy, Fla., and imported

Bavarian clays. The behavior of these clays is extremely varied, but all show the anticipated maxima of dissolved silica. The curve for the clay from Quincy is sharp, 560 parts per million at 0.08 normal, and that for the clay from Marianna is broad and a high concentration, 940 parts per million at 0.65 normal. Others are intermediate. The highest silica is shown by the Wyoming swelling bentonite, nearly 1,200 parts per million, far higher than that of silica gel in water, 300 parts per million in hot water, 180 parts per million in water at room temperature, which is exceeded by all the clays. The explanation seems to be that some silica is in solution as silicate.

These maxima may be readily accounted for in terms of ions. Hydrous oxides in dilute hydrochloric acid are known to adsorb chloride ions freely. With increasing adsorption of chloride ions on these clays, more and more silica is released. Finally the osmotic layer becomes so saturated with anions that they begin to attack the cations of the clay, new complexes are formed, and chlorides go into solution, "salting out" the silica; hence the quantity of silica at first increases, then decreases, or is even reversed.

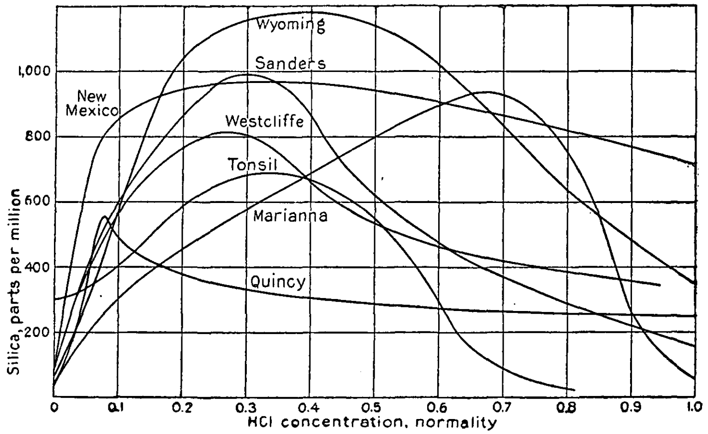


FIGURE 25.—Silica concentrations in acid solutions of clays.

Maximum solution of silica thus corresponds with maximum anion adsorption by the bentonite. The Quincy fuller's earth has a low anion adsorption capacity and is sensitive to changes in anion concentration. Wyoming bentonite has an enormous anion adsorption capacity and is not sensitive to ion concentration. The clay from Marianna is so stable that relatively strong acids are required to attack it. With the bentonite from Sanders maximum solubility of silica occurs at 0.3 normal, and it is at this concentration that iron begins to be removed and the bentonite increases in bleaching power. With pure silica gel there is little or no adsorption of anions and therefore enhanced solubility of silica.

In the final series of solubility tests 1 gram of clay and 1 gram of reagent, either hydrochloric acid or sodium carbonate, were added to 100, 200, 500, 1,000, and 2,000 cubic centimeters of water, digested 24 hours at 98°, and the solution analyzed for silica. This series was extended to still greater dilutions equivalent to 5 and 10 liters of water by taking less clay and reagent and by blanks run with distilled water alone.

The results are roughly graphed in figure 26 and given in detail in the table that follows. The solubility varies so rapidly near zero concentration of the reagent that complete curves cannot be shown. Maximum solubilities on the acid side are for about 1 gram of clay and 1 gram of hydrochloric acid to 500 milliliters of water. With the New Mexico bentonite the silica dissolved was about 0.25 gram from a gram of clay that contained by analysis 0.523 gram of silica, or roughly half the silica present went into solution. On the alkali side maxima of solubility are still higher and occur at higher dilutions. For the Wyoming bentonite 0.481 gram, out of a possible 0.596 in a gram of clay, went into solution when the ratio of clay, sodium carbonate, and water was 1:1:5,000.

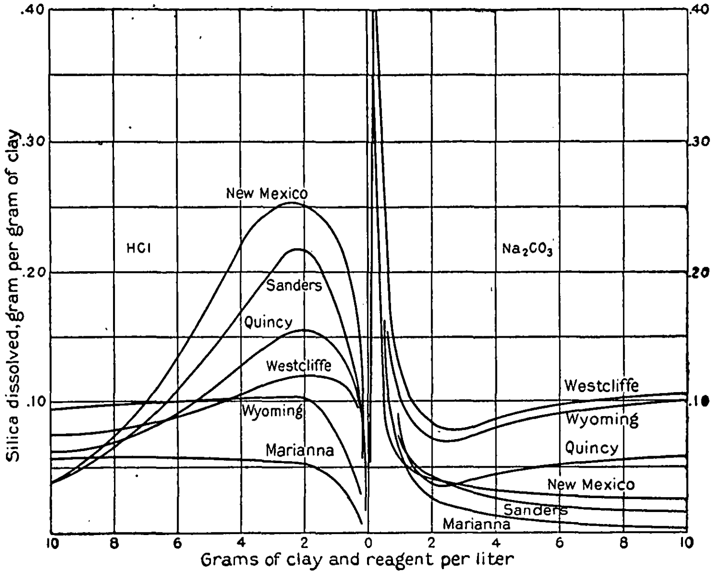


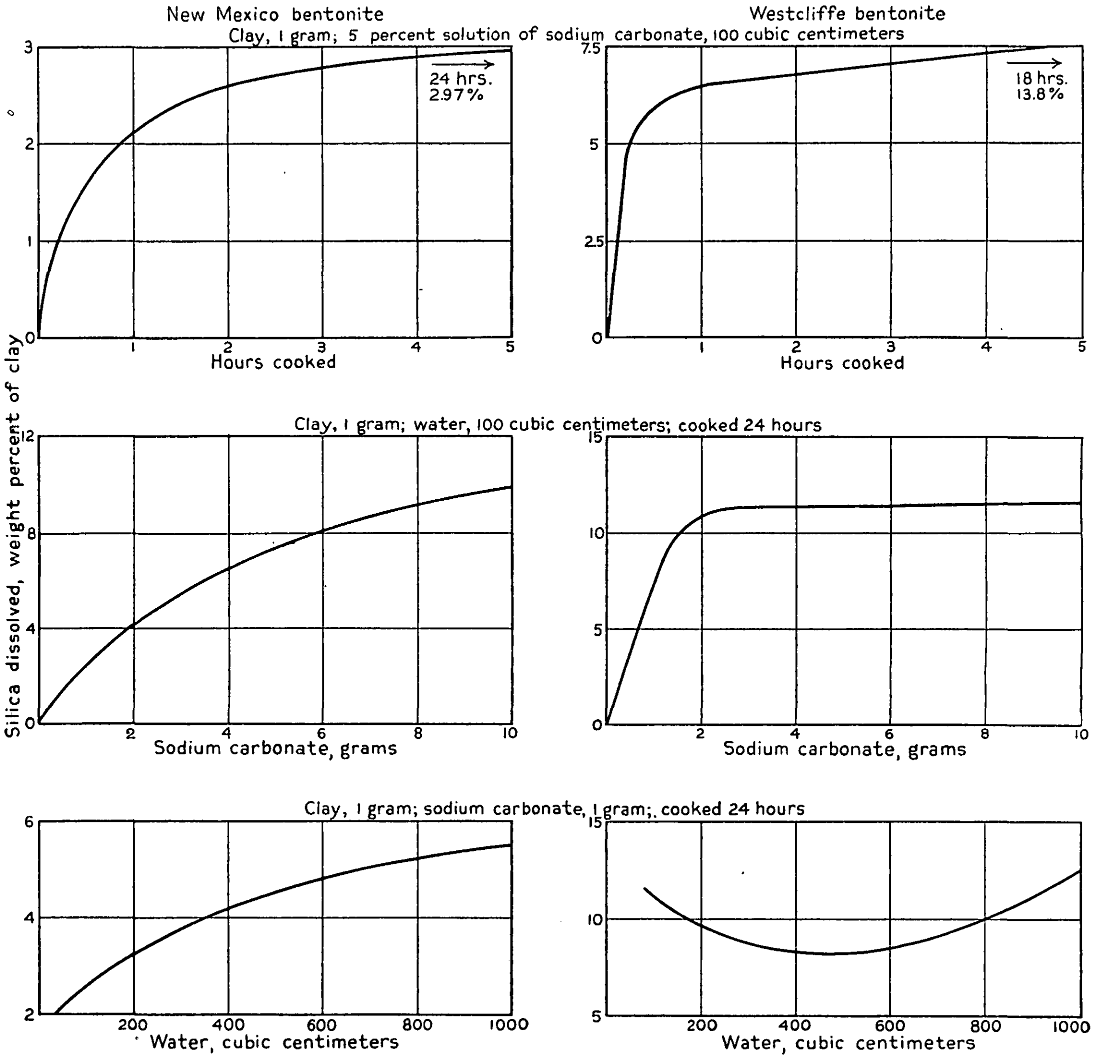
FIGURE 26.—Silica dissolved by dilute acid and alkaline solutions

