Smectite clay Minerals: Properties and Uses

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Smectite clay minerals: properties and uses

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[Plate 1]

The physicochemical properties of smectite clay minerals that determine their industrial utilization are reviewed. Smectite is the name used for a group of phyllosilicate mineral species, the most important of which are montmorillonite, beidellite, nontronite, saponite and hectorite. These and several other less common species are differentiated by variations in chemical composition involving substitutions of Al for Si in tetrahedral cation sites and Al, Fe, Mg and Li in octahedral cation sites. Smectite clays have a variable net negative charge, which is balanced by Na, Ca, Mg and, or, H adsorbed externally on interlamellar surfaces. The structure, chemical composition, exchangeable ion type and small crystal size of smectite clays are responsible for several unique properties, including a large chemically active surface area, a high cation exchange capacity, interlamellar surfaces having unusual hydration characteristics, and sometimes the ability to modify strongly the flow behaviour of liquids.

In terms of major industrial and chemical uses, natural smectite clays can be divided into three categories, Na smectites, Ca–Mg smectites and Fuller's or acid earths. Large volumes of Na smectites and Na-exchanged Ca–Mg smectites and Fuller's earth are directly used in the foundry, oil well drilling, wine, and iron ore and feed pelletizing industries, and are also used in civil engineering to impede water movement. Significant volumes of Na smectites are used for various purposes in the manufacturing of many industrial, chemical and consumer products. Large quantities of Ca–Mg smectites are used directly in iron foundries, in agricultural industries and for filtering and decolorizing various types of oils. A significant fraction of the Ca–Mg smectites used for decolorizing has been acid treated. Large volumes of Fuller's or acid earths are commercially used for preparing animal litter trays and oil and grease absorbents, as carriers for insecticides, and for decolorizing of oils and fats.

Natural Na smectites occur in commercial quantities in only a few places, but Ca–Mg smectite and Fuller's earth deposits of considerable size occur on almost every continent.

Introduction

There are many industrial and chemical uses for smectite clays, all of which depend on one or more of the unique properties of this group of minerals. During the past two decades, the various properties of smectite clays have been investigated intensively, with the result that many new uses have been introduced, especially in the environmental and chemical areas. Even today, almost every issue of journals devoted to clay mineral science contains one or more papers describing some previously unknown or poorly understood property of smectite clays.

The vast range of uses and the scientific interest in the smectite clay minerals stem from their physicochemical properties, many of which are not displayed by any other known natural minerals. The unique physicochemical properties displayed by smectite clays are the result of (i) extremely small crystal size, (ii) variations in internal chemical composition, (iii) structural characteristics caused by chemical factors, (iv) large cation exchange capacity, (v) large surface area that is chemically active, (vi) variations in types of exchangeable ions and surface charge, and (vii) interactions with inorganic and organic liquids.

Smectite clays are formed and are most stable in surface and shallow subsurface environments. At burial depths of 2000–4000 m smectite clays undergo alteration to illite–smectite mixed layer clays, and at greater depths the mixed layer clay is altered to illite through K adsorption in interlayer positions or even to chlorite if Mg is abundant (Eberl, this symposium). Smectite clays are ubiquitous components of soils, especially in semi-arid and arid regions. Continental and oceanic sediments from Cretaceous to Recent frequently contain smectite clays. Although very pure smectite clays as old as Jurassic are known, most of the commercial deposits are Cretaceous or younger in age.

The widespread occurrence of smectite clay minerals is related to multiple modes of origin including precipitation from fluids containing the appropriate chemical elements, from the alteration of Si-, Al-, Fe- and Mg-bearing minerals, and especially from the alteration of volcanic glass. The greatest number of commercial smectite clay deposits have formed from the hydrolysis of extrusive volcanics, although certain types of intrusive rocks have also been altered to smectite clays in weathering environments near the surface. Because of the vast amount of extrusive volcanism that began throughout the world in the Cretaceous period, smectite clay deposits are known on every continent, except Antarctica.

Large amounts of smectite clays have been used for many decades, and by 1982 the annual worldwide use, not including China and the U.S.S.R., had grown to more than six million tons†. Smectite clays have been important in the industrial revolution and in petroleum energy resource development, as these clays have extensive use in preparing metal moulds and in drilling oil wells. It has even been proposed that the beginnings of life originated when organic molecules were photochemically synthesized on the surfaces of iron-rich smectite clays.

PROPERTIES OF SMECTITE CLAY MINERALS

The physicochemical properties of smectite clay minerals are described in considerable detail in numerous textbooks, reference books and professional papers. Several of the properties of smectite clays are further described in other papers in this volume. The following discussion focuses on only those properties of smectite clays that are most important in their industrial and chemical uses. As far as possible, interrelations among physicochemical properties are stressed because many uses of smectite clays are dependent on more than one property.

Crystal structure and chemical composition

The smectite clay minerals have a layer lattice structure similar to micas, but they differ from micas in that the bonds between layers are weakened because of internal chemical substitutions. Only in the smectite clays are interlayer cations exchangeable and interlayer surfaces and cations hydratable. The smectite clays consist of layers of negatively charged oxygen atoms within which several types of positively charged cations are fixed in specific positions. In a two-dimensional schematic diagram of the structure (figure 1), four layers of oxygen atoms can be seen that define upper and lower tetrahedral sheets containing tetravalent (Si) and sometimes trivalent cations (Al^{3+} and Fe^{3+}). The apexes of the tetrahedra point toward each other, and the oxygen atoms at the apexes form part of an octahedral sheet that may contain

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† 1 ton ≈ 1016 kg.

trivalent cations, (Al, Fe), divalent cations (Fe, Mg), both divalent and trivalent cations, or divalent and monovalent (Li) cations. The presence of two tetrahedral sheets and one octahedral sheet is the basis for classifying the smectite structures as 2:1 phyllosilicates. This structural characteristic differentiates smectite clays from kaolinite clay structures containing one tetrahedral and one octahedral sheet and from chlorite clay structures that contain two tetrahedral and two octahedral sheets. Illite clay structures are similar to smectite clay structures, but in illite adjacent tetrahedral sheets are bonded by K^+ ions which are not exchangeable.

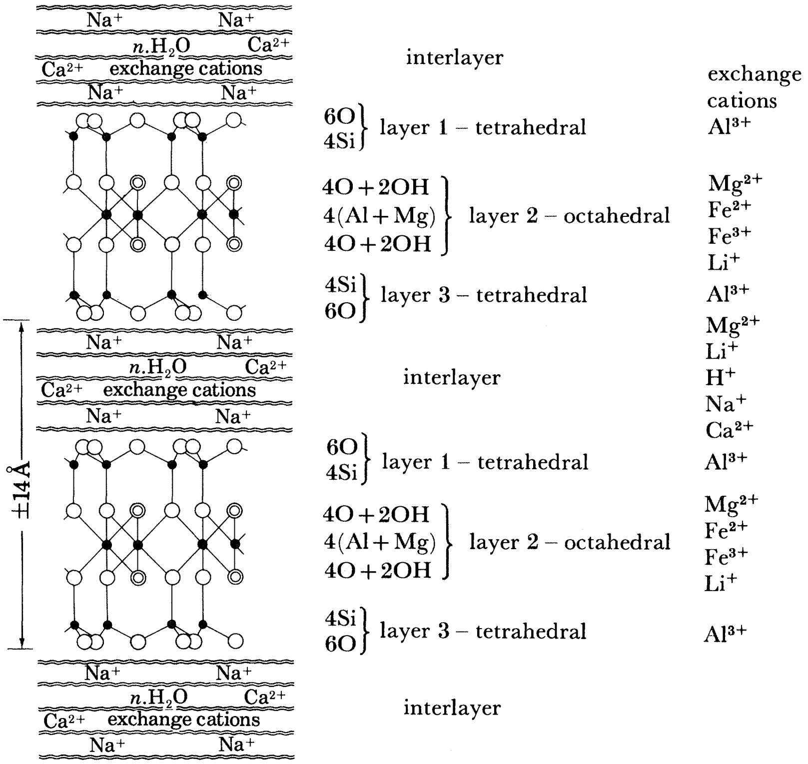

FIGURE 1. Structure of smectite clay minerals. The chemical composition shown is that of montmorillonite. Various ions that may be present in other smectite clay species are shown in column on right.

