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CLAY MINERALS – MINERALOGY AND PHENOMENON OF CLAY SWELLING IN OIL & GAS INDUSTRY

ABSTRACT

Among the minerals found in the earth's crust, clay minerals are of the widest interest. Due to the specific properties such as plasticity, absorbing and catalytic properties clay minerals are used in many industries (oil & gas, chemistry, pharmacy, refractory technology, ceramics etc.). In drilling, a phenomenon of swelling clays is frequently observed. It has an important impact on the cementing quality. During the last few decades clays have been the subject of research on a scale unprecedented in the history of mineralogy. This paper presents review literature on mineralogy of clay minerals and phenomenon of swelling in oil and gas industry. Unique ion exchange properties and clay swelling mechanisms are also considered.

Keywords: clay minerals, oil&gas, ion exchanging, swelling

INTRODUCTION

The name of the clay minerals define a group of minerals that are essential constituents of loam rocks, such as kaolins, clays, soils, shales, bentonites, etc., and determine specific properties of these rocks. As they occur in nature, clays consist of a heterogeneous mixture of finely divided minerals, such as quartz, feldspars, calcite, pyrites, etc. The definition of clay was first formalized in 1546 by Agricola. It has been revised many times since, although the fundamentals involving plasticity, particle size, and hardening on firing were retained by most. AIPE* Conference held in Brussels in 1958 and Copenhagen in 1960 adopted the following definition of clay minerals of crystalline structure:

Clay minerals of crystalline structure are the hydrated layered silicates (packets), formed from a layer containing a silicon-oxygen tetrahedral arranged in hexagons, which are connected with the layers of octahedral formed; clay minerals are usually fine-grained, and are capable of forming with water a more or less plastic mass.

Definition of clay minerals developed at the Copenhagen Conference is consistent with the definition adopted by the Academy of Sciences of the USSR [1].

Clay minerals are an extremely important group of minerals. Due to the specific properties such as plasticity, hydration and catalytic properties clay minerals are used in many industries. Agriculture, chemistry, pharmacy, refractory technology, ceramics etc. are the fields in which clay minerals found practical application [2].

In recent years, clay minerals have gained in importance in the oil & gas industry, where are used as a basic component in drilling fluid technology. Clay provides the colloidal base of nearly all aqueous muds, and rarely used in oil-based drilling fluids [3]. On the other hand, the presence of clay minerals in the soil, causing numerous problems at the steps of drilling and cementing the borehole. In drilling, a phenomenon of swelling clays is frequently observed. It has an important impact on the cementing quality [4]. The clay minerals e.g. chlorite, smectite, illite, kaolinite, etc. are present in the targeting rocks of oil and gas exploration. During the 1940s and 1950s of worldwide oil & gas exploration, when scientists tried to investigate the origin of oil and gas, clay minerals were studied a lot. Scientists sought to predict the quality of organic rich source rock and generation mechanism. The drilling fluid technologist should have a basic knowledge of fluid mechanics, colloid chemistry and clay mineralogy, because clays form colloidal suspensions in water, and also because a number of organic colloids are used in drilling fluids.

Phenomenon of swelling in oil and gas industry

Formation damage is an undesirable operational and economic problem that can occur during the various phases of oil and gas recovery from subsurface reservoirs including drilling, production, hydraulic fracturing, and work over operations [5]. Water-based drilling fluids are increasingly being used for oil and gas exploration, and are generally considered to be more environmentally friendly, easy to use and cheaper than oil-based or synthetic-based drilling fluids which makes them more acceptable. Unfortunately, their use facilitates clay hydration and swelling.

Problems caused shales in petroleum activities are not new. At the beginning of the 1950s, many soil mechanics experts were interested in the swelling of clays, which are important for maintaining wellbore stability during drilling, especially in water-sensitive shale and clay formations [6]. Wellbore instability is the largest source of trouble, waste of time and over costs during drilling. The swelling of clays and the problems that may so arise have been reviewed in the literature [7,8,9].

In drilling industry, a phenomenon of swelling clays is frequently observed. It has an important impact on the cementing quality. Inadequate cementing is often the result of the problem of swelling clay layers, which is often encountered at holes. The phenomenon of expansion of clay into the hole significantly influences the quality of cemented pipe sections. A number of adverse phenomena, such as the deposition (sticking) of rock formation with high viscosity to the surface of pipes: preventing proper bonding of the cement or casing contacting with clay stones, is just one of many threats shortening the lifetime of the hole and exposing the company to additional



costs. Clay swelling during the drilling of a subterranean well can have a tremendous adverse impact on many others drilling operations. The overall increase in bulk volume impedes the removal of cuttings from beneath the drill bit, increases friction between the drill string and the sides of the borehole, and inhibits formation of the thin filter cake that seals formations. Clay swelling can also create other drilling problems, such as loss of circulation drilling fluids [10]. Civan et al. [11] pointed out that fines migration and clay swelling are the primary reasons for formation damage measured as permeability impairment. Amaefule et al. [12] determined that poorly lithified and tightly packed formations having large quantities of authigenic, pore-filling clays sensitive to aqueous solutions, such as kaolinite, illite, smectite, chlorite, and mixed-layer clay minerals, are especially susceptible to formation damage. Formation damage also occurs as a result of the invasion of drilling mud, cements, and other debris during production, hydraulic fracturing, and work over operations [13]. With the drilled depth, the percentage of mixed layers and illite increases, while that of smectite decreases. In deposits of Silurian, Ordovician and Cambrian origin, illites are the dominant structure. Also the mixed package minerals contain smectite. The stability of the borehole depends to a large extent on interactions between the drilling fluid and exposed shale formations. Interactions between the mud filtrate and the clays present in producing horizons may restrict productivity of the well if the wrong type of mud is used. All of these point out the need for knowledge of clay mineralogy [3].