Milligrams of silica dissolved from 1 gram of clay in various amounts of water containing 1 gram of hydrochloric acid or 1 gram of sodium carbonate

Water (liters)	Wyoming	New Mexico	Westcliffe, Colo.	Sanders, Ariz.	Quincy, Fla.	Marianna, Fla.	Pumice
Hydrochloric-acid solution							
0.1	96	40	75	40	62	57	23
0.2	100	175	94	137	108	55	25
0.5	102	252	118	218	155	52	25
1	70	226	115	164	143	38	20
2	45	185	107	124	120	23	---------
5	22	130	85	73	80	7	---------
10	4	9	8	7	6	1	---------
Pure water							
----------	1.7	11	20	12	20	0	---------
Sodium-carbonate solution							
10	169	343	510	40	32	69	---------
5	481	336	275	415	253	452	---------
2	215	106	175	110	192	160	---------
1	104	54	125	72	79	62	70
0.5	70	42	83	42	87	23	47
0.2	86	31	94	24	50	10	25
0.1	100	26	105	17	59	3	15

These results appear to be highly significant in the study of the alteration of clays. Both acid and alkaline solutions, if sufficiently dilute, tend to lower the silica content of clays. Acid solutions tend to remove bases with the silica, the proportion varying with the concentration. At a certain critical concentration, montmorillonite is dissolved and may be redeposited as such. Most natural waters are more dilute than this critical concentration, remove more silica than bases, and therefore degrade bentonite toward laterite or bauxite. Alkaline solutions remove silica and alumina, and these results show that at extreme dilutions the complete removal of silica from bentonites is possible, impure iron oxide being left and silica redeposited on neutralization.

The standard test for "free" silica in a sample is to boil 1 gram in 100 cubic centimeters of 5 percent sodium carbonate for 15 minutes and determine the silica dissolved. To find the significance of these tests on bentonites, runs were made on the easily attacked New Mexico bentonite and the more resistant Westcliffe bentonite, varying alkali, water, and time of digestion. The results are shown in plate 13 in milligrams of dissolved silica per gram of clay. The standard test is without any special significance for either of these two bentonites. With the New Mexico clay, the amount of silica dissolved at the end of 15 minutes was 11 milligrams per gram, and it was rising rapidly; it reached 29.5 milligrams per gram in 5 hours and only 29.7 milligrams in 24 hours. With the clay from Westcliffe, Colo.,



SOLUBILITY OF TWO CLAYS IN ALKALINE SOLUTIONS.

the silica dissolved rose quickly to 50 milligrams per gram in 15 minutes and then rose slowly to 138 milligrams in 18 hours.

With 1, 2, 5, and 10 grams of sodium carbonate in 100 cubic centimeters of water, the two clays heated 24 hours gave the two middle curves. The two clays differ widely in their response under these conditions. The two lower curves show the results for 1 gram each of sodium carbonate and clay in 100 to 1,000 cubic centimeters of water. The silica of the New Mexico clay steadily increases in solubility with dilution, but that of the Westcliffe clay at first decreases, then increases.

Several tests indicated that dilute solutions of sodium chloride are no better solvents than pure water. Bentonites may be slightly activated by treatment with aluminum chloride solutions, but apparently only to the extent of the excess acidity. Hot salt solutions appear to have a loosening effect chemically on bentonites, making them more easily and uniformly leachable by acids. In activating glauconite, in which some grains are much more easily leached than others, the addition of iron and aluminum salts to the acid serves a useful purpose in securing a more uniform product.

The effect of sodium chloride in precipitating silica from a clear sol was reported by the writer[18] in 1932. Starting with a sol containing C_0 grams of silica per liter and adding 5 grams per liter of salt, it was found that $(C-C_0)/(C_0-C_\infty)=e^{-ks}$. The constant $k=0.30$. $C_\infty=0.10$. $C_\infty=100$ parts per million is the silica left with an excess salt. With $C_0=6$, half the silica is precipitated ($C=3$) on the addition of 2.37 grams of salt per liter. A similar law probably holds in all "salting out" effects.

From the investigation of the action of solvents on the montmorillonite clays described above it is evident that the attack on such clays by acids and alkalies varies widely in character as well as in degree with concentration of solvent. Strong acids remove the bases from a clay and leave the silica, whereas weak or very dilute acids dissolve silica and bases together or even chiefly silica. On these clays, as on the hydrous oxides investigated by Weiser,[19] anions are first adsorbed from acid solutions. When adsorbed to capacity, salts are formed and silica released. However, an extremely dilute alkali solution is most efficient in removing silica from adsorbent clay.

The results afford a plausible reason for the use of strong acids in activating clay and for the rapid deterioration of adsorbent clay freely exposed to natural waters. They also indicate how soil minerals may be broken down by dilute solutions and made available as plant food.

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[18] Nutting, P. G., The solution and colloidal dispersion of minerals in water: Washington Acad. Sci. Jour., vol. 22, no. 10, pp. 261-267, May 19, 1932.

[19] Weiser, H. B., and Milligan, W. O., The constitution of hydrous oxide gels and sols: Faraday Soc. Trans., vol. 32, pt. 1, p. 376, 1936.

SLOW ALTERATION WITH TIME

It has been noted that naturally active clays vary little in bleaching power with time of storage in either a dry or water-saturated atmosphere, the test being made on a thoroughly dried sample; on the other hand, an activable bentonite rapidly loses its activability on air drying—as much as 30 percent in a month. If stored in a saturated atmosphere (over water) when fresh from the ground, it may be preserved at full strength indefinitely. A sample that has been air-dried but a few days may be restored by soaking the finely ground clay in water over night. An activated (acid-treated) bentonite gradually loses adsorbent power on room-dry storage, rapidly in damp storage. A sample of clay from the Vicksburg group, although testing 2.1, 2.8, 3.4, 4.0 when freshly treated, tested 1.1, 1.4, 1.7, 2.0 after 4 years of storage in a bottle. The admixture of a small percentage of activated charcoal to an active clay is said by Wittka[20] to lessen its deterioration under tropical conditions. The effect of a treatment with dilute acid, 1 percent or less, in lowering the activability of a bentonite has also been mentioned.

Obtaining age-deterioration curves in the laboratory is tedious and difficult, but interesting results have been obtained on four bentonites for both the humidity and dilute-acid treatments. Some effects are common to all the four bentonites tested, and others are individual in character.

The samples selected for the humidity tests were bentonites from Westcliffe, Colo., Chito, Ariz., and Santa Cruz, N. Mex., and the Ordovician bentonites from Chattanooga, Tenn. They were all ground to 150 mesh, were alternately dried over night at 160° C., and then placed over water in a desiccator for a month, the alternate treatments continuing for 6 months. The three younger bentonites showed little difference in water sorption, which was as follows: At 28° C. and 100 percent humidity, 1.44 in relative weight equals 35.5 percent water; at 28° C. and 41 percent humidity, 1.26 in relative weight equals 20.6 percent water; at 160° C., 1.08 in relative weight equals 7.4 percent water; and at 600° C., 1.05 in relative weight equals 4.8 percent water. The Ordovician bentonite at 100 percent humidity took up only about one-fourth as much water as the younger bentonites (relative weight 1.124, in comparison with 1.44).