Smectite 2:1 structural units are separated by layers of loosely held hydrated cations. These cations are present to balance the negatively charged structure that results from internal substitutions of trivalent ions for silica in the tetrahedral sheet and especially from variations in trivalent and divalent ion content in the octahedral sheet. Interlayer surface and cation hydration between smectite structural units is a unique property of smectite clays.

The members of the smectite group of clays are distinguished by the species and location of cations in the tetrahedral and octahedral sites. Table 1 shows the currently accepted classification of smectite clay minerals and gives idealized structural formulas. This classification is based on both crystalline structure and chemical composition. In a half-unit cell containing ten oxygen and two hydroxyl ions, there are four tetrahedral cation sites and three octahedral cation sites. When two-thirds of the octahedral sites are occupied by trivalent cations, the structures are classified as dioctahedral, and when all three octahedral sites are occupied by divalent cations the structures are classified as trioctahedral. While wholly dioctahedral and trioctahedral structures exist, deviations in octahedral site occupations by divalent and trivalent cations produce structures that may be intermediate between dioctahedral and trioctahedral. Smectite clays have additional structural and chemical differences caused by limited substitutions of Al in tetrahedral sites.

A negative surface charge is characteristic of all smectite clay minerals and may range from 0.2 to 0.66*e* per S_4O_{10}. The net negative surface charge results from a structural positive charge deficiency due to the substitution of cations of lower charge for cations of higher charge, thus the net negative charge should theoretically equal the positive charge deficiency.

TABLE 1. CHEMICAL COMPOSITION OF MOST COMMON SMECTITE CLAY MINERALS

Modified from Brindley & Brown (1980)

	dioctahedral smectites
montmorillonite	$M^{+}_{y}\,nH_2O\ (Al_{2y}Mg_{y})\ Si_4O_{10}(OH)_2$
beidellite	$M^{+}_{x}\,nH_2O\ Al_2(Si_{4-x}Al_x)\ O_{10}(OH)_2$
nontronite	$M^{+}_{x}\,nH_2O\ Fe^{3+}_2(Si_{4-x}Al_x)\ O_{10}(OH)_2$
	trioctahedral smectites
saponite	$(M^{+}_{x-y}\,nH_2O)\ (Mg_{3-y}(AlFe)_y)\ Si_{4-x}Al_x)\ O_{10}OH_2$
hectorite	$(M^{+}_{y}\,nH_2O)\ (Mg_{3-y}Li_ySi_4O_{10}(OH)_2$

Dioctahedral montmorillonite has its structural charge originating from substitution of Mg^{2+} for Al^{3+} in the octahedral sheet whereas, in dioctahedral beidellite and trioctahedral saponite the surface charge comes from substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet. Hectorite is also trioctahedral, but its charge stems from substitution of Li^{+} for Mg^{2+} in the octahedral sheet. Nontronite is an analogue of beidellite that is iron rich.

The negative surface charge is balanced by cations intercalated between the structural units (interlayer sites). Typically, these cations are alkaline earth ions, Ca and Mg and, or, the alkali metal Na. These cations are always hydrated, as is the interlayer surface.

Other smectites having special structures or chemical characteristics include volchonskoite, sauconite, stevensite and lembergite. The basic properties of these smectites are briefly described by Brindley & Brown (1980). The structural and chemical characteristics of smectite clay minerals have been described in greater detail by others. Books by Grim (1968), Brindley & Brown (1980), and Weaver & Pollard (1973) include excellent discussions and many references to pertinent literature.

Crystal size and surface area

An excellent description of the crystal size and morphology of smectite clay crystals and aggregate types, based on high resolution electron microscopy, is given by Grim & Guven (1978). They show that smectite crystals may be as large as 2 µm and as small as 0.2 µm with an average size of about 0.5 µm. Individual crystal morphologies range from rhombic to hexagonal, lamellar to lath, and even to fibre shapes. Grim & Guven (1978) also describe a classification of aggregates including globular, mossy, lamellar, foliated, compact, and reticulated. The various aggregate types are determined by the habit or shape of individual crystallites and by their arrangement in the aggregate. Crystal shape and aggregate characteristics can have an important influence on physical and rheological properties. Even when dispersed in water, smectite crystals tend to occur in aggregates rather than in single crystals.

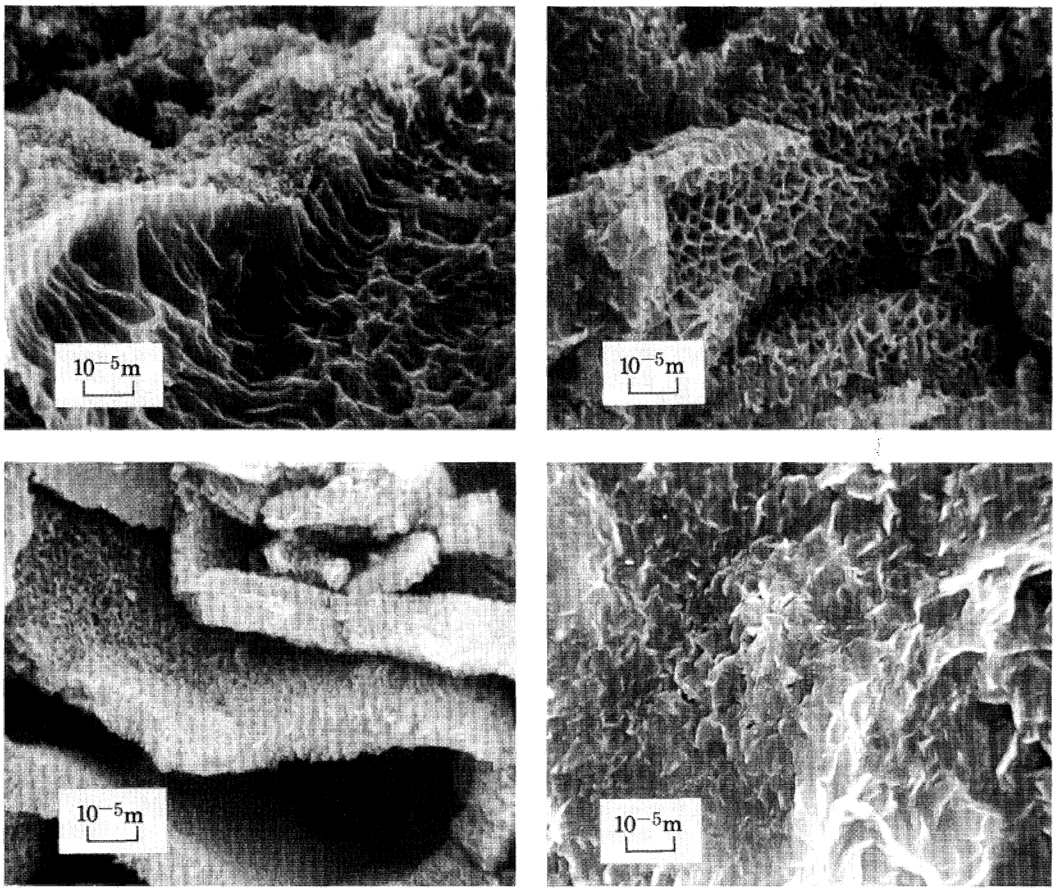

Figure 2. Electron micrographs showing the natural textures and crystal size variations of smectite clay minerals all of which formed from the hydrolysis of volcanic glass. The top two photographs are of Ca smectites; the bottom two photographs are Na smectites. Bar = 10 μm.

