



Clays and their Industrial Applications: Synoptic Review

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ABSTRACT

In this paper, the geology of clays is discussed alongside with their industrial applications. The term clay implies earthy, fine-grained material with upper limit of clay size at a particle diameter of 0.004 mm and it usually develops plasticity when mixed with limited amount of water. Clays are the most common minerals in argillaceous rocks, recent marine sediments and in many soils. Clays are made up of hydrous aluminosilicates, frequently with appreciable amount of Fe, Mg, Ca, Na and K. Clays are formed by the alteration of aluminium silicates both in weathering and low temperature hydrothermal processes. The study of clays can be used for paleoenvironmental reconstruction. Though there are two main schemes of classification of clays based on origin and structural chemistry, clays are also classified as phyllosilicates. Clays have several raw material applications in construction, ceramic, electrical, pharmaceutical, paint, paper, textile and petroleum industries, respectively, etc.

Keywords: *Clay Geology, Phyllosilicates, Clays Classification, Clay Crystal Structure, Ion Exchange, Industrial Raw Materials*

I. INTRODUCTION

Clay minerals are extremely fine-grained, so fine that ordinary microscopes are inadequate for studies of their crystal structures. Clays are best studied and identified using the following: X-ray diffraction, X-ray fluorescence, energy-dispersive X-ray analysis, electron diffraction, differential thermal analysis, infrared spectroscopy and electron microscopy [30],[10]. Clays are argillaceous alteration products due to hydrothermal action. There is usually a zonal arrangement of the clay minerals around the source of alteration with mica and kaolin being close to the source and chlorite and montmorillonite being more distant. Argillaceous alteration products are also known to be associated with hot springs and geysers. In addition, clays are formed as products of the weathering of aluminosilicates. The character of the clay mineral found in a given soil depends on the nature of the parent material, climate, topography, vegetation and time during which these factors have operated [11]. A major way in which climate, topography and vegetation influence weathering process is by their control of the character and direction of movement of water through the alteration zone. The character of the parent material is relatively more important in earlier stages of weathering than were the weathering has continued for long periods of time. Therefore, where climate and topography are such that the dominant movement of water is downward through the alteration zone, any alkalis or alkaline earths present in the parent material tend to be leached out. Primary minerals containing these compounds are broken down; in the case of the micas, they are first degraded and then broken down. If leaching is intense following the removal of the alkalis and alkaline earths, the aluminium or silica are removed from the alteration zone depending on the pH of the downward seeping waters. The pH of

such waters is determined in turn by the climate and vegetation cover. Under warm, humid conditions with long wet and dry periods, the surface organic material tends to be completely oxidized so that the downward seeping waters are neutral or perhaps slightly on the alkaline side, with a consequence that SiO₂ is removed and Al₂O₃ and Fe left behind and concentrated. The result is laterite soil type. Under more temperate conditions where the surface organic material is not completely oxidized, the downward seeping water contains organic acids so that Al₂O₃ and SiO₂ components are leached leading to development of podsol soil type. Illite and chlorite are formed in the earlier stages of leaching with the subsequent formation of kaolinite and finally oxides and hydroxides as leaching become complete. On the other hand, in the dry areas where the dominant movement of water is not downward so that leaching does not take place, the alkalis and alkaline earths remain close to the surface with the development of chernozem soil types which contain montmorillonite and chlorite clay minerals. Bentonites, composed essentially of montmorillonite, have high bonding strength and therefore, they are extensively used in metal foundry in the metallurgical industry [12].

II. GEOLOGY, CLASSIFICATION AND OCCURRENCE OF CLAYS

(A) Geology

(a) Structure and Composition

The atomic structures of the common clay minerals have been determined in considerable detail [22]. According to Grim [11], two units are involved in the atomic structure of most clay minerals. One unit consists of

closely packed oxygens or hydroxyls in which Al, Fe, or Mg atoms are embedded in octahedral coordination, so that they are equidistant from six oxygens or hydroxyls (Figure 1). When Al is present, only two-thirds of the possible positions are filled to balance the structure, which is the gibbsite structure and has the formula $Al_2(OH)_6$. When Mg is present, all the positions are filled to balance the structure, which is brucite structure and has the formula $Mg_2(OH)_6$. The normal O_2 to O_2 distance is 2.60 Å, and a common hydroxyl (OH) to hydroxyl (OH) distance is about 3 Å; in this structural unit, however, the OH to OH distance is 2.94 Å, and the space available for the atom in the octahedral coordination is about 0.61 Å. The thickness of the unit is 5.05 Å in clay mineral structure [11].

The second unit is built of silica tetrahedrons. In each tetrahedron, a silicon atom is equidistant from four oxygens, or hydroxyls if needed to balance the structure, arranged in the form of a tetrahedron with the silicon atom at the center. The silica tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of the composition of

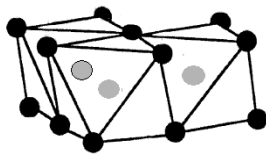


Figure 1: Octahedral Sheet (Source: [11],[5])
The black circles are hydroxyls and the filled grey circles are octahedrally coordinated cations (Al^{3+} , Mg^{2+} , Fe^{3+} , etc.)