Alteration of bleaching power of bentonites by moisture

	Westcliffe, Colo.		Chito, Ariz.		Santa Cruz, N. Mex.		Chattanooga, Tenn.	
	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
Fresh	0. 4–0. 5	1. 3–3. 2	0. 4–0. 5	1. 5–3. 5	0. 3–0. 4	0. 9–3. 0	0. 5–0. 6	1. 2–2. 9
Aged	. 3– . 4	1. 9–2. 6	. 3– . 4	1. 8–3. 3	. 2– . 3	1. 3–1. 4	. 3– . 5	1. 6–2. 6

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[20] Wittka, F., Seifenserder-Zeitung, vol. 63, pp. 938–940, 1936.

The alteration toward fuller's earth is evident, although the water sorption is little affected by the 6 months' treatment. All four clays remain activable after treatment, but with lowered color separation. The New Mexico clay loses practically all power, changing from 0.9–3.0 to 1.3–1.4, whereas at the other extreme is the clay from Chito which changes from 1.5–3.5 to 1.8–3.3.

The effect of a dilute acid treatment was studied in more detail. Twenty grams of 150-mesh bentonite was put in a liter of 0.5 percent hydrochloric acid (0.15 normal), kept at 50° C. for 10 days, then filtered, dried, ground again to 150 mesh, stored in loosely capped bottles (27–29° C., 30–50 percent humidity), and tested for both bleaching power and activability at 5-week intervals for 20 weeks. Silica and total solids in solution were determined. Under these conditions, silica as well as bases dissolves freely, but in a proportion less than in the clay. The four bentonites chosen were commercial "fuller's earth," XL brand, from England, and clays from Marianna, Fla., Otay, Calif., and Box Elder County, Utah. During the first 5 weeks after treatment small portions of each clay were stored also under water and in water-saturated air, but these tested practically the same as the main room-dry sample, and the results of that test are omitted. The chief results, showing details of separation, are given in the table following and in figures 27 and 28. To avoid confusion, only the water-white and extreme red bleaching limits are reproduced.

Alteration of bleaching power of bentonites by treatment with hydrochloric acid

	English		Marianna, Fla.		Otay, Calif.		Box Elder County, Utah	
	Raw	Treated	Raw	Treated	Raw	Treated	Raw	Treated
Untreated stock	1. 2–1. 2	1. 3–1. 4	1. 1–1. 3	1. 5–1. 7	0. 2–0. 3	0. 3–0. 3	0. 5–0. 6	0. 6–0. 6
Activated	1. 6–2. 6	3. 1–3. 5	1. 8–2. 9	3. 6–4. 0	1. 0–1. 9	2. 6–3. 3	1. 3–2. 1	2. 5–3. 1
Solids removed grams	4. 3663		3. 4567		3. 9165		4. 6721	
Silica removed do	. 3738		. 4258		. 3829		. 5689	
1 day after treatment	1. 2–1. 3	1. 3–1. 3	1. 2–2. 0	2. 2–2. 5	. 4– . 5	. 5– . 5	. 6– . 7	. 7– . 7
Activated	1. 9–2. 3	2. 6–2. 7	1. 4–2. 1	2. 5–3. 2	1. 1–1. 9	1. 9–1. 9	1. 3–2. 1	2. 7–2. 8
5 weeks after treatment	2. 0–2. 1	2. 2–2. 2	2. 2–3. 6	4. 4–5. 0	. 4– . 5	. 5– . 5	. 6– . 7	. 7– . 7
Activated	2. 8–3. 0	3. 1–3. 1	2. 2–3. 6	4. 2–4. 7	1. 1–1. 2	1. 2–1. 2	1. 3–1. 4	1. 4–1. 4
10 weeks after treatment	1. 1–1. 1	1. 1–1. 1	1. 3–2. 2	2. 4–2. 5	. 4– . 5	. 5– . 5	. 5– . 6	. 6– . 6
Activated	2. 3–2. 3	2. 3–2. 3	1. 5–2. 5	2. 8–3. 0	. 8– . 9	. 9– . 9	1. 1–1. 1	1. 1–1. 1
15 weeks after treatment	1. 1–1. 1	1. 1–1. 1	1 3–1. 7	1. 7–1. 7	. 3– . 4	. 4– . 4	. 4– . 5	. 5– . 5
Activated	1. 6–1. 7	1. 7–1. 7	1. 4–2. 0	2. 3–2. 5	. 8– . 9	. 9– . 9	1. 2–1. 3	1. 3–1. 3
20 weeks after treatment	1. 1–1. 1	1. 1–1. 1	1. 1–1. 4	1. 4–1. 4	. 3– . 4	. 4– . 4	. 4– . 5	. 5– . 5
Activated	1. 2–1. 2	1. 2–1. 2	1. 2–1. 9	2. 1–2. 2	. 8– . 9	. 9– . 9	. 9–1. 0	1. 0–1. 0

The low activability characteristic of fuller's earths is attained by each of the four earths, but the time required for internal readjustment is great and with the English and Marianna clays is preceded by a considerable rise in bleaching power during the first 5 weeks. The first test of the freshly treated bentonite shows a slight but barely perceptible activation and a lowered activability compared with the untreated clay. The bleaching powers of the Otay and Utah bentonites remain constant, but their activabilities drop to nearly constant values during the first few weeks. The bleaching power of the English clay returns to its original value after 10 weeks and then remains constant, with complete loss of color separation, that is, the percolated oil goes directly over from water white to black. The activability of the English earth drops to zero after 20 weeks, but a little color separation is retained. The clay from Marianna behaves similarly but retains a very considerable color separation even after 20 weeks.

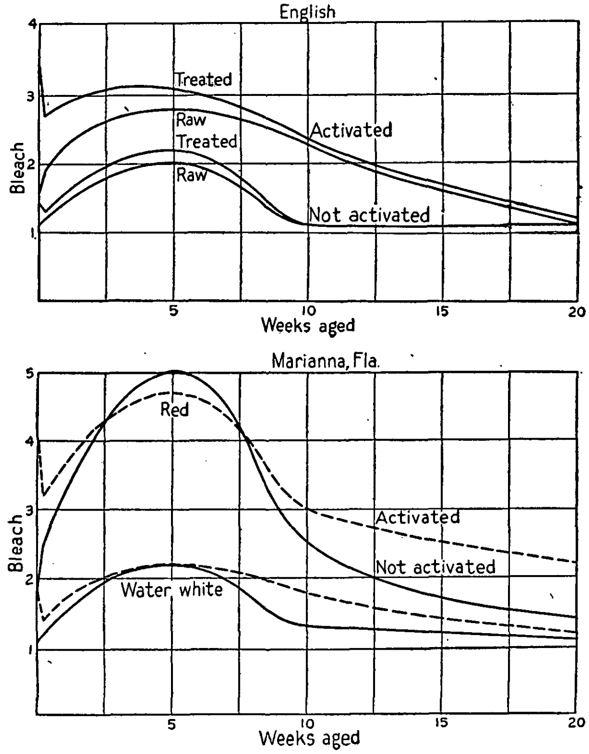

FIGURE 27.—Aging of commercial fuller's earth from England and bentonite from Marianna, Fla., after treatment with dilute acid.

These preliminary results indicate the time scale of alterations in active and activable clays due to internal readjustment. Tests used in obtaining the first part of these curves should be repeated, using shorter time intervals, and the study should be extended to other clays. Age curves for freshly mined clays should be determined by test laboratories near the mines. The aging of fully activated commercial clays is an important field of which little is known, but an effect similar to those described above is to be anticipated. Low storage deterioration may require special treatments such as electrodialysis or a second washing after the first drying to remove the last traces of acid and salts or possibly a final wash in a dilute solution of a magnesium salt to stabilize them.

It is to be noted that the low color separation observed in many field samples is shown by these laboratory experiments to be correctly interpreted for all four bentonites. This effect takes place from 5 to 15 weeks after treatment with dilute acid. Even the negative activitiability characteristic of a few fuller's earths is shown by the treated English earth after 20 weeks' aging. The most highly activable bentonites having the highest color separation are evidently those that have been subjected to least weathering.