In the industrial use of smectites, it is important to recognize that because of aggregation the effective particle size and surface area of smectite clays are often considerably less than the actual particle size and surface area. This relation exists because during the growth of smectite clays by either transformation or neoformation crystals become interlocked and become difficult to separate except by a strong shearing force. Differences in the effective particle size of smectite clays are extremely important in the determination of properties such as ion exchange (Neal & Cooper 1983), viscosity and fluid loss. Natural smectites containing sodium as the predominant exchangeable ion yield the smallest effective crystal size and the largest surface area in clay–water systems because their natural crystal size tends to be small and swelling pressure tends to disrupt interlocked crystals. Smectite clays formed from volcanic ash may show considerable variation in primary texture (figure 2, plate 1), and this texture may persist to various degrees in clay–water systems.

Exchangeable ions and ion exchange

Perhaps the most unique property of smectite clays is the presence of exchangeable cations that are primarily adsorbed on interlamellar surfaces. The most common of these exchangeable ions are Ca, Mg, Na and H, but small amounts of exchangeable K and Li occur in some smectites. It is now generally realized that exchangeable Mg may be very abundant in some smectite clays, but as a rule Ca and Mg occur together and only in rare instances does the amount of exchangeable Mg exceed the amount of exchangeable Ca. As exchangeable ions, the chemical properties of Ca and Mg are similar, apparently because these ions have similar hydration characteristics. Among the major commercial smectite clay deposits, a far greater number contain Ca and Mg than contain Na or H as exchangeable ions.

The cation exchange capacity of relatively pure smectite clays ranges between 70 and 130 meq/100 g. According to Weaver & Pollard (1973), of the c.e.c. of smectite clays, about 80% is due to charges resulting from structural substitution, and about 20% is due to charges from broken bonds at the edges of crystals. Owing to natural chemical and physical factors and to methods of analysis, the abundance of natural exchangeable ions in even relatively pure smectite is usually less than the c.e.c. of the same smectite. If the abundance of exchangeable ions should exceed the c.e.c., then the presence of soluble salts should be suspected.

The exchangeable ions associated with smectite clays are easily and reversibly replaceable. Owing to its valency, Na is readily replaced by Ca and Mg, so that smectite clays tend to be depleted of Na when subjected to leaching conditions. For example, in local situations the Na originally present in South Dakota and Wyoming Cretaceous bentonites has partially been replaced by Ca and Mg in relatively recent times by groundwater leaching (figure 3). The Ca and Mg were derived from overlying shales or limestones, and the amount of Ca plus Mg exchange for Na increases as overburden thickness decreases. If present in sufficient concentration in groundwater, Na could easily replace Ca and Mg. Natural examples of replacement of Ca and Mg by Na are rare, but some examples are known in the western U.S. desert region where alkaline lake waters have percolated through smectite clays.

Exchangeable ions play a dominant role in the commercial use of smectite clays. Where Na is the predominant exchangeable ion, smectite clays, regardless of species, may have a high swelling capacity. Na tends to promote the development of many oriented water layers on interlamellar surfaces. The hydration associated with Na may produce swelling to the extent of complete dissociation of the individual smectite crystals, the result being a high degree of dispersion and maximum development of colloidal-like properties, that is, high natural viscosity. On the other hand, smectites having similar internal chemistry but containing exchangeable Ca plus Mg even when fully hydrated show only a small degree of swelling. Differences in ion hydration characteristics are discussed more fully in a later section.

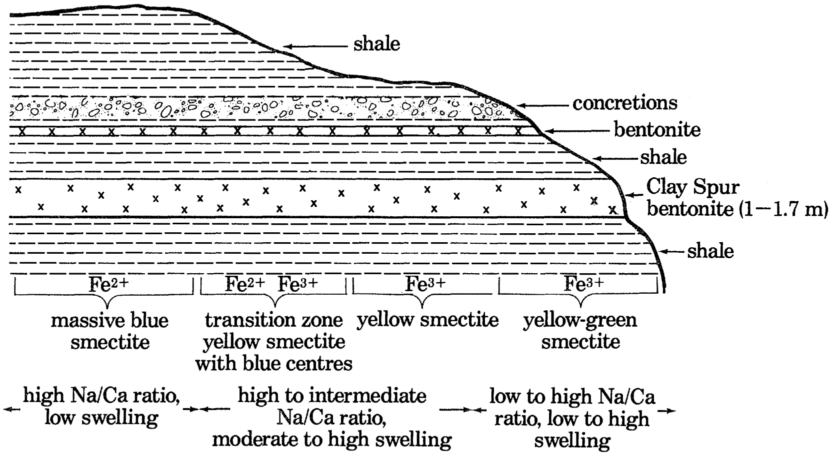

FIGURE 3. Diagrammatic cross-section of Clay Spur bentonite bed, Wyoming, showing variations in colour, iron oxidation, exchangeable ion ratio and swelling. The variations noted are caused by groundwater action and are related to overburden thickness and soluble ion content.

Exchangeable ion content of potentially commercial smectite deposits should be thoroughly studied or serious economic consequences could result. The exchangeable ions of smectite clays are usually determined initially by the chemical composition of the parent material if origin is by transformation, or by the concentration of ions in solution when formed by precipitation. The exchangeable ion content of smectite clays formed by transformation of volcanic glass that was desposited in a marine environment may be secondarily influenced by ions from pore solutions. These factors in addition to possible ion exchange from groundwater leaching can produce considerable variation of exchangeable ion content within a single smectite clay deposit.

Hydration and swelling

The hydration and dehydration of interlamellar surfaces are other unique properties of smectite clays, and these properties are of crucial importance in several industrial uses. Although hydration and dehydration occur regardless of the type of exchangeable cation present, the degree of hydration is dependent on the species of exchangeable ion, on the size and charge of the cations, and on the magnitude and location of the layer charge of the adjacent silicate sheets. Presently, it is generally accepted that the hydration of the interlamellar surfaces of smectite clays occurs in a series of steps when these clays are subjected to increasing relative humidity levels. At high humidity levels between one and four layers of water molecules may be formed, depending on the cation adsorbed. Most researchers believe that when only a few water layers are adsorbed, the water molecules (also organic liquids) are arranged in a highly ordered manner.

According to MacEwan & Wilson (1980), the hydration of smectites is controlled by three interrelated factors, (i) the magnitude of the negative charge on the clay mineral interlamellar surface; (ii) the exchangeable cations which occur between the interlamellar surfaces and balance the overall negative charge on the layer surface; and (iii) the interaction of the water molecules (or other neutral molecules) with the cations and with the clay mineral interlamellar surface.

The total net negative charge and the origin of this charge (octahedral or tetrahedral substitution) play an important role in the point localization of cations, especially multivalent species, on the layer surface. Charge resulting from tetrahedral Al substitution appears to cause ordering especially of multivalent cations on the silicate sheet. The tendency for exchangeable cation ordering is not found in octahedrally substituted smectites, since the net charge is more randomly distributed among the surface oxygens. This is a matter of great importance in certain areas of industrial use of smectites because it plays an important role in swelling behaviour.

The type of exchangeable cations and their tendency to hydrate has a strong influence on the arrangement of the water molecules and on the thickness to which oriented water layers could develop. Several investigators have demonstrated that multivalent ions tend to enhance the rigid structures of the first few adsorbed water layers, but as additional water layers are adsorbed these ions promote disorder or act to make the water more fluid. Monovalent ions such as Na and Li, however, tend to reinforce the rigid structure of water layers probably because they dissociate from the layer surface. The greater the degree of dissociation the less they disrupt the quasicrystalline water layers, thus these ions are, in effect, 'dissolved' in the water structure.