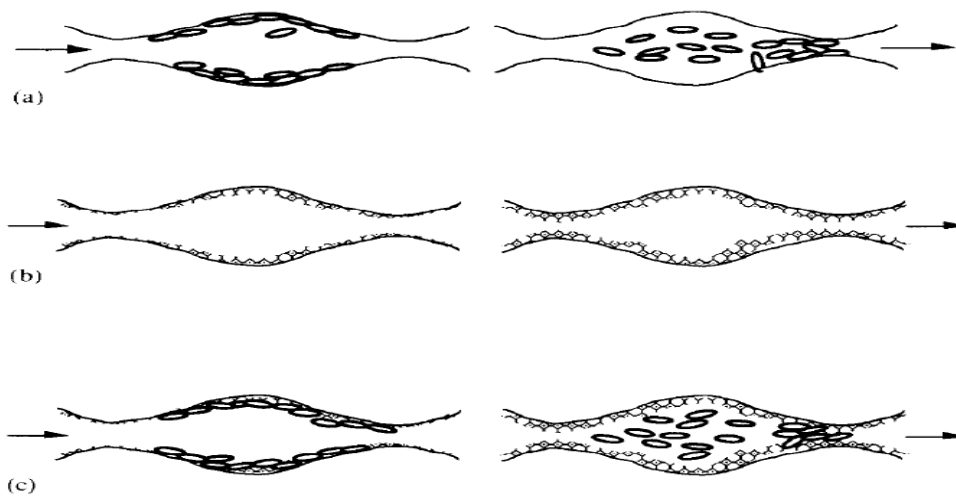


Fig. 1. Mechanisms of permeability reduction caused by clays in porous media. (a) Migration: changing ionic conditions cause the release of clays from pore walls and result in pore blockage. (b) Swelling: changing ionic conditions cause swelling of clays lining the pores and reduce cross-sectional area for flow. (c) Swelling-induced migration: changing ionic conditions cause swelling of clays lining the pore walls and dislodge fines in the process [14]

CLAY MINERALOGY

Clay minerals are usually ultrafine-grained, so may require special analytical techniques for their identification/study. The development of X-ray diffraction techniques in the 1920s and the subsequent improvement of microscopic and thermal procedures enabled investigators to establish that clays are composed of a few groups of crystalline minerals. Current identification/study methods include x-ray diffraction, electron diffraction methods, various spectroscopic methods such as Mössbauer spectroscopy, infrared spectroscopy, Raman Spectroscopy, and SEM-EDS or automated mineralogy solutions.

The formation of the clay minerals by weathering processes is determined by the nature of the parent rock, climate, topography, vegetation, and the time period during which these factors operated. These factors influence weathering processes by their control of the character and direction of movement of water through the weathering zone.

General Description of the structure

Clay minerals are an assemblage of crystalline minerals that provide plasticity and cohesion to soil. A clayey soil, in addition to non-clay minerals such as quartz, feldspar, mica, and calcite, may contain one or two clay minerals made of microscopically thin sheets. Chemically, the clay minerals are composed of aluminum silicate or a combination of iron and magnesium silicate, some also contain alkaline earth [15].

The upper limit of the particle size of clays is defined by geologists differently: Wentworth [16] adopted 1/256 mm, i.e. approx. 3,9 μm , Ruhin [17] 5 μm , Pettijohn [18] recommended 2 μm . It is generally accepted that soil clay fraction comprises plate-like particles $<2 \mu\text{m}$ in diameter and is formed mainly of clay minerals [19].

Ordinary chemical analysis plays only a minor part in identifying and classifying clay minerals of a crystalline nature. The atomic structure of their crystals is the prime factor that determines clays properties [3]. Grim [20,21], Marshall [22] and Weaver et al. [23] carried out identification and classification mainly by analysis of X-ray diffraction patterns, adsorption spectra, and differential thermal analysis.

The structure of clay minerals should be seen against the background of the construction of all layered silicate to which they belong. Their flakes are composed of tiny crystal platelets (packets), normally stacked together face-to-face. A single platelet is called a *unit layer*, and are made up of 2-3 planar sheets arranged in parallel to each other. Two types of sheets are noticed:

Silica tetrahedral sheet (SiO_4)⁴⁻, where each silicon atom being coordinated with four oxygens (O) or hydroxyls (OH) groups as shown in Figure 1a. The tetrahedra are arranged in a sheet like hexagonal network (Fig. 2b.) by the sharing of oxygen atoms at the basal corners of the tetrahedra. This hexagonal arrangement is reflected in the symmetry of the bright spots in the electron diffraction patterns [24]. In many tetrahedral layers of clay minerals the substitution of Si^{4+} by Al^{3+} or Fe^{3+} take placed. In minerals such a *muscovite* and *biotit* every fourth silicon ion is replaced by aluminum, and in *margarite* every second [2].