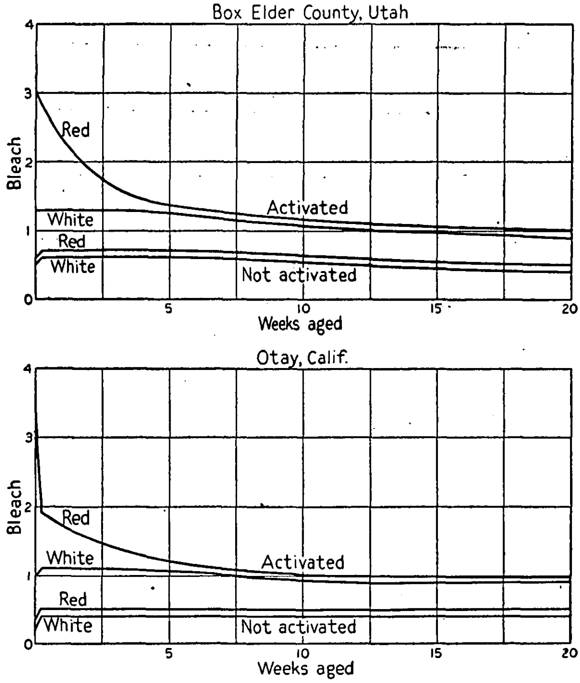

FIGURE 28.—Aging of bentonites from Otay, Calif., and Box Elder County, Utah, after treatment with dilute acid.

ADSORPTION POTENTIAL AND ACTIVATION

It is of interest to know whether there is a relation between the power of selectively adsorbing oil, as shown by decolorizing tests, and the adsorption potential of a clay for water given by its thermal dehydration curve. Two series of tests experiments on the same sample of pure activable bentonite indicates a close correlation between water adsorption and oil adsorption.

A 50-gram sample of bentonite of the Vicksburg group from Polkville, Miss., the purest activable bentonite known, was dried, ground to 150 mesh, thoroughly mixed, divided into four portions and acid treated to remove 0, 15, 30, and 40 percent by weight of the clay. Each of the four portions was then divided into two, one for the oil test and the other for a weight-temperature determination.

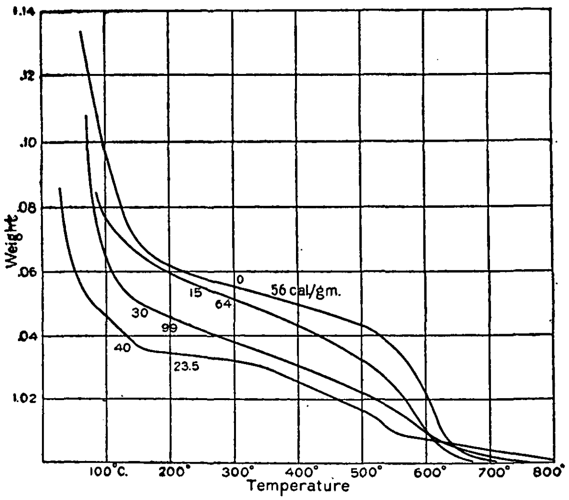

FIGURE 29.—Weight-temperature curves for different acid treatments.

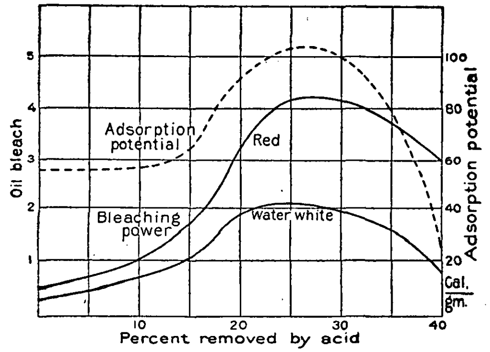

FIGURE 30.—Adsorption potentials and oil-bleaching efficiencies for different acid treatments.

The four thermal dehydration curves are shown in figure 29. The clay treated to 40 percent loss in weight was reduced almost to pure isotropic silica.

The slopes of the flatter central portions of the four curves, representing adsorption, gave the following adsorption potentials:

Percent removed by acid	0	15	30	40
Adsorption potentials..calories/gram	56.3	64.2	98.7	23.5

These results are graphed with the corresponding curves from the oil-bleaching tests in figure 30. The correlation between bleaching efficiency and adsorption potential is striking. Maxima are in the same position. The extremes of the curves would indicate a higher bleaching power for the untreated clay than is commonly found. This higher power is actually found, it is said, when the test is conducted at higher temperatures.

From the set of weight-temperature curves (fig. 29) it may be noted that the first drop (0–15 percent) is much greater at 500° than at 200° (1.1 versus 0.2 percent). This would indicate that what has been called lattice water (the 500° shoulder) yields far more rapidly to acid than the hydrate water. With 30-percent removal of base, the lattice water has all but disappeared, yet the water adsorption is even more powerful than in the natural clay. It is the removal of the last of the bases (30 to 40 percent weight loss) that drops the adsorption potential to a low value—lower than that of silica gel. There appears to be a slight hydrate shoulder at 350°, even in the residual isotropic silica.

PROCESSING AND TESTING OF ADSORBENT CLAYS

GENERAL CONDITIONS

With supplies of all kinds of adsorbent clays abundant and widely distributed, competition in their production is necessarily keen and likely to continue so. The greater part of the market will go to those who produce the best naturally active and activated clays at the lowest prices. Economical and efficient methods of mining and processing are at a high premium. The presence in the field of large producers with extensive plant equipment need not discourage the small producer or the beginner, for equipment and experience are expensive and mean large overhead and amortization charges. New uses for active clays, some requiring special preparation, are constantly appearing. Special methods adapted to local conditions and special shipping advantages are also to be considered.

DRYING

After stripping, mining, and hauling these clays to the plant, the first major problem is that of drying. As mined, both active and activable clays contain 50 to 60 percent of moisture and are soft and plastic. Before they can be ground, or slaked for acid treatment, the moisture must be reduced to 20 or 25 percent. When freight charges are of importance, a reduction of moisture content to 5 to 10 percent is advisable. Natural drying under cover would suffice for grinding and for slaking but would require 1 to 6 months, which would mean extensive and expensive drying sheds. Six months of natural drying is said to be used at a diatomite plant in Nevada where the output is not large.

On the other hand, artificial drying means a very considerable expense for fuel and special equipment. To vaporize water requires roughly 1,000 British thermal units per pound of water or the condensation of an equal amount of steam and the clay is 50 to 60 percent water as it comes from the ground. The clay must not be overheated, for that would destroy its bleaching power, nor should it be exposed to flame gases, which consist largely of water vapor and gases that are partly adsorbed by active clays, thus lowering their bleaching power.

In one plant producing excellent fuller's earth, the moist clay is formed into bricks by extrusion to secure uniform drying. These bricks are then dried over night in sheet iron ovens heated to not more than 180° by protected oil burners. In another plant the clay was pushed along a metal tube by a screw impeller, the tube being heated externally by direct flame. A worse method could hardly be devised. In large plants the standard method of drying is by flame heat in long, inclined, double-walled rotating drums, the flame not coming in contact with the clay. The simplest method of artificial drying known to the writer is a trench covered with sheet iron on a slope. A wood fire in the trench provides the heat, and the clay, in small lumps, is raked by hand along the sheet-iron cover of the trench, drying being complete in about half an hour. It is possible to dry 5 to 10 tons a day in this way.

Other methods of drying, apparently worth a trial, may be mentioned. A steam-heated tunnel kiln, with the clay in a half-inch layer on a slowly moving belt, would doubtless give excellent results but would be costly. Without doubt the most rapid method is the exploding kettle. Strong drums of about 1 barrel capacity are charged with raw clay and filled with superheated steam for a short time. Then the pressure is suddenly released, exploding and drying the clay. Some preliminary experiments at the masonite plant at Laurel, Miss., indicated that a modified wood exploding kettle might prove satisfactory.

After drying, grinding and screening are simple operations by ordinary methods. For use on petroleum, active clays are reduced to 30–60 and 60–90 mesh for market. The fines are usually thrown away but are sometimes pulverized with a Raymond mill for use by the contact process. An interesting account of the equipment and processing methods used in the modern Filtrol plant at Jackson, Miss., is given by Trauffer.[21]

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[21] Trauffer, W. E., Pit and Quarry, June, 1937.