White & Pichler (1959) found that for air-dried smectite clays having Ca and Mg as adsorbed ions there is an initial rapid adsorption of water up to, or slightly in excess of, the liquid limit after which little further adsorption occurs, but when sodium and lithium are the adsorbed ions there is generally no sharp break in the adsorption rate and water may continue to be adsorbed far beyond the liquid limit. In naturally occurring smectites the highest water adsorption capacities are not always directly associated with the highest sodium ion content. The highest adsorption sometimes occurs when approximately one quarter to one fifth of the total exchangeable ions are Ca and Mg (figure 3). This relation suggests that Ca and Mg may strengthen the structure of water layers closest to the silicate layers, which then permits a greater number of rigid water layers 'reinforced' by Na ions to develop. In this situation, Na can diffuse a greater distance from the basal oxygen planes. The writer believes the primary reason some high-Na smectites have a low swelling capacity (figure 3) is that the crystallites are interlocked.

In summary, natural smectite clays range from strongly swelling to non-swelling depending on the smectite clay species and on the ratio of exchangeable Ca plus Mg present. The vast majority of naturally occurring smectite clays have Ca and Mg as the predominant exchangeable cations and are essentially non-swelling. Some Na and Li forms are particularly susceptible to swelling by water adsorption, and the layers may be separated by water layers many Ångstroms† thick, even to the point that dissociation of the layers may occur. A simple determination of hydration characteristics should be given priority in the evaluation of smectite clay deposits as so many industrial uses are dependent on this unique property.

Attempts to change Ca–Mg smectites to so-called Na smectites are a common practice in

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† 1 Å = 0.1 nm = 10^{-10} m.

the clay industry, especially in Europe where naturally occurring Na smectite deposits are rare. The ion exchange is usually performed by mixing soda ash (sodium carbonate) with crude, moist clay using various mechanical methods. After the soda ash is added, it is a general practice to stockpile the clay for several days or weeks to permit maximum exchange to occur. In Europe, smectite clays are often 'activated' using several forms of extrusion. In addition to intimate mixing with the soda ash, extrusion effects considerable shear of the clay platelets making more interlamellar surfaces accessible for exchange. The main objectives of activation are to increase hydration and swelling, wet tensile strength and thermal resistance.

The author's investigations of activation indicate that the maximum improvement in hydration is usually attained when Na constitutes approximately one quarter of the natural exchangeable ions. Perhaps the presence of some natural sodium permits more complete exchange of Ca plus Mg when additional Na (soda ash) is added to the system.

Colloidal properties

When certain smectite clays are added in very small amounts to water, their chemical and hydration properties cause the crystals to separate and disperse. In addition, their electric potential causes the particles to repel each other, and because the crystals are so small they may remain suspended in the liquid indefinitely, so that a colloid state is attained. The same smectite clays when added to water in larger concentrations (5–6 %) may cause the liquid to become highly resistant to flow or viscous, and when the shear stress on the liquid is removed the smectite particles usually develop a rigid gel structure. The ability to impart high viscosity and to develop thixotropy are unique properties of naturally occurring montmorillonite, hectorite and some saponite clays having high amounts of exchangeable sodium. Ca–Mg smectites, on the other hand, neither give high viscosity values or display thixotropic behaviour even when the percentage solid is very high. The viscosity developed by Na smectites is believed to be due mainly to small particle size, large surface area, and high dispersibility, and secondarily to the electrical forces between the particles. Thixotropy results because the negatively charged basal surfaces and the positive charges present on crystal edges attract each other, and so forms an internal 'card house' structure. A thixotropic smectite clay system can be returned to a viscous system through shear or agitation. Both viscosity development and thixotropic behaviour are essential properties of smectite clays used for preparing drilling muds.

The viscosity properties of smectite clays within a single deposit or bed may be uniform or highly variable. Figure 4*a* illustrates the large natural apparent viscosity variations possible in a natural montmorillonite at various locations over a small pit in a bentonite bed in eastern Wyoming, U.S.A. In contrast, figure 4*b* shows that in a second pit located near Belle Fourche, South Dakota, the natural apparent viscosity of the Na montmorillonite is much lower and very uniform. These natural viscosity differences are primarily related to degree of dispersibility and secondarily to natural ion exchange. The montmorillonites yielding high viscosities (figure 4*a*) usually occur under moderately shallow overburden, have a yellow colour as Fe^{2+} iron has been oxidized to Fe^{3+} iron, and have some Ca and Mg exchangeable ions introduced by groundwater which have replaced Na ions. The montmorillonites having lower and more uniform viscosities (figure 4*b*), on the other hand, occur under more than 10 m of overburden, have a very high Na to Ca + Mg ratio, and a blue or green colour, indicating that little groundwater action or oxidation has occurred. The combined action of ion exchange and oxidation caused by groundwater has increased the hydration and dispersibility of the montmorillonite,

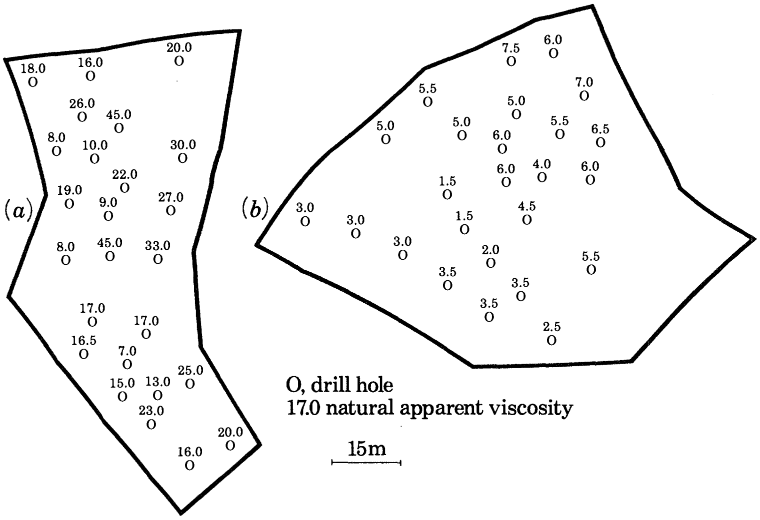

Figure 4. Variations in the natural viscosity of high Na smectite clays in different pits in South Dakota (*a*) and Wyoming (*b*). Numbers represent apparent viscosity in centipoises. Measurement made on a slurry containing 22.5 g in 350 ml of water using a direct-indicating viscometer.

Table 2. Colloidal properties of smectite clay samples from a single active pit, Mediterranean area, before and after soda ash activation

	crude smectite		soda ash activated smectite	
	apparent viscosity	fluid loss	apparent viscosity	fluid loss
sample number	cP	ml	cP	ml
1	2	31	26	15
2	2	21	39	13
3	2	40	7	21
4	2	30	10	16
5	2	31	13	18
6	2	26	5	20
7	2	20	54	14
8	2	27	16	19
9	2	23	19	24
10	2	36	24	14

Total Na content after activation is approximately 75 meq 100 g^{-1}. Measurement made on slurry containing 22.5 g in 350 ml of water using A.P.I. procedures.

leading to greatly increased natural viscosity. Table 2 shows the low natural viscosities of smectite clays from a bentonite deposit in the Mediterranean area in which approximately one quarter of the natural exchangeable ions are Na. Although these smectite clays initially have a low degree of dispersibility, treatment with sodium carbonate (table 2) greatly increases the dispersibility which in turn causes a dramatic improvement in the colloidal properties. In general, the influence of replacement by Na ions on the colloidal properties of Ca–Mg smectites is unpredictable and a careful evaluation of each deposit should be made.

Dehydration and rehydration

When smectite clays are heated two forms of water are lost, adsorbed and crystalline. The adsorbed water loss, most of which is interlayer water, occurs at low temperatures (100–200 °C). The amount of adsorbed water loss is contingent upon the nature of the adsorbed ions, if pretreatment of the samples is the same, and also to a lesser degree on the structure of the smectite (Farmer & Russell 1971). When Na is the predominant adsorbed cation, adsorbed water is usually lost in a single stage, but when Ca and Mg are predominant the adsorbed water is sometimes lost in two stages (figure 5).