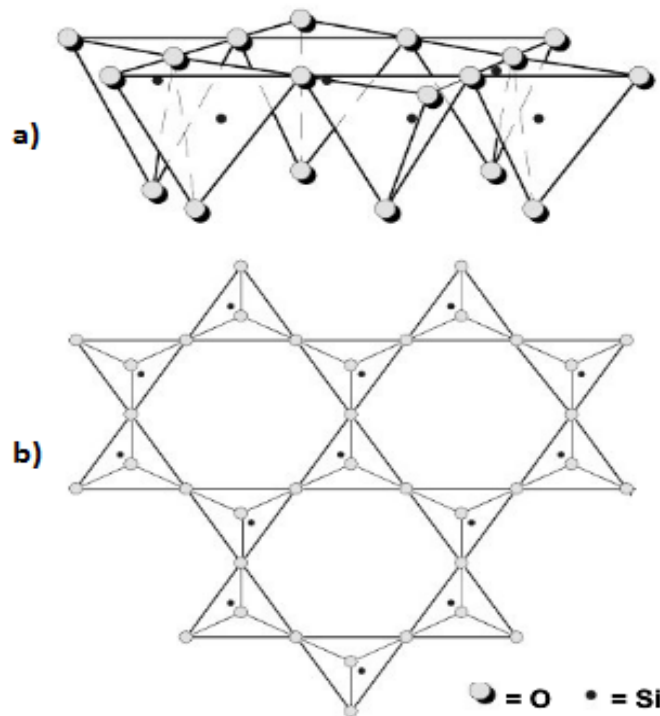


Fig. 2. Diagrammatic sketch of sheets of silicon tetrahedral: (a) in perspective; (b) looking on the tetrahedral, i.e., projected on the plane of the base of the tetrahedral (after Grim) [25]

An octahedral sheet, made up of coordination octahedra, where middle of each octahedron is placed by metal cation, and the corners are occupied by oxygens and OH^- or F^- groups. Inside the octahedra tetravalent ions (Ti^{4+}), trivalent (Al^{3+} , Fe^{3+} , Cr^{3+}), divalent (Mg^{2+} , Ca^{2+} , Fe^{2+}), and especially monovalent (Li^+) may be located. If the metal cations are trivalent, only 2/3 possible octahedral positions can be filled with metal cations to total charge compensation of layers, so the sheet is termed *dioctahedral*. If, on the other hand, the metal cations are mono- or divalent, in this case all three positions are filled with the metal cations, and the structure is termed *trioctahedral*. If the metal atoms are aluminum, the structure is the same as the mineral *gibbsite*, $\text{Al}_2(\text{OH})_6$ (Fig. 3.). If, on the other case, the metal atoms are magnesium, the structure is that of *brucite*, $\text{Mg}_3(\text{OH})_6$. Aluminum and magnesium ions in octahedral layers may be isomorphically substituted by Fe^{3+} , Fe^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} and others ions. The most common substitution is the replacement of Al^{3+} by Fe^{3+} or Mg^{2+} by Fe^{2+} .

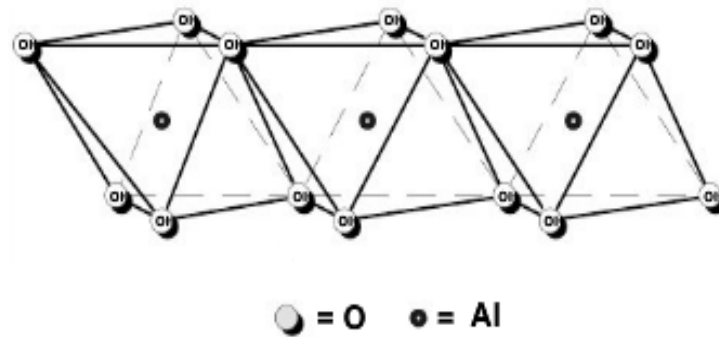


Fig. 3. Octahedral sheet; structure shown is that of gibbsite (after Grim) [20]

The sheets are tied together into larger units called packets (*unit layer*) sharing common oxygen atoms. Packets with layering parallel to each other's give the full structure of the mineral. There are known two and three-layer packets. Two-layer packets, made up of one tetrahedral and one octahedral sheet are called as *packets 1:1*. The two sheets are held together in such a way that the tips of the silica sheet and the layers of the octahedral sheet form a single layer. Kaolinite (Fig. 4.) is an example of two-layer dioctahedral clay mineral. Kaolinite structure is characterized by the formula $Al_4[Si_4O_{10}](OH)_8$.

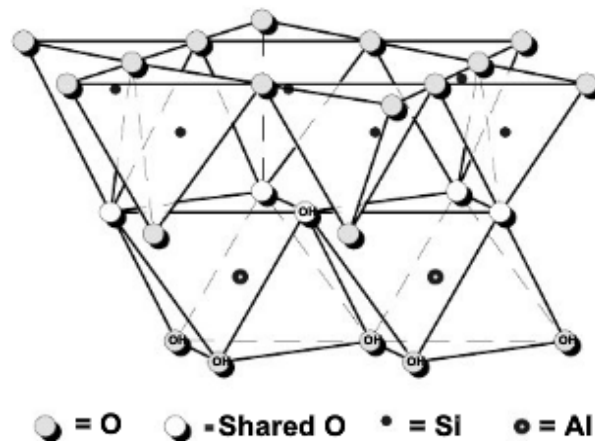


Fig. 4. Atomic structure of kaolinite, e.g. of 1:1 mineral (after Grim) [25]

When there are two tetrahedral sheets, the octahedral sheet is sandwiched between them (packages 2:1), as shown in Figure 5a. Typical examples of minerals with 2:1 structure are talc and pyrophyllite.