ACID TREATMENT OF ACTIVABLE CLAYS

Although activating a bentonite by partial leaching with acid is one of the simplest of chemical operations in theory, in practice it is one of the most difficult because of the extreme nicety of control required to secure just the right result for maximum bleaching power. For acid treatment, as for drying, a wide variety of equipment and methods is acceptable. Tanks may be of wood or of lead-lined steel. For heat, steam at 220° F. seems to be in universal use. Sulfuric acid is generally used on account of its low cost, but near alkali works where cheap hydrochloric acid is available, that may be preferable. So far as results are concerned there is no choice between the two acids but hydrochloric is cleaner to use, as it is volatile and produces only readily soluble salts. Lime-free water must be available in large quantities for final washes, as hard water destroys the activation obtained by acid treatment. The rate of attack of clays by acids doubles for about 20° C. in the ordinary heating range from 70° to 110° C. for ordinary concentrations (20 percent) of acid and ratios of acid to clay, as shown in figure 31.

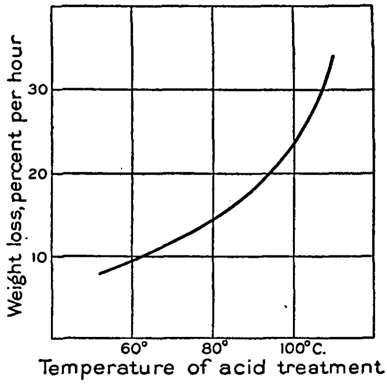

FIGURE 31.—Rate of solution of clay bases at various temperatures.

Although the continuous flow, and in part counter-current, process is used in the largest clay-treating plants, it must be admitted that the batch process, using separate tank units, has much in its favor, as it eliminates precise control of rates of flow. On the other hand, the acid treatment and washing of 10 to 50 tons of clay per day require enormous tank capacity. Tanks permit settling and decantation in washing, whereas flow processes resort to mechanical thickeners. The suction drum filter (continuous) appears to be generally used in the final process of treating rather than the centrifuge. The final processes of drying and grinding offer no difficulty, as the treated clay is almost incoherent.

The uniformly high quality and long storage life of imported activated adsorbent clay are to be attributed to close control of processing, just the optimum acid digestion followed by thorough washing and drying. The bentonite from which it is prepared is similar to the domestic clay most used and slightly inferior to the best. In efforts at quantity production, much improperly processed clay was formerly marketed in this country.

TESTING ADSORBENT POWER

The numerous methods of measuring the adsorbent power of active clays fall into two classes, the percolation method and the contact method. In the percolation method the sample is ground to a certain mesh, placed in a porous-bottomed tube and a reference oil allowed to percolate through it. In the contact method a weighed proportion of clay is mixed with the test oil, heated and stirred for a time, then strained out. Each method has its advantages. The contact method gives rough practical information quickly and is preferred by clay users; the percolation method gives much more detailed information about the nature of the clay and is preferred for research and for the technical work required to formulate treating practice.

CONTACT METHOD

In the simplest contact method, 16 grams of 200-mesh clay are mixed with 100 cubic centimeters of test oil, heated to 200° F. (with constant stirring) for 20 minutes, then filtered out and the color of the residual oil read off on a set of red glass color standards. The test oil used is usually a cylinder stock, free from sulfur and not dewaxed. The standard temperature may be any one between 100° and 400° F. The higher the temperature the better the product, but above 300° F. oxidation by air is rapid unless the hot oil is protected from it. The bleaching action occurs chiefly in the first half minute but continues to increase and is practically complete in 20 minutes.

To obtain a complete color curve for a given clay by the contact method, a group of tests similar to that just described is run with 2, 4, 8, 16, and 32 percent of clay by weight added, and the resulting colors are plotted against weight of clay used. The variation in this curve from clay to clay shows significant differences related to the nature of the clay, its fineness, and its moisture content at the start of the test.

PERCOLATION METHOD

Percolation tests are made on clay ground to pass a 150-mesh (0.1 millimeter) sieve. This is just fine enough to permit action by all the clay and sufficiently coarse to permit the test oil to pass at a reasonable rate. About 3 grams, or a level teaspoonful, of this ground clay is dried for an hour in an oven at 160° C. (320° F.), then put in a porous-bottomed tube to the depth of an inch or more. To avoid channeling it is first wet down with gasoline, stirred, and allowed to settle and drain before the test oil is introduced. The first oil through is water white and contains the gasoline, for which an allowance of half the volume of the clay is made. Then follow green, yellow, and red oil, ending with black unbleached oil. In daylight the eye is very sensitive to the first green and to the golden yellow, which is between lemon and orange. The recognition of the first red following the orange and the first black is less certain but not difficult with practice.

Thus four volumes corresponding to the four colors are obtained. The ratios of these oil volumes to the volume of the clay bleaching them are the color indices given in the writer's tests. In practice the measurement of actual volume is avoided by making clay and oil-drip containers of the same glass tubing and simply comparing the height of clay and oil passed. Thus a rating of 1.5 means that the oil bleached was 1.5 times the volume of the clay bleaching it. A set of four numbers such as 1.5, 2.2, 2.8, 3.6, refers to the four colors—water white, green, yellow, and red.

The tubes used for testing are of glass and have an inside diameter of 8 millimeters. (See fig. 32.) A 9-inch piece of tubing is constricted at about one-third its length and cut off. The shorter piece is shaped into a small test tube with slightly flaring top, and the longer piece is formed with a tapered carbon rod to seat a ¼-inch disk of blotting paper, cut with an ordinary file punch. A set of 5 or 6 pairs of such tubes mounted in a frame is convenient for testing. Similar sets of 1-inch metal tubes holding 6 inches of clay and surrounded by a bath of hot oil for controlling temperature, have been used in works tests.

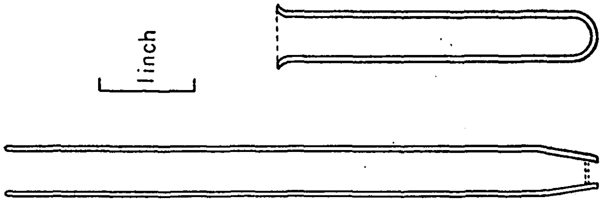

FIGURE 32.—Tubes for testing bleaching efficiency.

As a test oil, the writer prefers a black, sulfur-free crude oil. This is diluted with gasoline until Floridin clay tests 1.0 to 1.1 for water-white bleach, the complete run being 1.0, 1.3, 1.5, 1.7. Floridin clay is chosen for a reference standard, because it changes little with age. If the test oil is such as to give too low yellow and red separations, these may be increased as desired by adding cylinder stock. A few ounces of 150-mesh clay are kept in reserve for check tests. An advantage of the small glass tubes is the small amount of clay sample required for a test and the small amount of test oil used up; a gallon of test oil is ample for a thousand tests.

Unfortunately there appears to be no possibility of an absolute method of testing bleaching clays and no escape from the necessity of using reference standard clays and arbitrarily chosen test oils. The substitution of known concentrations of dyes in benzine for test oils has been suggested, but the adsorption of such solutions on clays differs so widely from that of petroleum as to be of little value.

PRELIMINARY TESTS OF CLAYS

If a clay sample passes inspection as an active or activable clay, about 10 grams are ground to 150 mesh and divided into three portions. One portion is set aside for the test of the bleaching power of the raw clay, and the other two, about 3.5 grams each, are put in 250-cubic-centimeter flasks with 100 cubic centimeters of 1:1 (20 percent) hydrochloric acid and heated to boiling for 1 and 2 hours, respectively, filtered, washed, dried, and sifted. All three samples are then dried at 160° C. for an hour and given the oil test described above. This test is sufficient to determine natural activity and activability. Testing fifteen clays in 3 batches of 5 each is a day's work, and several thousand such tests have been made at the Survey.

COLOR CURVES

If a clay shows pronounced activability in the preliminary test it may be worth a more detailed test to determine the utmost of which it is capable and the precise amount of acid treatment that will give optimum bleach. Five portions of about 3.5 grams each are weighed out of a supply that has been ground to 150 mesh and left over night to come to room humidity, put in five 250-cubic centimeter flasks with 100 cubic centimeters of hydrochloric acid ranging from 10 to 30 percent in concentration, and heated from about 40 minutes for the 10 percent to 4 hours for the 30 percent. The clay samples are filtered on weighed filter paper, washed and dried, left over night to come again to room humidity, and carefully weighed. Losses in weight should be about 5, 10, 20, 30, and 40 percent, the last residue usually being pure silica. The samples are then ground, dried at 160°, and tested for bleaching power.