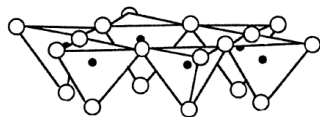


Figure 2: Tetrahedral Sheet or Silica Sheet (Source: [11],[5])
The open circles are oxygens and the black circles are tetrahedrally coordinated cations (Al^{3+} , Mg^{2+} , Fe^{3+} , etc.)

$Si_2O_6(OH)_4$ (Figure 2). The tetrahedrons are arranged so that the tips of all of them point in the same direction, and the bases of all tetrahedrons are in the same plane (there may be exceptional cases in which some of the tetrahedrons are inverted). The structure is made of three planes, namely: oxygen, silicon and hydroxyl atoms, respectively. The first plane is made up of oxygen atoms and it is the plane of the base of the tetrahedral groups; the second plane is made up of silicon atoms that occupy the cavity at the junction of three oxygen atoms and thus forming a hexagonal network. The third plane is made of hydroxyl atoms lying directly above the silicon at the tip of the tetrahedrons. The observed open hexagonal network is composed of three strings of oxygen atoms intersecting at angles of 120° . The O_2 to O_2 distance in the silica tetrahedral sheet is 2.55 Å, and the available space for the atom in the tetrahedral coordination is about 0.55 Å. The thickness of the unit is 4.93 Å in clay mineral structures [10]. Figure 3 shows the crystal structure of montmorillonite clay mineral, while Table 1 shows the average chemical composition in weight percent of clays in weathered zones.

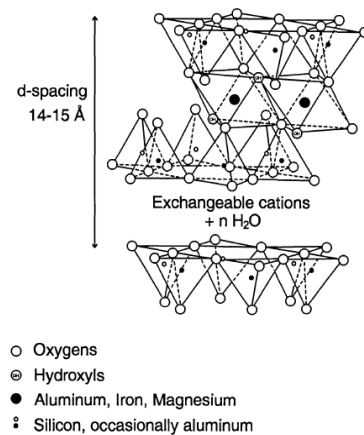


Figure 3: Crystal structure of Montmorillonite (Source: [11],[23])

Table 1: Average Chemical Composition of Clays (Source: [19],[26],[17],[21], [7])

OXIDE/ SAMPLE NO.	Greyish Clays			Reddish-Brown Clays				Reference Samples			
	NH2	NH3	NH4	RNG1	RNG4	RNG5	RNG6	S [26]	M [17]	P [21]	E [7]
SiO_2	60.50	56.20	54.29	48.03	49.30	47.70	46.70	67.50	38.67	51.00-70.00	59.97
Al_2O_3	24.21	29.25	28.01	33.81	33.98	34.22	30.28	26.50	9.45	32.44	24.66
MnO	Trace	Trace	Trace	Trace	Trace	Trace	Trace	-	-	-	0.01
Fe_2O_3	1.90	1.50	2.30	2.30	2.80	3.70	3.80	0.50-1.20	2.70	0.50-2.40	3.32



P ₂ O ₅	0.03	0.02	0.03	0.03	0.05	0.02	0.02	-	-	-	-
TiO ₂	1.12	1.10	1.14	1.23	1.24	1.27	1.24	0.10-1.00	-	1.00-2.80	20.20
CaO	0.50	0.75	0.65	0.62	0.75	0.88	0.08	0.18-0.30	15.84	0.10-0.20	0.46
MgO	-	0.09	-	0.50	0.08	0.08	0.10	0.10-0.19	8.50	0.20-0.70	0.27
K ₂ O	1.50	1.57	2.08	1.30	1.29	1.08	1.00	1.10-3.10	2.76	-	0.48
Na ₂ O	1.98	1.35	1.45	1.20	1.20	1.15	1.20	0.20-1.50	2.76	0.80-3.50	1.78
LOI	6.38	6.25	7.04	8.30	8.30	7.30	8.09	-	-	-	16.14

(b) Ion Exchange Capacity of Clays

The characteristic property of clays is their ion exchange capacity. This is the property of clays to adsorb certain anions and cations and their capacity to retain them in exchangeable state. In other words, the adsorbed ions are exchanged for other anions and cations in an aqueous solution, though such an exchange reaction can also take place in non-aqueous environment. The exchangeable ions are held around the outside of the silica-alumina clay mineral structural units, and the exchange reaction generally does not affect the structure of the silica-alumina packet [14],[11]. A simple and well known example of the ion exchange reaction is the softening of water by the use of zeolites, permutites, or carbon exchanges. The property of exchange capacity is measured in terms of milliequivalent per gram (meq/g). One equivalent of Na expressed as Na₂O would be a combining weight of 31 and 1 meq/100g would be equal to 0.031% Na₂O. Ion exchange capacities are determined at pH = 7.