An important group of layered clays minerals are chlorites. Their structure is defined as 2:1:1. Between packages 2:1 type are in fact single octahedra layer Figure 4b. Loads of packages and additional layers of octahedral mutually compensate each other. Chlorites also divide for dioctahedral and trioctahedral. The first ones are found rarely.

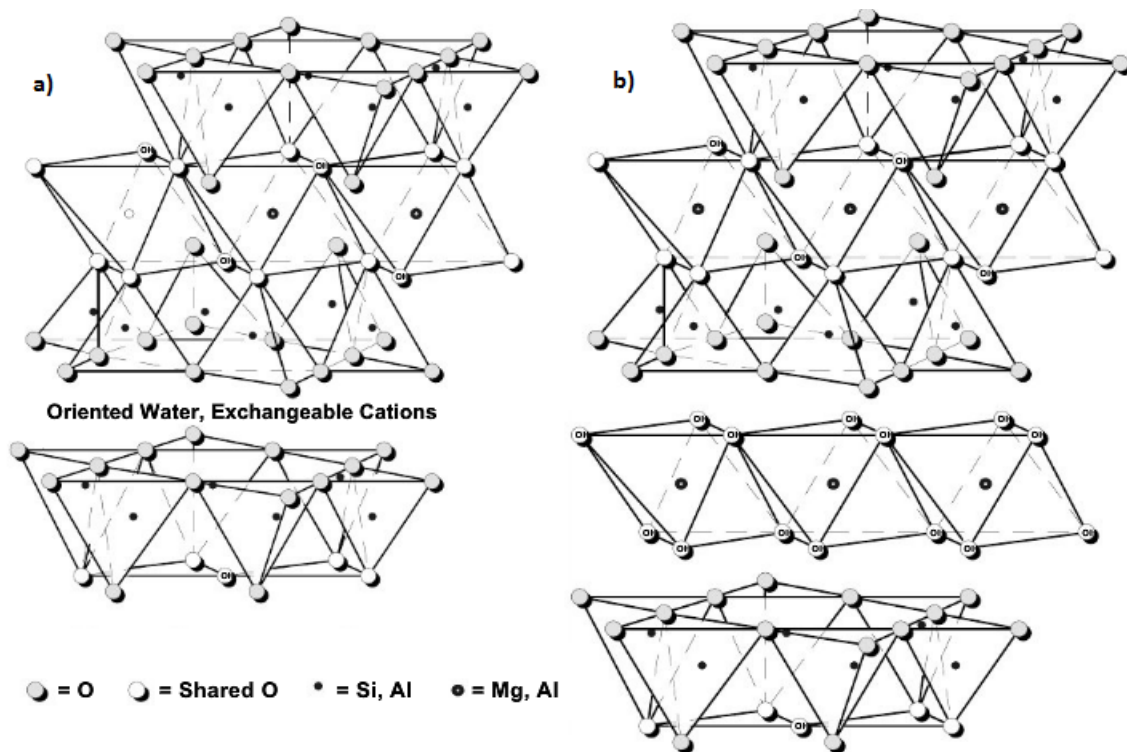


Fig. 5. a) Atomic structure of montmorillonite, e. g. of 2:1 mineral (after Hendricks et al.) [26] b) Atomic structure of chlorite, e.g. of 2:1:1 mineral (after Mac Murchy) [27]

The *unit layers* are stacked together face-to-face to form what is known as the *crystal lattice*. The distance between a plane in one layer and the corresponding plane in the next layer (see Figure 6) is called either the *c-spacing*, the *001*, or the *basal spacing*. This spacing is 9.2 Angstroms for the standard three-layer mineral and 7.2 Å for a two-layer mineral. The crystal extends indefinitely along the lateral *axes*, *a* and *b*, to a maximum of about one micron [3].

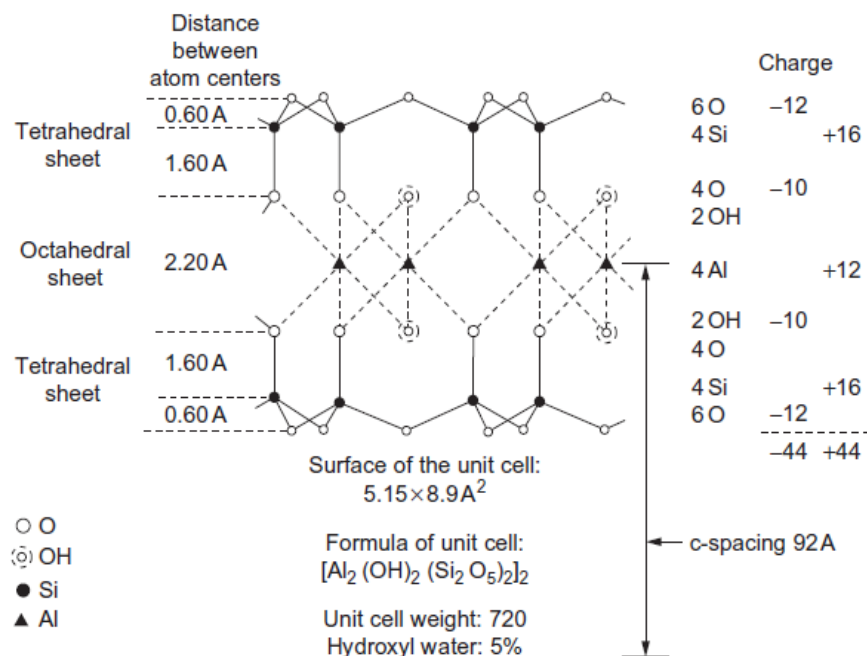


Fig. 6. Atom arrangement in the unit cell of a three-layer mineral (schematic) [3]