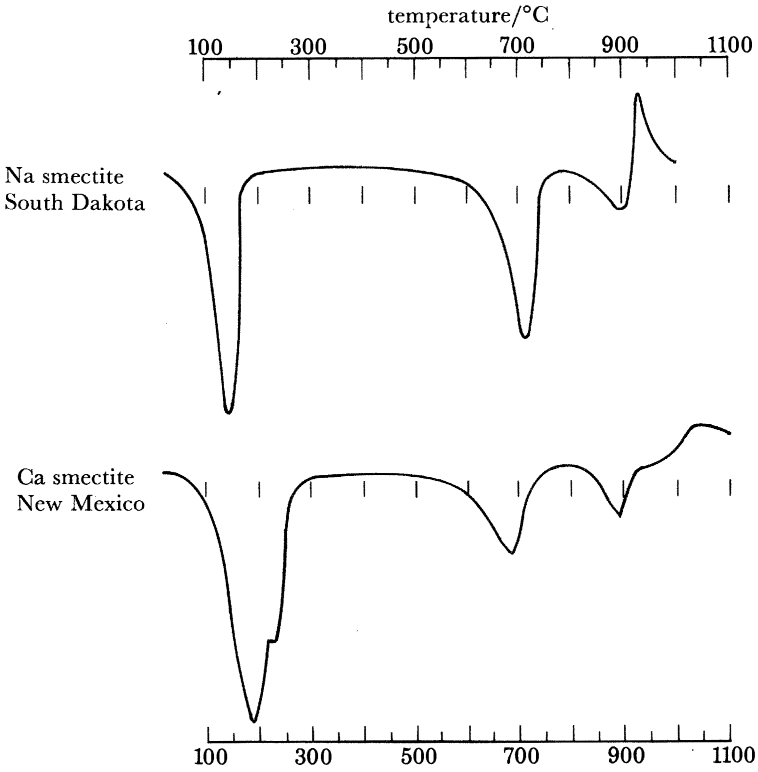

Figure 5. Differential thermal analysis patterns illustrating the single stage loss of adsorbed water that is typical of Na smectites and the two stage loss of adsorbed water that is often shown by Ca smectites.

Various smectites show wide variations of the temperature at which loss of OH or lattice water occurs. These variations are primarily related to crystalline structure, strength of cation-OH bonds, and chemical composition, since the OH loss involves a breakdown of the silicate structure. Among dioctahedral smectites, montmorillonites with low substitution of Fe and Mg for Al and having Na as the predominant exchangeable ion show loss of OH at the highest temperature, beginning gradually at 550 °C and ending at about 750 °C, with a peak at about 680–700 °C. Large replacement of Al by Fe or Mg causes a reduction in the temperature of the reaction, and for nontronite the peak temperature of OH loss is 500–600 °C. In magnesium-rich trioctahedral hectorite, however, the rapid loss of OH may not begin until 700 °C, possibly because the fluorine atoms that replace some hydroxyl groups are more tightly held within the lattice structure than the hydroxyl groups themselves. Other factors having some importance in the temperature of dehydroxylation of smectites are the intimate mixing of two smectites varying in composition and, or, structure (Grim & Kulbicki 1961), and possibly defect structures (Greene-Kelly 1957).

The rehydration characteristics of smectite clays after heating to various temperatures are not as well understood as the dehydration characteristics. If all of the adsorbed water is removed from smectite clays, some rehydration will occur, the amount depending on the relative humidity level and the properties of the clay. Smectites containing primarily exchangeable Ca and Mg usually rehydrate more rapidly, and at a lower humidity level, than do smectite clays containing exchangeable Na. This effect is due to the hydration properties of Ca and Mg ions. Also, the rate and amount of moisture a Ca–Mg smectite may adsorb seems to be greater if there is a moderate substitution of Mg for Al in the octahedral layer. The Ca–Mg smectite from Cheto, Arizona, has this chemical characteristic, and it rehydrates rapidly at low relative humidity levels (40%). Because of its rapid rehydration and textural properties, the Cheto smectite is used extensively as a desiccant.

When smectite clays are not heated much above 200 °C, most will rehydrate completely in the presence of liquid water, but generally there are some effects on certain properties such as swelling and, or, dispersion. Experience in drying bentonites commercially has shown that to retain primary properties it is unwise to remove the last traces of interlayer water, and in most industrial processing absorbed water content is seldom reduced below 8%.

In the presence of liquid water, smectite clays will generally rehydrate to some degree even after heating to temperatures as high as 500–700 °C. The degree of rehydration depends mainly on the degree of structural change owing to loss of OH lattice water. Naturally occurring Na montmorillonite having high thermal resistance (figure 6) is preferred for use in green sand moulding because the green compression strengths of the clay bonded sand moulds, which is a function of the rehydration of smectite, will be essentially the same even after the clay is heated repeatedly to temperatures of 600 °C.

Organic reactions

The absorptive and catalytic effects of smectite clays on organic compounds were long ago recognized as having fundamental importance in petroleum forming reactions, in soil forming processes, and in the chemical evolution of certain organic compounds. In the past 50 years an immense literature has developed on the properties of various smectite clay–organic interactions. This field of investigation has gained new vigour in the past decade as a result of the potential for using smectite clays as absorbents of various organic pollutants. Smectite clays have a large surface area for the adsorption and catalysis of organic molecules because of their small particle size and the large size and chemical activity of the oxygen layers forming the basal surfaces of the negatively charged 2:1 structure.

There are an almost endless number of organic compounds that interact in a variety of ways with smectite clays. The list is large because of the many types of bonding that are possible between the oxygen surfaces and the organic molecules (Mortland 1970). A simple example of a smectite clay–organic reaction that has great utility for the identification of smectite clays is the glycerol or ethylene glycol solvation technique. These organic compounds replace water layers on interlamellar surfaces and expand the interlayer distance to a nearly constant 17 Å spacing, which greatly aids identification by X-ray diffraction. In recent years, there has been considerable interest in organic molecules that are capable of carrying various metal ions as complexes, and that upon absorption may serve as pillars to prop open and increase the catalytic activity of smectite clay interlamellar surfaces (Pinnavaia 1983). These so-called pillared smectites are believed to have considerable promise for use as petroleum cracking catalysts. There is a growing use of smectite clays for absorbing various organic and inorganic contaminants from industrial waste water. In these processes a small amount of clay is added to the water to adsorb the contaminants, then other chemicals are added to flocculate the clay for easy removal from the system. Other uses of smectite clays related to their interaction with or action on organic compounds are discussed in later sections of this paper.

USES OF SMECTITE CLAYS

Smectite clays used in industry and in chemical and commercial products can be separated into three main types; Na smectites, Ca–Mg smectites and Fuller's or acid earths. The latter type may include materials that do not necessarily contain a large amount of smectite clays.

TABLE 3. PRIMARY INDUSTRIAL AND CHEMICAL USES OF SMECTITE CLAY MINERALS

large volumes	small volumes
foundry sand binder	medical, pharmaceutical, cosmetic
oil well drilling	paint
filtering, clarifying, decolorizing	building – brick, sewer pipe, roofing tile
pelletizing – iron ore	gypsum products
pelletizing – animal feed	radioactive waste disposal
waterproofing, water impedance	glazes
pet absorbent	pottery – ceramics
pesticide carrier	lubricants
oil and grease absorbent	fertilizers
	detergents
	mortar
	catalysts
	paper coating
	seed coating
	adhesives
	water purification
	other miscellaneous

Table 3 shows the primary uses of smectite clays. The uses are divided into two categories based on volume or tonnage used. Neither the large or small volume uses are necessarily ranked according to actual volume used, since annual consumption by various industries can change drastically depending on economic and political factors. However, over the past two decades the foundry, oil well drilling, and iron ore pelletizing industries have been the largest users of smectite clays, and these industries are likely to continue to be the largest users through the next several decades.