Finally the oil-test results are plotted against percentage removed by acid, and a set of four curves for the four colors, such as are shown in figure 23, are obtained. The lowest curve shows the limit of water-white bleached fraction for different amounts dissolved by acid. This curve usually shows a maximum of 20 to 25 percent removal of soluble material. The effect of low leaches is slight, the action being chiefly an exchange of hydrogen for calcium. When alumina and iron are attacked, the bleaching power rises sharply to a broad optimum. Finally, with overtreatment with acid, the bleaching power drops considerably, to about that of silica gel or fuller's earth. The curves for limiting green, yellow, and red fractions are similar but with maxima farther to the right, that for the red fraction (petroleum lubricants) being usually at about 30-percent removal of solid materials.

Such sets of color curves are indicative of the nature of the clay, whether or not it has been weathered or kept too long in storage, and show the range of tolerance in plant control. The color curves of most good clays are so flat at their maxima that a departure of 5 percent either way from the optimum leach is of little consequence. A clay being treated for use in bleaching cottonseed, linseed, or palm oil should be slightly undertreated. An overtreated clay is almost valueless.

WORK TESTS

The tests above outlined are still lacking in the data necessary to establish a formula or recipe for plant operation. Although a 2-hour treatment in 20 percent acid may be best for some clays, for others a 3-hour treatment in 10 percent acid may give better results or be more easily controlled in practice. The data required are obtained by running tests that give sets of solubility curves, as described under chemical properties, and making a bleaching test of each portion treated. (See fig. 23.) Weighed samples are digested for 0.5, 1, 2, 3.5, and 5 hours in acid of 1.5, 3.0, 6.0, and 9.0 normality. The four sets of color curves indicate which acid concentration and time of treatment give best results and the range of tolerance in time and concentration.

A quick test to determine the degree of leaching would be valuable in plant control, but no such test is known. To remove a sample from the batch being treated and give it a regular bleaching test would require far more time than is permissible. A sample quickly washed and dried will form a hard cake if much underdone, but will be incoherent if correctly treated to overdone, but this test is not conclusive. Titration of a sample of spent liquor requires little time but is insensitive on account of the large excess of free acid that is always present. The determination of refractive index requires little time but is not very sensitive. An absorption test on a quickly washed clay sample with a water dye solution would be quick and might be servicable if done by a practiced observer. In the absence of any such quick tests, clay-treating must continue to be by formula alone.

The cracking of oil by clay is not shown by contact methods of testing, but is easily apparent in percolation testing. When the sample of dried clay under test is wet down with gasoline in the regular bleaching test, the top of the clay may turn red, pink, or brown, even though the gasoline used has been previously treated with active clay. Highly purified laxative oil and fused paraffin crack even more readily than gasoline, the longer chain molecules being more readily broken than the shorter ones. Many activated adsorbent clays and some fuller's earths crack gasoline, and there is no way known of preventing it without a considerable sacrifice of adsorbing power, although the addition of chlorinated hydrocarbons is of some assistance. When a bentonite is activated in steps, as for color curves, it is found that maximum cracking occurs at maximum absorbing power and that a fully leached clay shows little or no cracking. Among different clays, cracking and adsorbing power do not always go together.

Granular clays for percolation bleaching must be thoroughly dried just before use, as the hot oil cannot maintain a temperature sufficient to dehydrate the clay. Tanks for percolation bleaching are commonly 8 feet in diameter and two stories high and are charged with 20 tons of clay at a time. Drying is usually done with a Wedge furnace, which is a cylindrical tank provided with a series of shelves, the clay being raked from one to another in circulating hot air. Drying at a temperature of 300° to 500° F. is continued until the moisture content is reduced to 5 or 6 percent. Activated clays are used only room-dry and work best with an initial moisture content of 15 to 25 percent, as escaping steam assists oil impregnation.

Reburning used clays for reuse is common practice with the granulated fuller's earths and activated bauxites and if carefully done, to avoid overheating, may be continued until the adsorbing power has dropped 60 to 70 percent. The fine activated clays are never reburned. Wet combustion with concentrated chromic acid completely restores the original adsorbing power of both kinds of bleaching clays, but it is too expensive for practical use. Reburning is done in a Wedge furnace, such as is used for the final drying of new clays before use.

ECONOMICS OF PRODUCTION OF ADSORBENT CLAYS

GENERAL CONDITIONS

Although the market for adsorbent clays is already well supplied and potential reserves of both raw clay and processing capacity are considerable, there is yet room for new developments because of the diversity and wide distribution of consumption. The dominant producers are vulnerable, despite large-scale operations and long experience, because of heavy overhead charges and, in part because of unwise location with respect to clay deposits and markets. There is still considerable room for improvement, particularly in the activated clay industry, in the matter of quality and location of the clay worked, wastes in processing, and improvement in the quality and stability of product.

TRANSPORTATION

As there are few workable beds of either kind of adsorbent clay in the North and as freight charges from the far West are almost prohibitive, clay consumers of the North and East must look chiefly to the Gulf Coast for shipments by rail, and to California, England, and Germany for shipments by water. Refiners of the midcontinent region have abundant local supplies, but these are not of the highest quality. Most fuller's earth is now shipped at the lower rate applicable to "raw clay," but some is still billed as 'processed clay." In fairness, activated clay alone should pay the higher rate. Per ton per mile, shipments by water are of course far less expensive than by rail.

ACTIVE CLAYS

As to active clays, there is little to suggest in the way of improving the transportation picture, and there is little choice as to quality. At present the chief producers are at Macon and Attapulgas, Ga., Quincy and Ocala, Fla., Olmsted, Ill., Nacogdoches, Tex., and Creede, Colo. The clays produced are of high and nearly equal quality and are as well located as possible with respect to markets. The sole change suggested is the opening up of the enormous deposits at Pinson Hill, in western Tennessee (Porters Creek Clay), and at Epley's Bluff, near Cunningham, Ala. (Tallahatta). Both these are between the Olmsted and Quincy clays in quality, extremely hard when dry, and after drying do not slake in water. The only American substitute that has yet appeared for the English fuller's earth, which is used extensively for refining lard, is from St. Paul, Minn. Nearest like it in properties is the clay from Creede, Colo.

ACTIVATED CLAYS

Clay is activated at Los Angeles and El Segundo, Calif., Beaumont, Tex., and Jackson, Miss., and at a number of oil refineries where it is treated as used. That treated at Los Angeles is from Chambers, Ariz., and that used at El Segundo is from Otay, near San Diego. The Beaumont plant activates clays from Riverside, Tex., and elsewhere. The new plant at Jackson, Miss., is treating bentonite from the Vicksburg group. No attempt has yet been made to develop the extensive beds of excellent activable clay near Westcliffe, Colo., Santa Cruz, N. Mex., Browndell, Tex., Vienna, Ga., and Marianna, Fla. The very considerable expense of plant construction and operation has been a powerful deterrent. The market would appear to warrant an additional treating plant at Marianna or Cottondale, Fla. The large beds of easily available glauconite in the tidewater parts of New Jersey and Maryland should be of considerable local interest.

IMPORT DUTIES

A duty of about $21 a ton on activated clay and $3 a ton on fuller's earth has been in effect for some years. Such duties have not prevented the entry of either kind of adsorbent clay but have offset the lower ocean freight rates, the American market remaining fairly stable at about $80 a ton retail for activated and $15 to $20 a ton for naturally active clay. These prices are in the ratio (4:1) of the decolorizing powers of the two kinds of clay for petroleum, the chief advantage of the higher-powered clay lying in the lower handling costs.

MAPPING AND MINING

Given a location as favorable as possible from the transportation standpoint, the next consideration is the quality, extent, depth, and thickness of the clay bed to be worked. Mapping and testing in some detail is an essential preliminary to successful operation. Much mapping has been based on exploration with the old-fashioned spud drill, but for most clay deposits a 3-inch Iwan post-hole auger is far more rapid and less expensive to operate. A stem of ¾-inch iron pipe in 5-foot sections is used. With this tool samples are easily taken to a depth of 30 feet and have been taken to 50 feet. A gang of three men can easily prospect and map a 40-acre bed in a week or two.