Classification of Clay Minerals

Grim [20,29] and Hughes [28] classified The clay minerals into four main groups:

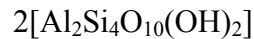
- Kaolinite – a highly stable 1:1 (silica:gibbsite) mineral (Fig.3.), which is non-swelling with a relatively small surface area, and a low adsorptive capacity.
- Smectites – are 2:1 (silica:gibbsite) minerals which swell on wetting and shrink on drying, they have a large surface area due to the access of soil solution to all lamellae surfaces which, together with isomorphous substitution, contributes to their relatively high adsorptive capacity. This group of minerals include montmorillonite and bentonite.
- Illite – a 2:1 clay like the smectites with a lower adsorptive and swelling/shrinking capacity and properties intermediate between kaolinite and smectites.
- Chlorites – are a group of clay minerals whose characteristic structure consists of a layer of brucite alternating with a three-sheet pyrophyllite-type layer, as shown in Figure 5. Chlorites occur both in macroscopic and in microscopic crystals. In the latter case, they always occur in mixtures with other minerals, which makes determination of their particle size and shape very difficult

In addition, there are mixed-layer clay minerals formed from several of these four basic groups [23]. The description of the various clay minerals of the sedimentary formations is given by Degens [30].

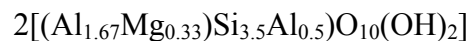


Chemical analysis of minerals does not give a direct image of the quantitative proportions in which individual elements are present in the mineral structure. For this reason, the chemical analysis are translated into the structural formula, which better reflects the construction of the unit cell of the mineral.

Note that the convention for writing the formulas of clay minerals is as follows: Suppose the prototype mineral is pyrophyllite from smectites group, which has the formula:



If one of six aluminum atom in the octahedral sheet is replaced by magnesium atom, and one of eight silicon atom in the tetrahedral sheet is replaced by aluminum atom, then the formula would be written:

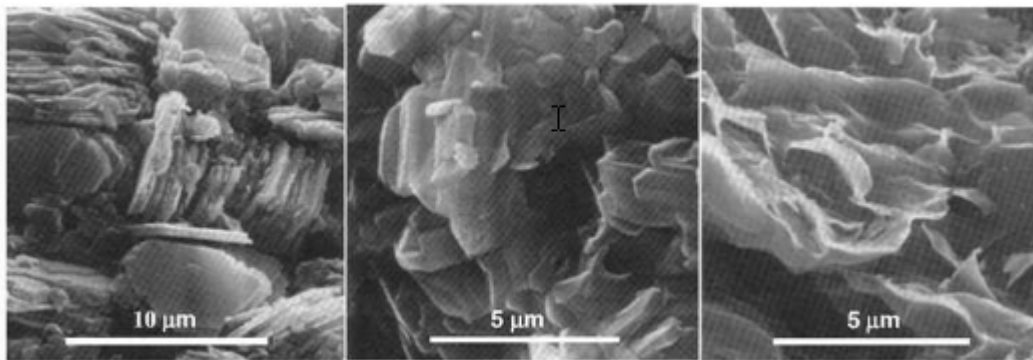


Typical clay minerals are described in Table 1 [13,31]. However, the near-wellbore formation may also contain other substances, such as mud, cement, and debris, which may be introduced during drilling, completion, and work over operations, as depicted by Mancini [32].

Table 1. Description and typical problems caused by the Authigenic Clay Minerals [13,31]

Mineral	Chemical Elements	Morphology	Surface area (m ² /gm)	Major reservoir Problems
Kaolinite	$\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$	Stacked plate or sheets	20	Breaks apart, migrates and concentrates at the pore throat causing severe plugging and loss of permeability.
Chlorite	$(\text{Mg}, \text{Al}, \text{Fe})_{12}[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_{16}$	Plates, honeycomb, cabbage-head rosette or fan	100	Extremely sensitive to acid and oxygenated waters. Will precipitate gelatinous $\text{Fe}(\text{OH})_3$, which will not pass through pore throats.
Illite	$(\text{K}_{1-1.5}\text{Al}_4[\text{Si}_{7-6.5}\text{Al}_{1-1.5}\text{O}_{20}](\text{OH})_4)$	Irregular with elongated spines or granules	100	Plugs pore throats with other migrating fines. Leaching of potassium ions will change it to expandable clay.
Smectite (or montmorillonite)	$(1/2\text{Ca}, \text{Na})_{0.7}(\text{Al}, \text{Mg}, \text{Fe})_4[(\text{Si}, \text{Al})_8\text{O}_{20}] \cdot n\text{H}_2\text{O}$	Irregular, wavy, wrinkled sheets, webby or honeycomb	700	Water sensitive, 100% expandable. Causes loss of microporosity and permeability.
Mixed-Layer	Illite-Smectite and Chlorite-Smectite	Ribbons substantiated by filamentous morphology	100-700	Breaks apart in clumps and bridges across pores reducing permeability.