Foundry moulding sands

Several million tons of smectite clays are used annually in the metallurgical industry for preparing moulding sands. In Europe and Asia, foundry use is the main market for smectite clays, whereas in North America foundry use currently ranks second behind oil well use. In foundry usage smectites, in amounts varying from 5 to 10%, are mixed with sand and water to make the sand plastic and cohesive so that it can be moulded around a pattern. After the pattern is moulded and removed the smectite clay must give the sand sufficient strength to maintain the shape of the cavity before, during and after the pouring of the hot metal into the mould. The properties of smectite clays that are crucial in foundry usage are green compression strength, dry compression strength, wet tensile strength, hot compression strength, flowability and durability. The methods for analysis of the above foundry properties are described in detail by Parkes (1971).

Green compression strength is the strength of the moulded sand–clay mixture at a specified water content. It is measured by determining the compressive force necessary to cause failure in a test specimen containing a fixed amount of tempering water that is compacted by ramming to a specific compactibility. An alternative method for preparing the test specimen is to add only the amount of tempering water that is necessary to obtain a specified compactability. The green strength of smectite clays varies with crystallinity, the type of exchangeable ions, the percentage of clay, and the percentage of tempering water. When evaluating the green strengths of smectite clays from a single deposit or different deposits, it is advisable to make all tests with a specific type of sand and at a fixed clay and tempering water content. Table 4 shows the green compressive strength of several smectite clays presently used in foundries containing various amounts of exchangeable Na, Ca and Mg determined at 2.5 % tempering water and 5 % clay. In general well-crystallized smectites of high purity that contain primarily exchangeable Ca or Ca and Mg have somewhat higher green compression strength than natural Na smectites or Na exchange Ca–Mg smectites. The green strength differences between Na and Ca smectites are related to the influence that the various exchangeable ions have on the shear strength of a relatively small number of adsorbed water layers. Replacing Ca and Mg ions with Na usually decreases green strength.

TABLE 4. FOUNDRY AND OTHER PROPERTIES OF SMECTITE CLAYS AS RELATED TO EXCHANGEABLE ION CONTENT. SOME SAMPLES WERE ACTIVATED BY PRODUCER USING SODIUM CARBONATE. AMOUNT OF SODA ASH USED IN ACTIVATION IS NOT KNOWN

	green compression strength	dry compression strength	green compression durability (%)		liquid limit (%)
	pounds per square inch†	pounds per square inch†	500 °C	600 °C	
Na smectite, United States	10.9	104	100	100	670
Na smectite, Africa	9.3	125	100	100	465
Na–Ca–Mg smectite, Australia	8.6	85	100	42	338
Na–Ca–Mg smectite, Europe	11.3	84	75	31	225
Na–Ca–Mg smectite, Europe – activated	13.7	100	100	74	610
Ca–Mg smectite, Europe	13.6	54	11	0	200
Ca–Mg smectite, Europe – activated	14.6	53	78	44	430
Ca–Mg smectite, Europe	12.8	91	64	20	—
Ca–Mg smectite, Europe – activated	12.6	121	100	51	525
Ca–Mg smectite, Australia	11.1	58	70	16	200
Ca smectite, United States	13.8	56	50	16	200
Ca smectite, Europe	14.3	60	55	14	—
Ca smectite, Europe – activated	13.2	82	87	29	—

† 1 pound per square inch ≈ 6895 Pa.

Dry compressive strength is the force necessary to cause failure in a rammed specimen after all tempering water is removed by drying in an oven at 100 °C before cooling in a desiccator. Again, for routine comparative analysis of the dry strength of smectite clays, it is advisable to make all tests at a fixed moisture and clay content. Differing amounts of tempering water or clay content cause significant variations in dry compressive strengths as well as green compression strengths.

In smectite clay–sand systems containing 5% clay and 2.5% tempering water, the dry strength of Ca smectites is usually lower than that of Na smectites (table 3). If the tempering water is increased the dry strength of both Na and Ca smectites also increases. These variations in dry strength again illustrate the influence that the different common exchangeable ions have on the rigid structure of those absorbed water layers remaining after drying. It is possible that the higher initial dry strength of Na smectites is in part related to the dispersibility of the clay as Na smectites are more dispersible at lower moisture contents. Treating Ca smectites with Na salts tends to raise dry strength slightly or leaves it essentially unchanged (table 3).

When metal is poured into a smectite clay-bonded sand, the heat drives adsorbed water and water resulting from OH loss from the clay within a given distance from the metal–sand interface deeper into the mould. The excess water then condenses and concentrates in a narrow zone where the temperature is less than that required to remove absorbed water layers. The amount of water that condenses in this zone is in excess of the amount required for optimum green strength. Since green strength decreases with increasing moisture content, the mould becomes weak in the zone of moisture condensation or build-up. If the smectite clay in the mould contains an abundance of Na ions, the excess water is adsorbed on the clay surface in an organized or rigid structure, whereas if Ca–Mg are the predominant adsorbed cations the water remains in a liquid form. As a result of the ability of the Na ion to develop rigid water layers, the saturated zone becomes stronger and more resistant to tensile and compressional stresses that might cause a part of the mould wall to separate from the remainder of the mould (Patterson & Boenisch 1967). Natural Na smectites give high wet tensile strengths, whereas Ca–Mg smectites have very low wet tensile strengths. The wet tensile strength of many Ca smectites can be greatly improved by Na exchange.

In the preparation of moulds, the sand–clay mixture is compacted by a variety of mechanisms. In order to achieve the minimum porosity, the clay coated sand grains must ‘flow’, that is, the clay–water system acts as a lubricant reducing friction between the sand grains. Flowability is, of course, influenced by grain shape, clay, and moisture content, but for smectite clay–sand mixtures containing the same amount of clay and moisture Ca smectites generally have better flowability than Na smectites. The Na smectites tend to develop a greater number of water layers that have a rigid structure, whereas there is a sharp break between rigid and non-rigid water layers absorbed on Ca smectites.

When metal is poured into a mould, the clay–sand mixture inward a short distance from the metal–mould interface is heated to high temperatures, the maximum being dependent on the temperature of the metal. Smectite clays heated in the range 800–1100 °C begin to vitrify, and the compression strength of the clay-bonded sands through this temperature range shows a moderate to sharp increase, then a sharp decrease.

Natural Na smectites have much higher hot compression strengths than Ca smectites. These differences in hot compression strengths are primarily related to the influence different exchangeable ions have on the strength of the glass-like or mineral products formed during vitrification (when the mould is hot). Although the hot compression strength of Na-exchanged Ca smectites is often increased, the high strength characteristic of natural Na smectites is seldom attained.

Clay–bonded moulding sands are recycled many times in the mould making process. Each time metal is poured into a mould, a certain percentage of the clay is heated above the temperature where OH ions are removed from the clay structure. After loss of OH ions, the smectite loses its ability to develop green and dry compression strength properties. The OH loss from most smectite clays generally occurs in the range of 500 to 750 °C. As a general rule the higher the temperature of OH loss the greater the durability of the smectite clay. Although durability is primarily related to the temperature of OH loss, it is secondarily influenced by the type of exchangeable ions. An approximation of the durability of smectite clays can be obtained from differential thermal analysis (d.t.a.) (figure 6), but actual tests after heating and re-use of the smectite clays provide a more definitive measure of durability. As a general rule durability is greater for Na than for Ca smectite clays, and the durability of some Ca smectites can be improved by Na exchange.