Clay at least equal in thickness to overburden is an old rule. For bentonite a minimum overburden of 3 feet is required for protection against deterioration by weathering. Fuller's earth is very much less susceptible to weathering. Formerly operations ceased when overburden exceeded 15 feet, but where the power shovel has been displaced by the dragline much greater thicknesses are removed. Nearly everywhere clay improves in quality with depth in the bed. In removing overburden, the last foot in contact with the clay is usually left to protect it until mined, when it is removed by hand. At Creede, Colo., and Chambers, Ariz., clay has been produced for years by underground mining methods, but it is doubtful if either will continue long in competition with other deposits where strip mining is practiced.

COST OF DRYING

Various drying processes have been mentioned in the previous pages. Their relative costs are largely undetermined, and the writer is unable to add to the knowledge concerning them. In granulating fuller's earths, waste fines are minimized by drying and grinding in three or more steps, and the finished product ready for shipment should not cost more than $4 a ton. Dried bentonite ready for acid activation should cost no more, but it generally does, owing to inefficient methods of mining and handling.

COST OF ACID ACTIVATION

Acid activation costs from $15 to $25 a ton. This includes acid at $9 to $15 a ton, head, skilled supervision, washing, drying, sacking, and plant overhead and amortization. The cost of the finished product will be at least $30 a ton and should be less than $40 a ton at the plant. Naturally even a small percentage of underdone or overdone clay adds materially to the cost of the good product. Underdone clay cannot be reprocessed at a profit, and most overtreated clays are quite useless.

A complete modern plant for the acid activation of 50 tons of clay a day costs upwards of $300,000, but a plant of the same capacity operated by the batch process with wooden tanks need cost hardly a tenth of that figure. Operating costs of the two types of plant are approximately equal. Final drying, screening, and sacking costs are eliminated when refiners acid-treat their own clay, injecting it as mud into the hot oil after the final washing, but the over-all saving by this method is doubtful.

An acid-sprayed Texas fuller's earth called Millwhite, which bleaches the same as the Georgia-Florida fuller's earth at 350° F. and twice as well at 700° F., has been in use for some years, but it has yet to show a sufficient saving in bleaching costs to have a distinct advantage over either fuller's earth or activated clay. Acid-sprayed clays are said to leave the bleached oil less stable than acid-leached clays, whereas fuller's earths improve stability.

USES OF ADSORBENT CLAYS

As the bleaching clays can function efficiently as decolorizing, deodorizing, and catalytic agents only when free from all but essential or lattice water (H and OH), they are commonly used only on mineral oils at high temperature and on the more stable fatty acids, such as lard, palm oil, and cottonseed oil, at moderate temperature. For the nonfatty acids and carbohydrates (sugar and fruit acids), activated carbon is used or a mixture of carbon black and fuller's earth. For dehumidifying, silica gel, activated alumina, and bauxite are perhaps best. In "aging" raw wines, a mild fuller's earth is used for selective adsorption of the higher alcohols and unsaturated constituents.

Treatment of oils.—The universal use of adsorbent clays on lubricating oils is primarily to decolorize them and in this way enhance their sales value. However, careful engineering tests show a definite but small improvement in lubricating value of the oil as a result of clay treatment and a very considerable increase in its life, as measured by oxidation and sludging. All lubricating oils are clay processed. Clay removes not only tarry coloring matter but other unsaturated compounds that are colorless and more readily oxidized, including some olefins. The very considerable cost of treating lubricants with clay is simply charged to sales, and the writer knows of no attempt to justify it in actual lubricating value.

The older percolation and contacting methods of treating lubricants are well known. The use of any of the modern solvent extraction methods of preparing lubricants means the use of considerably less bleaching clay, but no solvent process yet devised obviates the use entirely. The application of bleaching clays to the decolorizing of distillates in vapor phase is simple and effective and an already established practice. Only a moderate amount of clay is required, and the demand is for a highly active clay in granular form. Clay-treating a crude oil before distillation has been shown to be feasible, provided the oil is not too high, more than 1 percent, in sulfur. The advantage of this method lies in the far greater fluidity of the crude oil. The clay requirement is the same as when only the heavy fraction is clay treated.

Active clays are not efficient decolorizers of either used lard from doughnut machines or for rosin oil, probably on account of their strongly acid character. Of the clays, those of type III are best, but the electro-positive activated carbon is more suitable. However, active clays are highly efficient in removing taste and odor from fish oils.

The treatment of vegetable and mineral fats, oils, and waxes with clays may be for decolorizing alone, if they are to be used for varnishes and soaps, or for removal of odor and taste. Animal and synthetic fats for shortening or other cooking purposes are treated only with the naturally active fuller's earths. For varnish and soap oils both active and activated clays are used. Even menhaden oil may be deodorized without difficulty. The laxative mineral oils are treated in succession with acid, alkali, and clay several times until a high finish is obtained that is not possible with clay alone. Oil lost by retention on bleaching clay, an important item when treating valuable oils, is of course less the more powerful the clay used, but there is a limit to this saving, as powerful clays crack oils and lower their stability.

Renovating dry-cleaning fluids.—The use of adsorbent clay for renovating dry-cleaning fluids (gasoline, naphtha, and chlorinated hydrocarbons) is simple, effective, and well established. Contacting and percolation methods are both effective in the complete removal of dirt and grease and in restoring the water-white condition of the solvent. If the proper amount of clay is added to the batch being cleaned, the cleaning fluid remains water-white at all times, acting merely as a solvent and carrier between fabric and clay.

Catalysts.—Activated clay already has a firm place in the rank of catalysts used in the polymerization of olefins into high-class lubricating oils. Aluminum chloride and certain metal oxides have been used for this purpose for some time, but activated clay is particularly adapted to it because of its ability to split and reform hydrocarbon chains. The catalytic effect is at its best at high temperatures and pressures. When a catalyst is used, a single closely related group of hydrocarbons may be produced, but without a catalyst the result is a whole series of hydrocarbons of widely divergent properties as the result of heat and pressure treatment.

The most highly active clays make the best catalysts, but these are incoherent, and a fairly open structure is required to obtain the preferred pea-size granules. A binder is required, but such binders as water glass contain alkalies and lower the power of the clay. Iron oxide and aluminum phosphate are used as a binder without any great sacrifice of adsorbing power. Firm structures may also be obtained by using fibers such as cellulose, spun glass, asbestos, or steel wool as binders. The demand for activated clay for catalysts is likely to reach a considerable volume.

Treatment of water solutions.—In the treatment of water solutions and suspensions it is well to recall that active clay is electronegative on its surface and seeks to adsorb electropositive ions and particles of matter. Activated carbon is the reverse and seeks to adsorb negative ions and particles. Active clay is used for removing hardness from boiler feed water. For sugar juices activated carbon is used. For removing suspended clay from city water supplies, carbon is indicated. When clay and carbon are both to be used, they should be applied in succession, not as a mixture.

In dealing with microorganisms, the problem is very complex and lies chiefly in the field of the microbiologist. Cataphoresis shows that such organisms are either positive or negative, and that death frequently changes the sign. Fuller's earths have long been used to collect vitamins from yeast and from whey and are better for that purpose than the more powerful activated clays, which apparently decompose the vitamins even when weakened by moisture. Similar studies should be made of the algae and cocci and of the many kinds of spores found in water supplies. When not too expensive, the obvious treatment in most cases would be active clays followed by active carbon.

Bleaching crude sulfur.—For bleaching crude sulfur, acid-activated clay of high power is used to minimize loss of sulfur. The clay is contacted at about 300° F., the temperature of maximum fluidity. On removal of impurities, chiefly organic, the color changes from a chocolate brown to a clear straw yellow. The spent clay, reground, is suitable for use as a fungicide dust.

Fungicides.—As a fungicide dust spray for grain fields, a combination of bentonite and sulfur has been found to be an efficient preventive of rust and smut and is now used in large quantities in dust form spread by airplanes. For this purpose, however, the less expensive Wyoming bentonite has been found to be as effective as the activable bentonites. The strongly hydrophilic nature of the swelling bentonite doubtless aids the fungicide in adhering to growing plants.