The occurrence of diagenetic filamentous illitic clay in the pores of sandstones associated with hydrocarbon reservoirs has become more widely recognized since the initial scanning electron microscope (SEM) observations of Stalder (1973) on the Permian Rotliegend sandstones of north-west Europe [33]. Similar material has been described by Sommer (1975) [34] and Hancock & Taylor (1978) [35] from Jurassic sandstones of the Viking Graben of the North Sea, and by Given et al. (1980) [36] from Mesozoic and Tertiary sandstone reservoirs in the United States.



a) *Kaolinite*

b) *illite*

c) *montmorillonite*

Fig. 7. Scanning electron microscopic photos of typical clay minerals [37].

ION EXCHANGE

The metal atoms in the clay lattice can be substituted with others. For example, if an atom of Al^{+3} is replaced by an atom of Mg^{+2} , a charge deficiency of one results. This charge is compensated for by cations located in the interlayer region, which can be freely exchanged. In the presence of water, the adsorbed cations can exchange with cations of another species in an aqueous, and they are therefore known as the *exchangeable cations*. In addition, ions may also be adsorbed on the clay crystal edges and exchange with other ions in the [34]. Isomorphous substitutions may occur in either the octahedral or tetrahedral sheets. Diverse species may be exchanged, giving rise to innumerable groupings and subgroupings of clay minerals. The cation exchange capacity (CEC) of the mineral depends on crystal size, pH, and the type of the cation its involved. These may not only be small ions, but poly-cations also (Blachier et al., 2009) [35].

The degree of substitution, the atoms involved, and the species of exchangeable cations are of enormous importance for agriculture, technology and engineering. In drilling fluids technology they influence exert on such properties as swelling, dispersion, and rheological and filtration characteristics.

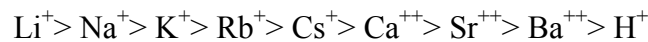
The exchange reaction is governed primarily by the relative concentration of the different species of ions in each phase, as expressed by the law of mass action. For example, for two species of monovalent ions, the equation may be written:

$$\frac{[A]_c}{[B]_c} = \frac{K[A]_s}{[B]_s} \quad (1)$$

where $[A]_s$ and $[B]_s$ are the molecular concentrations of the two species of ions in the solution, and $[A]_c$ and $[B]_c$ are those on the clay. K is the ion exchange equilibrium constant, e.g., when K is greater than unity, A is preferentially adsorbed.

The extent to which ions from the soil solution will exchange places with ions adsorbed on colloids in outer sphere complexes will depend on several a number of characteristics of cation exchange reactions, including: reversibility, charge equivalency (one mol of charge exchanges with one mol of charge), the ratio law (after equilibrium is approached, the ratio of species in the solution will equal the ratio of ion species adsorbed on the colloid), the anion effect, the selectivity for particular ion species, and the complementary ion effect.

Grim (1942) determined the order of replaceability of the common cations in clays from most to least easy cations as [29]:



Sodium-montmorillonite swells more than calcium-montmorillonite because the calcium cation is strongly adsorbed compared to the sodium cations.

The cation exchange capacity (CEC) is one of the basic properties of clay minerals. Several methods to determine the CEC have been developed. One of the first method to determination CEC developed by Mehlich in 1948 [36] was performed by saturating the clay with one metal cation salts solution, then washing out excess salt and finally replacing the cation by several exchange/washing cycles with another cation salts solution. The collected solutions were employed for the determination of the amount of the replaced cation. The method proposed by Alexiades and Jackson in 1965 [37] utilizes the phenomenon of stabilization removable potassium in the structure of the vermiculite, after heating at a temperature of 110°C. This method assumes a relatively constant density of electric charge of sorption capacity of the packet and vermiculite. Kloppenburg [38] proposed further methods by using cationic surfactants.

Table 2. Surface area and CEC of clay minerals (Eslinger et al.) [39]

Type of mineral	Surface area [m ² /g]			CEC [meq/100 g]
	Internal	External	Overall	
Smectite	750	50	800	80-150
Illite	5	15	30	10-40
Kaolinite	0	15	15	1-10
Chlorite	0	15	15	<10



MECHANISM OF CLAY SWELLING

Swelling is one of the most characteristic and important features of the minerals and argillaceous rocks. The type of substitutions and the exchangeable cations adsorbed on the crystal surface greatly affect clay swelling, which is a primary importance property in the drilling fluid industry. The laboratory studies by many researchers, have concluded that clay swelling primarily occurs by crystalline and osmotic swelling mechanisms [40,41].

Crystalline swelling (sometimes called surface hydration) occurs when the clays are exposed to concentrated brine or aqueous solutions containing large quantities of divalent or multivalent cations. The type of exchangeable cations found in clay minerals is reported to have a significant impact on the amount of swelling that takes place.