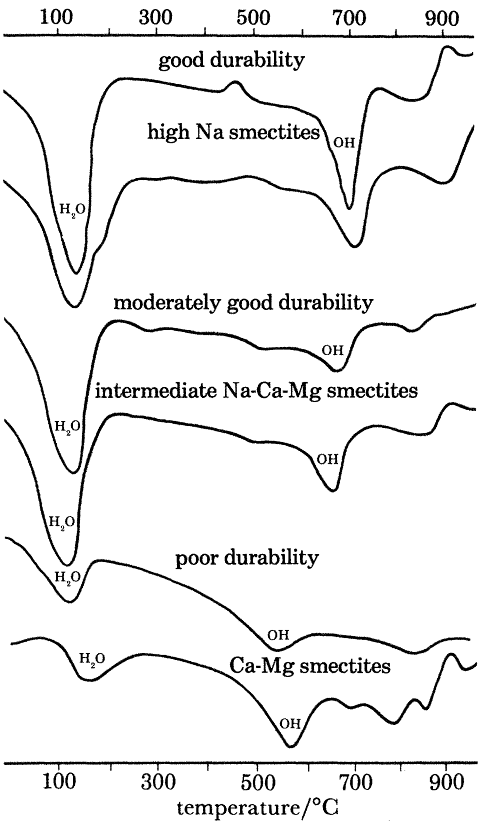

Figure 6. Differential thermal analysis patterns showing the relation of temperature of crystalline water (OH) loss to the thermal durability of some Na, Na–Ca–Mg, and Ca–Mg smectite clays.

The type of smectite clay used in each foundry depends on a variety of factors including geography of source, type of foundry practice, particular application, and price. Most foundries have their own specifications for green, dry and hot strengths, wet tensile strength, and liquid limit. Natural Na smectites have better durability and higher fusion temperatures, and are favoured for use in steel foundries. Na smectites, Ca smectites, and Na exchanged Ca smectites are suitable for preparing moulds for iron castings. In actual practice, many iron foundries specify a blend of specific types of Na and Ca smectites to achieve optimum green, dry, hot and wet tensile properties.

Drilling muds and related uses

The preparation of drilling muds currently constitutes the second largest end use of smectite clays, amounting to approximately 2.5 million tons in 1982. Smectite clays used for drilling muds must meet the American Petroleum Institute (A.P.I.) or the Oil Companies Materials Association (O.C.M.A.) standards set for grit, viscosity and related rheological properties, and fluid loss. Only certain natural Na and Na-exchanged Ca smectites have the potential for meeting the A.P.I. and, or, O.C.M.A. specifications. A.P.I. specifications require that 2000 pounds† of smectite clay (bentonite) yield at least 90 barrels‡ of drilling mud having a minimum apparent viscosity of 15 cP§, a plastic viscosity to yield point ratio not greater than 1:3, and a fluid loss of 15 ml or less. Although O.C.M.A. specifications are the same as the A.P.I., a higher concentration of smectite clay, 7.5 rather than 6.4%, is permitted to achieve the required properties and yield.

The worldwide occurrence of smectites that will meet all of the A.P.I. specifications is limited to a few geographic locations. However, if a Na or Na-exchanged Ca smectite clay meets the A.P.I. or O.C.M.A. fluid loss requirement, a small amount of a suitable polymer can be added during processing to develop the necessary minimum viscosity. Both fluid loss and viscosity of smectite clays can sometimes be favourably influenced by adding sodium carbonate and, or, certain types of polymers, but the cost of such additives is often prohibitive. There are many types of organic and inorganic additives used to improve or regulate the properties of drilling muds, the effectiveness of which depends on the surface, colloidal and ion exchange properties of the smectite clays used.

A relatively new and growing use of high-swelling Na smectites is to seal shallow exploration drill holes to prevent contamination of groundwater aquifers by surface or interformational leakage. The clay is compacted into large pellets that sink in the hole, after which hydration and swelling begin.

Na smectite clays specially formulated to resist high temperatures have recently been introduced for drilling deep wells and geothermal areas. These high temperature-stable smectites are not subject to the large increase in viscosity that elevated temperatures may induce in common well drilling grade smectites.

Pelletization

Smectite clays are extensively used as a binding agent in the pelletization of animal feeds, iron ore and other fine-grained solids. Smectite clays are added to animal feed in amounts of approximately 2% as a binder and to reduce die friction during the pelletization process. In addition, smectite clays are known to increase the nutritional benefits animals derive from the feed. Both Na and Ca smectites are used in feed pelletization.

The beneficiation of low grade iron ore (taconite) requires that the rock containing the ore be ground to a fine particle size so that impurities can be separated from the iron. The separation is usually done in a fluid medium. Pelletization of iron ore derived from taconite using smectite clays as a binder was introduced in the U.S.A. in the mid-1950s, and by the mid-1970s this was the largest single use of smectite clays. Both natural Na and Na-exchanged smectite clays are used for iron ore pelletization. Only the Na smectites promote good pellet

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† 1 pound = 0.45 kg.

‡ 1 barrel = 0.159 m^3.

§ 1 cP = 1 centipoise. 1 P = 10^{-1} Pa s.

development and give the pellets the required green and dry strengths and a high strength after calcination. Another important factor is that Na smectites are required to adsorb excess water that is not removed from the ore by vacuum filters. For this reason Na smectites having a high moisture adsorption capacity are preferred, and minimum moisture absorption capacity is often specified by iron ore pelletizing companies.

Civil engineering

The use of smectite clays in civil engineering applications first began in the mid-1950s, and these uses have grown substantially in the past three decades. In civil engineering smectite clays are used to grout cracks and fissures in rocks, to impede water or chemical waste movement through sand, gravel and permeable soils, to provide nonmechanical support of excavation and tunnel walls, to lubricate caissons and piles, to increase the plasticity of mortar, to make concrete pliable as well as impermeable, to waterproof concrete walls and floors that are below grade, and to lubricate cables and pipe for pulling through conduit.

The properties of smectite clays that are most significant in civil engineering uses are viscosity, thixotropy, impermeability and plasticity, thus smectites having a high swelling capacity and good dispersibility are normally required. Only natural Na smectites as well as certain Na exchanged Ca smectites have the necessary properties for engineering use.

Absorbents

Clay materials containing smectite clays and Fuller's earth or acid earth having absorbent properties are extensively used for pet litter, for absorbing oil and grease from floors, as a carrier for certain types of agricultural insecticides, and for packaging desiccant. In the preparation of pet litter, local customs or disposal methods may determine the type of smectite-containing clay material used. In the U.S.A., pet litter granules must be resistant to disaggregation in the dry state and resistant to slaking when wetted. Since high purity Na and Ca bentonites are not normally resistant to disaggregation or slaking, they are seldom used in the U.S.A. for pet litter. In some parts of Europe, however, granular Ca bentonites are used for pet litter because the favoured disposal method is to flush the litter into the sewage system, thus it is desirable for the litter to slake into fine particles when saturated.

Granular clay materials suitable for absorbing oil and grease from floors must not become slippery when wet. For this reason, only certain types of absorbent smectite clay materials are suitable for this use. Sometimes the slipperiness can be reduced and the absorbency increased by calcination. Smectite clays that have some hydrogen absorbed on surface exchange positions seem to be especially effective as carriers of agricultural insecticides, but high purity Na and Ca smectites are also used for this purpose. Ca smectite clays having high moisture absorption capacity at low relative humidity levels and high hardness are used for packaging desiccants.

Filtering, decolorizing and clarifying

More than 150000 tons of smectite clays are used annually for the treatment of animal and mineral oils and greases, for decolorizing vegetable oils and for clarifying wine. Most of the smectites used for the filtering and decolorizing of oils are Ca smectite that has been acid treated to increase the decolorizing property. To qualify for these uses, a small amount of the acid-treated smectite must cause a large amount of colour reduction. Some natural acid or Fuller's earths are also used for filtering and decolorizing.

A moderately large amount of smectite clay is used to remove colloid impurities in wine. The colloidal organic impurities in wine carry a positive charge, and these particles are coagulated by mixing a small amount of a negatively charged smectite clay into the wine. Na smectites having a light colour and high dispersibility are preferred for use in the wine industry. Smectites are also used to clarify beer, vinegar and fruit juices.