As carriers of nicotine applied to fruit trees to kill the coddling moth, active clays have been found very efficient. They adsorb and hold the nicotine sulfate against too rapid evaporation and serve to bind it to the moist fruit buds and young leaves. The present high price of nicotine, however, has prevented its extensive use despite its efficacy against moths, eggs, and larvae.

Supplying adsorbed food to plants.—The use of active clay for supplying adsorbed plant foods to vegetation has received some attention and offers decided possibilities. The active clay is contacted with the required plant food to the limit of adsorption, then mixed with soil for the growing plant. The less powerful naturally active clays appear to be better adapted to this purpose than those highly activated, as the latter do not readily release adsorbed material. The class III bleaching clays (active and further activable), such as the English and Marianna, should be best adapted to the adsorption of diverse ions. Whether or not this use of active clay is of practical value, it offers a means of evaluating the power of plant roots to remove food from soils.

Increasing bonding power of sands.—For increasing the cohesiveness of foundry molding sands the Wyoming swelling bentonite is of course ideal, as a very small proportion, 2 to 3 percent, is sufficient to greatly enhance the bonding power between moist sand grains. Some fuller's earths and activable bentonites function nearly as well as the swelling bentonites. The Olmsted, Ill., Porters Creek clay has been used in molding sands for some time and is rated 80 percent as efficient as the swelling type of bentonite. For this use the demand is small but steady.

In drilling muds.—Bentonitic clays are much used for increasing the density, viscosity, and plasticity of drilling muds. Many low-grade deposits of the midcontinent region, high in iron and lime, are well adapted for this use. The iron contributes to the desired weight, and lime and organic impurities give body to the fluid. There is a considerable demand for this sort of clay, but marketing is difficult and uncertain. A comprehensive discussion of the properties, methods of testing, and standards of performance has been presented by Reistel, Cannon, and Buchan.[22] Drilling muds may be made from any montmorillonite clay by soaking it in sodium carbonate solution to produce swelling and gelling properties and adding either baryta or hematite to give weight.

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[22] Reistle, C. E., Cannon, G. E., and Buchan, R. C., Field testing of drilling fluids: Oil Weekly, June 7, 1937, pp. 26–32. See also 13 references in Oil & Gas Jour., June 10, 1937, p. 54.

In ceramics.—The addition of bentonite to the clay of whiteware has been found not only to increase plasticity but to increase the modulus of rupture both dried and fired. It also increases the shrinkage after both drying and firing as well as the vitrification. The white and pink bentonites and pyrophyllite should best serve the purpose.

In portland cement.—The use of bentonite and similar clays as pozzuolanic material in portland cement is well known. Its chief function is to increase workability, but it decreases permeability to solutions and to some extent increases the resistance of the cement to weathering as well.

Waterproofing.—The swelling bentonites are very effective in waterproofing earth dams and reservoirs when properly applied. Such bentonite by itself is of course useless, as it becomes fluid in excess water and cracks in drying. Nor is it effective when introduced by means of isolated well points, because its diffusion is very limited. The most effective method of application is to mix soil with 5 to 10 percent as much dry ground bentonite and apply the mixture at least several inches thick as the core of a dam or an inner coating of a reservoir. The soil or sand serves as a support for the bentonite, which swells and fills the pores of the soil as it becomes wet. Tests are readily made with a porous-bottomed tube to find the proper proportion of clay and soil and the thickness required to withstand a given head of water.

SUMMARY

Production and uses.—The production of adsorbent clay keeps pace with the petroleum and automotive industries, to which it is closely related. The production of active clay is roughly 270,000 tons annually and of activated clay 40,000 tons. Most of this is used for decolorizing and stabilizing petroleum lubricants. The remainder is used chiefly in the fat and vegetable-oil industries. Deposits of active and activable clay of the highest grade appear to be far in excess of every prospective need.

Distribution.—The adsorbent clays range in geologic age from Ordovician to Pliocene.

The principal workings of naturally active clay are near Macon and Attapulgus, Ga., and near Quincy and Ocala, Fla. Reserves include a broad belt of the Barnwell formation extending northeastward from Macon into South Carolina and extensive deposits in the Hawthorn formation to the east of Attapulgus, north of Quincy, and northward from Ocala. Very large deposits of slightly inferior fuller's earth occur near Cunningham, Ala., and throughout the Porters Creek clay of Mississippi, Tennessee, Kentucky, Illinois, and Missouri. In the West, excellent active clay occurs near Browndell, Tex., Creede, Colo., Princeton, British Columbia, and Olancha, Calif. Active clay is known to occur in Japan and Argentina but not in Europe.

Clay that is both active and highly activable, class III, is now known to exist in large quantities in this country, but none has yet been produced as activated clay. The deposit at Browndell, Tex., has been used as fuller's earth for several years. Clay of Class II occurs in Georgia near Vienna and in southeastern Brooks County. In northwestern Florida it occurs in a belt beginning west of Marianna and extending eastward along the Georgia-Florida border to Brooks County, Ga. A deposit near Hachita, N. Mex., is in this class, as is the English clay sold as fuller's earth.

Clays that are almost inactive but highly activable, class II, have come chiefly from the Puerco region in northeastern Arizona (from Chambers to Allentown) and from Otay, Calif. Others from the Vicksburg group in Smith County, Miss., are now being worked. Large additional deposits are available near Pontotoc and Amory, Miss., Westcliffe, Colo., Box Elder, Utah, Milk River, Alberta, in the State of Veracruz, Mexico, and in southern Germany. As to activability, classes II and III are equally good. Distance from prospective markets is a factor in the development of deposits.

Physical and chemical properties.—All activable montmorillonite clays and at least some of those naturally active originated in volcanic ash or tuff. Where this ash contained sufficient alkalies and was exposed to water, the alkalies, most of the alkaline earths, and part of the silica escaped in water solution, and the remainder of the ash crystallized as montmorillonite, beidellite, or even halloysite, depending on the amount of alkalies and silica in the original ash.

Tentative field identification of montmorillonite clay can be made from its soapy texture and absence of grit. The montmorillonite clays fall into five natural classes, differing widely in their behavior toward water and oil. The class of the clay and its value for decolorizing can be determined only by laboratory test. The chemical composition of the five classes of montmorillonite clays shows no essential correlation with either activity or activability.

A clay is active, according to the writer's view, when open bonds capable of selective adsorption exist over its grain surfaces. Montmorillonite clay is well adapted to carrying a high surface density of open bonds.

Water is associated with clay in at least four different ways, which are evaluated by means of observations of vapor pressure and thermal dehydration. Active clays do not slake in water; all activable clays slake but leave nonslaking granules. The cause of this behavior is not yet known. Bentonites that swell in water do not activate, and they leave no unslaked granules.

The bases of montmorillonite clays dissolve readily in 20 percent hydrochloric or sulfuric acid, leaving nearly pure silica. Activation is best with a little more than half the bases removed. In dilute acids, silica as well as bases goes into solution up to a maximum concentration of about 1 gram per liter. Most activable clays after treatment with dilute acid undergo a slow internal change lasting from 1 to 10 weeks, with an alteration in bleaching power. The solubility of the silica of a montmorillonite clay reaches a maximum at a definite low concentration (0.08 to 0.8 normal) of acid, which is probably related to the maximum adsorption of acid by clay. The adsorption potentials of partly leached clays vary with the severity of the acid treatment in a manner closely paralleling the oil-bleaching efficiency.

The lattice structure of the montmorillonite clays indicated by X-ray analysis suggests an explanation of selective adsorption that is plausible but incomplete as to details. The refractive indices of montmorillonites vary with water content as much as 0.04, and after acid-leaching to about the same degree. The interlattice spacing varies with water content by more than 10^{-7} cm. During the acid treatment of montmorillonite clay, lattice water appears to be lost more readily than interlattice water.

The decolorizing action of clay on oil and the activation of clay are interpreted in terms of selective adsorption. The bleaching of an oil by clay is a selective adsorption of the darker constituents of the oil by the active clay surfaces. The decolorizing power of both naturally active and acid-activated adsorbent clay approaches a fixed upper limit.

The active clays change little in decolorizing power with age, but the activable clays deteriorate rapidly both before and after activation. Raw activable clays keep best in very moist air, activated clay in very dry air.

All attempts to produce a superior bleaching clay by the chemical treatment of inferior or impure clays have met with failure.

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