Table 3. *c*-Spacing of Monoionic Montmorillonite Flakes in Pure Water by Norrish [42]

Cation on the Clay	Maximum <i>c</i> -Spacing, Angstroms
Cs ⁺¹	13,8
NH ₄ ⁺¹	15,0
Ca ⁺² , Ba ⁺²	18,9
Mg ⁺²	19,2
Al ⁺³	19,4

Process results from the adsorption of mono molecular layers of water on the basal crystal surfaces - on both the external, and, in the case of expanding minerals, the inter layer surfaces. Hydrogen bonding holds a layer of water molecules to the oxygen atoms, which are exposed on the crystal surfaces. In this phenomenon, water molecules surround a clay crystal structure and position themselves in such a way as to increase the structure's *c*-spacing, thus resulting in an increase in its volume (Fig. 8.)

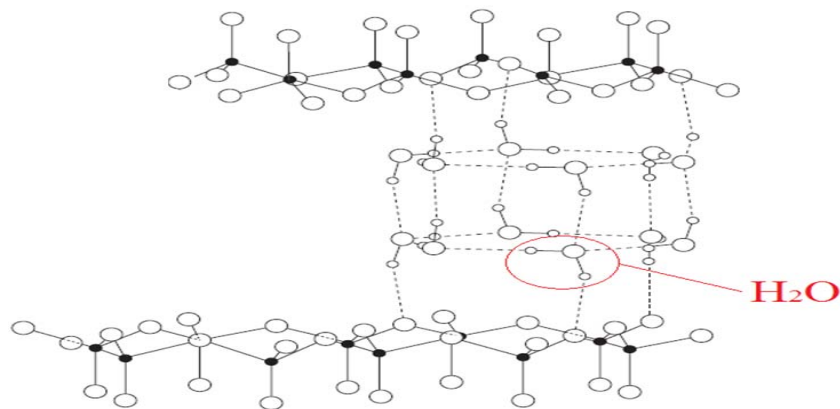


Fig. 8. Combined water layers between layers of partially dehydrated vermiculite (after Hendricks et al.) [26]

The exchangeable cations influence the crystalline water in two ways. Firstly, many of the cations are themselves hydrated, i.e., they have shells of water molecules (exceptions are NH_4^+ , K^+ , and Na^+). Secondly, they bond to the crystal surface in competition with the water molecules, and thus tend to disrupt the water structure. Exceptions are Na^+ and Li^+ , which are lightly bonded and tend to diffuse away.

Osmotic swelling is a second type of swelling. Osmotic swelling occurs because the concentration of cations between the layers is greater than that in the bulk solution. Where the concentration of cations between unit layers in a clay mineral is higher than that in the surrounding water, water is osmotically drawn between the unit layers and the c-spacing is increased. Although no semipermeable membrane is involved, the mechanism is essentially osmotic, because it is governed by a difference in electrolyte concentration. Osmotic swelling results in larger overall volume increases than surface hydration, but only a few clays, like sodium montmorillonite, swell in this manner [35]. These phenomena create repulsive forces to separate the clay flakes from each other.

Mohan and Fogler [41] observed a discontinuity in the value of the interplanar spacing as the salt concentration was varied and defined the region as the critical salt concentration. Crystalline swelling occurs above the critical salt concentration while osmotic swelling occurs below this point.

CLAY SWELLING COEFFICIENT

The rate of clay formation swelling is derived from the definition of the isothermal swelling coefficient given by Collins [43]:

$$\lambda_{sw} = \left(\frac{\partial V}{\partial V_w} \right) \quad (2)$$

V and V_w are the volumes of the solid and the water absorbed, respectively. Ohen and Civan used the expression given by Nayak and Christensen (1970) [44] for the swelling coefficient:

$$\lambda_{sw} = \frac{\zeta_1 CI^m}{c} \zeta_2 \quad (3)$$

in which c is the water concentration in the solid and CI is the plasticity index. ζ_1 and ζ_2 , are some empirical coefficients, m is an exponent. Chang and Civan [45] used the expression given by Seed et al. [46]:

$$\lambda_{sw} = k' PI^{2.44} C_c^{3.44} / (C_1 c - 10)^{12.44} \quad (4)$$

where C_c is the clay content of porous rock as weight percent, PI is the plasticity index, and k' is an empirical constant.



SWELLING INHIBITORS

Wellbore instability is in fact the most significant technical problem area in drilling and one of the largest sources of lost time and trouble cost. Shales make up over 75% of the drilled formations, and over 70% of the borehole problems are related to shale instability [47]. When the wellbore walls become unstable, the spilling of cuttings causes a disastrous change in the rheological properties of the mud [48]. Several studies on shale–fluid interactions confirm that various causes are at the origin of borehole instability: water adsorption, osmotic swelling and cation exchange. Different approaches to WBM design are suggested by Bol et al. [49], and Van Oort [50].