Miscellaneous uses

There are so many miscellaneous small volume and speciality uses of smectite clays that only a few can be briefly mentioned. More than ever before, speciality uses of smectite clays are being investigated by numerous producing companies.

(i) Adhesives. Smectite clays having high dispersion and suspension characteristics are used in latex and asphaltic materials. Organic-clad smectites are used in some types of adhesives because of their gelling properties in certain organic liquids.

(ii) Atomic waste disposal. There has been a small use of Na smectites having high c.e.c. for absorbing radioactive isotopes of strontium and caesium and then fixing them against groundwater leaching by calcining the clay to the vitrification point. More recently, Na smectites have been used for sealing around buried canisters containing radioactive wastes.

(iii) Emulsifying suspending and stabilizing agents. Highly colloidal Na smectites and organic-clad smectites are used as suspending agents in liquid fertilizers and in many organic liquids.

(iv) Greases. Organic-clad smectites are widely used for stabilizing the gel properties of lubricating greases. The greases prepared with organic-clad smectites are said to have superior properties (Jordan 1950).

(v) Ink. Small quantities of organic-clad smectites are used in certain types of inks to control consistency, penetration and misting during the printing operation. The current extent of this use is not known. Smectites are also used to de-ink old newsprint through their ability to disperse and absorb ink pigments.

(vi) Medicines, pharmaceuticals and cosmetics. There is an increasing use of Na smectites in the preparation of medicines, pharmaceuticals and cosmetics. These uses generally require water washed Na smectites having a high brightness, and in some uses the smectite must also be high in magnesium.

(vii) Paint. Natural, Na-exchanged Ca and organic-clad smectites are used in both oil and water-based paints. The smectite clays act as suspending and thickening agents and the gel structure is said to improve brushability and spraying characteristics and to reduce pigment penetration into porous surfaces.

(viii) Catalysts. Certain types of Ca smectites were previously used for manufacturing petroleum cracking catalysts, but synthetic zeolites have largely replaced the clay catalysts. A small volume of Ca smectite is still used for manufacturing dimer acid.

(ix) Soaps. Because of the environmental problems caused by phosphates, there has been renewed interest in Na smectites as a component in soaps. Na smectites, in addition to their detergent action, have a beneficial water softening effect. The patent literature mentions a variety of cleaning and polishing compounds containing smectites.

(x) Ceramics. Smectite clays are not used in large volumes as ceramic raw materials because of their high water of plasticity. However, small amounts of low-iron smectites are added to ceramic bodies to impart strength and to give desired vitrification or colour properties. Smectites are sometimes added to kaolin slips to improve their suspension characteristics and to structural clay products to increase plasticity required for extrusion.

(xi) Anti-stick and drying agents. A moderately large tonnage of both Na and Ca smectites are used as absorbents to reduce moisture content and to prevent sticking of various types of grains and fertilizers. The potential use of granular Ca smectite as a substitute for natural gas for drying pecans has recently been reported.

(xii) Seed coating. Certain types of seeds are coated with Na smectite to improve germination and to increase their size to permit mechanical planting.

(xiii) Soil conditioners. There has been considerable research on the use of smectite clays having moderate to high water-holding capacity to retain moisture in porous and sandy soils. Because of costs, this use is limited to high profit crops. Ca smectites have been added to certain types of soils to improve tilth and to modify the pH.

(xiv) Water clarification. There are several commercial processes that use smectite clays for purification of water containing various types of industrial oils and organic contaminants. Na smectites are preferred for this use because of their dispersion and absorptive properties.

(xv) Mortar mixes. Specially formulated mortar mixes containing a small amount of sodium smectites are commercially available. The smectite clay improves the water retention, plasticity and general workability of the mortar. Microfine smectite clays are used for essentially the same purpose in the tape–joint compounds, plasters, putties and caulking compounds.

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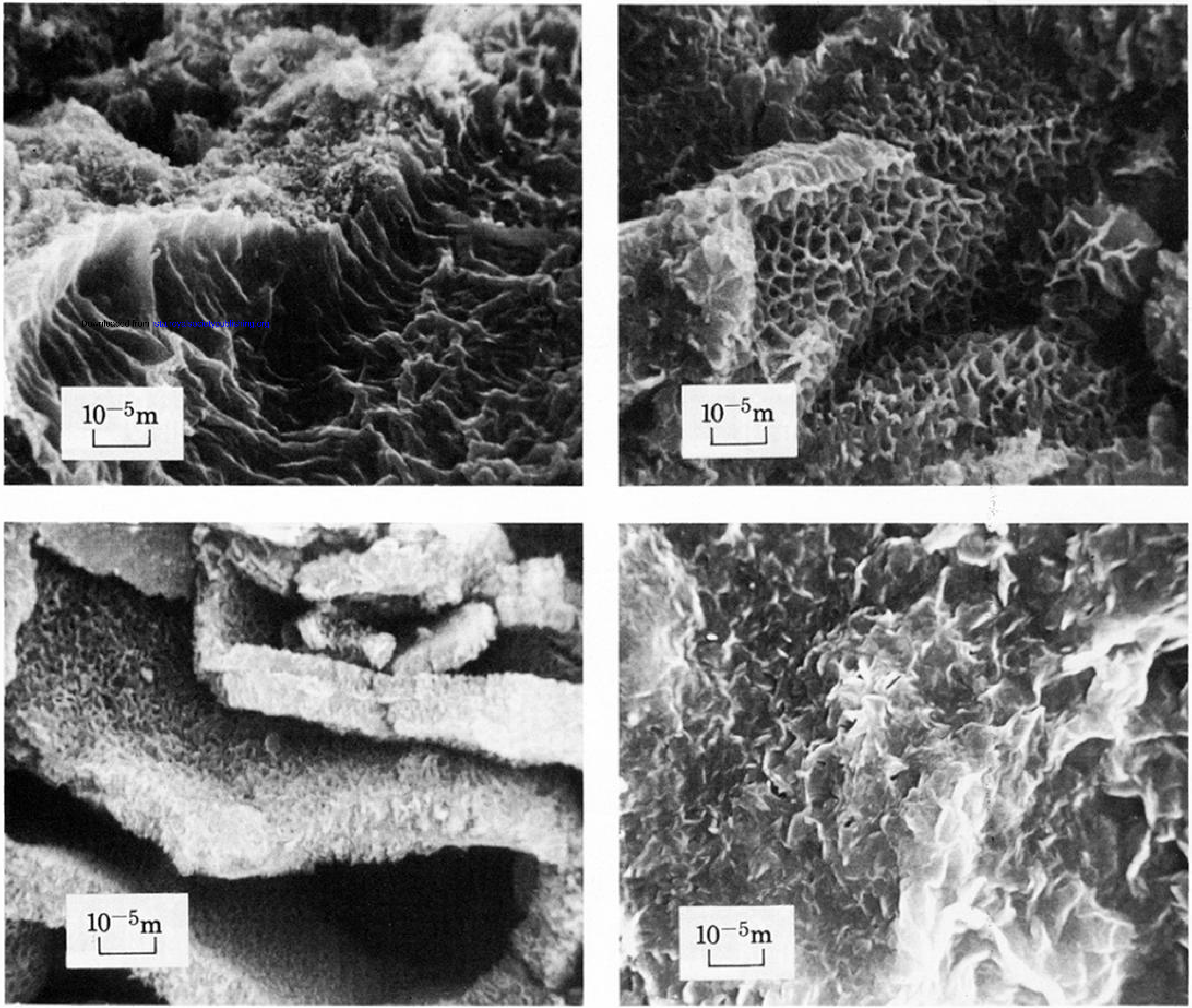

FIGURE 2. Electron micrographs showing the natural textures and crystal size variations of smectite clay minerals all of which formed from the hydrolysis of volcanic glass. The top two photographs are of Ca smectites; the bottom two photographs are Na smectites. Bar = 10 μm.