Table 4. Various additives for clay stabilization are shown in table (by Fink) [6]

Clay Stabilizers	
Additive	References
Polymer latices	Stowe et al. (2002)
Polyacrylamide	Zaitoun and Berton (1990) Zaltoun and Barton (1992)
Partially hydrolyzed poly vinylacetate	Kubena Jr., et al. (1993)
Nitrogen	Sloat (1989, 1991)
Partially hydrolyzed acrylamide-acrylate copolymer, potassium chloride, and palyanionic cellulose (PAC)	Haliday and Thielen (1987)
Hydroxyaldehydes or hydroxyketones	Westerkamp et al. (1991)
Polyols and alkaline salt	Hale and van Oort (1997)
Aluminum/guanidine complexes with cationic starches and polyalkylene glycols	Branch (1988)
Pyruvic aldehyde and a triamine	Crawshaw et al. (2002)
Quaternary ammonium compounds	Coveny et al. (1999a,b)
In situ crosslinking of epoxide resins	
Tetramethylammonium chloride and methyl chloride quaternary salt of polyethyleneimine	Afen and Gabel (1992a,b, 1994)
Oligomer (methyl quaternary amine containing 3-6 moles of epihalohydrin)	Himes and Vinson (1989)
Quaternary ammonium carboxylates	Himes (1992)
Quaternized trihydroxyalkyl amine	Patel and Mc Laurine (1993)
Polyvinyl alcohol, potassium silicate, and potassium carbonate	Alford (1991)
Copolymer of styrene and substituted maleic anhydride (MA)	Smith and Balson (2000)
Potassium salt of carboxymethyl cellulose	Palumbo et al. (1989)
Copolymer of anionic and cationic monomers: Acrylic acid (AA), methacrylic acid, 2-acrylamido-2-methyl-1-1propane sulfonic acid, dimethyl diallyl ammonium chloride	Aviles-Alcantara et al. (2000) Smith and Thomas (1995a,b, 1997)

The stability of clay-rich shales is profoundly affected by their complex physical and chemical interactions with drilling fluids. Optimization of drilling fluid parameters such as mud weight, salt concentration, and temperature is essential to alleviate instability problems during drilling through shale sections. The selection of suitable mud parameters can benefit from analyses that consider significant instability processes involved in shale-drilling–fluid interactions [51].

Inhibitors of swelling act by a chemical mechanism, rather than in a mechanical manner. They change the ionic strength and the transport behavior of the fluids into the clays. Both the cations and the anions are important for the efficiency of the inhibition of swelling of clays (Doleschall et al., 1987) [52].

Clay stabilizers reduce clay swelling. They function through ion exchange, where the clay stabilizer provides a cation to replace the native, solubilized clay cation such as sodium. Potassium chloride (KCl) is commonly used to reduce clay swelling, where the potassium ion is effective at preventing swelling. It presents certain challenges. Potassium chloride solution is often used at high levels (2-4%) and requires handling at the site of use to prepare a solution.

One potential mechanism by which polymers may stabilize shales is by reducing the rate of water invasion into the shale. This is not the only mechanism involved in shale stabilization (Ballard et al., 1993) [53] there is also an effect of the polymer additive.

The stability of shales is governed by a complex relationship between transport processes (e.g., hydraulic flow, osmosis, diffusion of ions, pressure) and chemical changes (e.g., ion exchange, alteration of water content, swelling pressure). They have the ability to absorb water, thus causing the instability of wells either because of the swelling of some mineral species or because the supporting pressure is suppressed by modification of the pore pressure. The response of a shale to a water-based fluid depends on its initial water activity and the composition of the fluid [6].

INDUSTRIAL MINERALS AND THEIR USES

Clays are perhaps the oldest materials from which humans have manufactured various artifacts. The making of fired bricks possibly started some 5,000 years ago and was most likely humankind's second earliest industry after agriculture. Such microporous materials as zeolites and clay minerals have many applications in the industrial sector. They can be used as catalyst carriers [54], catalysts themselves [55,56], molecular sieves, and sorbents [57]. They have a tremendous number of miscellaneous uses, and for each application a distinct type with particular properties is important. Clays composed of kaolinite are required for the manufacture of porcelain, whiteware, and refractories. Talc, pyrophyllite, feldspar, and quartz are often used in whiteware bodies, along with kaolinite clay, to develop desirable shrinkage and burning properties. Sodium smectites are therefore used as rheology control agents because of the colloidal structure their delaminated particles form in water. Recently, clays have become important for various aspects of environmental science and remediation. Dense smectite clays can be compacted as bentonite blocks to serve as effective barriers to isolate radioactive wastes. Smectites can also absorb polar liquids other than water and will accommodate organic cations in exchange for their native counterions. This enables them to be used as absorbents and as

rheological agents in nonaqueous systems. Tons of kaolinite clays are used as paper fillers and paper coating pigments. Palygorskite-sepiolite minerals and acid-treated smectites are used in the preparation of no-carbon-required paper because of the colour they develop during reactions with certain colourless organic compounds [58].

The intercalation of smectites with hydroxy-metal polycations is a method of mineral modification developed in the late 1970s [59].

The United States is the world's largest producer of both bentonite and kaolinite. Turkey, Greece, and Brazil are also large producers of bentonite. and Uzbekistan, Greece, and the Czech Republic are major suppliers of kaolinite.

CONCLUSIONS

The clay minerals are important compositions in source rocks and reservoir rocks that can generate and store oil and gas respectively. The presence of clay minerals strongly influences the physical and chemical properties of conventional sandstone, carbonate and unconventional shale. The modern innovative technologies have been playing key roles in the identification and quantitative characterization of clay minerals, which help define the best brittle reservoir interval and avoid exploration failure by choosing the compatible drilling and hydraulic fluids.

The number of applications for the clay minerals kaolinite, Na- and Ca-montmorillonite and sepiolite continues to expand. New and improved processing, continued research and development and new market opportunities will require continued exploration and development of new deposits in all areas of the world.

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