(B) Classification of Clays

There are two main schemes of classification of clays, namely:

- (i) Based on origin [15], clays may be exogenous (fluvial, weathering and sedimentary) and endogenous (hydrothermal or pneumatolytic).
- (ii) Based on Structural Chemistry:

Based on structural chemistry, clays are classified into two main types, namely: the dioctahedral (gibbsite-type

layers) and trioctahedral (brucite-type layers), according to the nature of octahedral layer and into two-layer and three-layer structures, according to whether the octahedral layer is linked on one or both sides with a tetrahedral [4]. Examples of the two-layer structures are kaolinite, nacrite, dickite, halloysite (Al₄Si₄O₁₀(OH)₈ and antigorite (platy serpentine), and chrysotile (fibrous serpentine) with the formula Mg₆Si₄O₁₀(OH)₈ and a common smectite, montmorillonite (Al₂Si₄O₁₀(OH)₂ xH₂O). On the other hand, examples of the three-layer structures are prophyllite (Al₂Si₄O₁₀(OH)₂), muscovite (KAl₂(AlSi₃O₁₀(OH)₂)), margarite (CaAl₂(Al₂Si₂O₁₀(OH)₂)) and talc (Mg₃Si₄O₁₀(OH)₂), vermiculite (Mg₃Si₄O₁₀(OH)₂ xH₂O), phlogopite (KMg₃(AlSi₃O₁₀(OH)₂)), etc.

Bailey [1] and Reider et al. [24] classified clays into seven phyllosilicate groups, namely: kaolinite-serpentine, talc-prophyllite, smectites, vermiculites, chlorites, micas and the inverted ribbons groups, respectively. Minerals of the kaolinite sub-group have compositions corresponding to the formula Al₄Si₄O₁₀(OH)₈, and structures of Si₄O₁₀ sheet alternating with gibbsite-type sheets. The smectite group has structures similar to prophyllite, but with exchangeable cations and a variable number of water molecules between the layers, which results in swelling when these minerals are immersed in water. Clay mica is essentially fine-grained muscovite, often intimately mixed or inter-layered with montmorillonite. Chlorite in clays is always mixed with other clay minerals and it is often difficult to detect. Allophane clay minerals are those constituents of clay materials which are amorphous to X-ray diffraction [10]. Figure 4 shows classification of phyllosilicates.



A. Construction Industry

Clays and bricks are used as construction raw materials. Bricks are made up of 100% earth materials which include shales, clays, and fine-grained lateritic soils. Clay minerals in the natural lime rock or in the clay or shale mixed the limestone would contribute SiO_2 , Al_2O_3 and possibly Fe, alkalis, and alkaline earths depending on the identity of clay minerals for the manufacture of Portland cement. Kaolinite is best suitable for the manufacture of white Portland cement [3].

(B) Agricultural Industry

(a) Fertilizers

Phlogopite, illite, and glauconite clays are used as agromineral additive to enhance soil fertility for crop production because of their high content of potassium. Also, clays are used as diluents in chemical fertilizers to provide the optimum relative concentration of the elements [27].

(b) Pesticides

Clays composed of montmorillonites and kaolinites are used in pesticide preparations as diluents to enhance the even dispersion of the toxicant and the retention of the pesticide by plants [10],[27].

(c) Animal Feed Additives

Vermiculites and montmorillonite clays are used as feed additives for poultry, cattle and other animals [10],[27].

(C) Textile and Paper Industry

Clays are used for filling, sizing and backing textiles of various kinds. Very fine-grained kaolinite clays with particle sizes from 2-5 μm are best suitable fillers for textiles and papers [29].

(D) Pharmaceutical Industry

Clays, especially kaolinites, have been used for centuries in pharmaceutical preparations of intestinal adsorbent drugs and other therapeutically useful applications [2],[9]. Clays such as montmorillonite, kaolinite and attapulgite are used in the preparation of pastes, ointments and body lotions. These clays are used in cosmetic formulations because of their properties such as softness, dispersion, gelling, emulsifying, adsorption, etc. [8].

(E) Ceramic Industry

Clays are very valuable prime raw materials in the manufacture of several ceramic products, namely:

- (i) Ceramic building materials (bricks, tiles, stoneware pipes, domestic sanitary wares, and fittings for sewage and drainage).
- (ii) Domestic ceramics (table wares, dinner ware, flower vases, dental wares, e.g. artificial teeth, etc.).
- (iii) Chemical and technical ceramics (chemical engineering apparatus/equipments, hospital equipments and acid resistant tiles and sinks, etc.).
- (iv) Specialized laboratory and engineering ceramics (jet nozzles, crucible, pestle mortars, rocket motors, and spark plugs).
- (v) Ceramic in electrical industry (electrical insulators, motor brushes and battery carbons).

(F) Atomic (Radioactive) Waste Disposal

The disposal of waste waters and solutions carrying radioactive materials of high biological toxicity is a vital problem in the development of nuclear energy. Clays are used in disposal of highly radioactive (nuclear) wastes by adsorbing the ions and then fixing them against leaching by calcifying to temperature in excess of 1000 $^{\circ}\text{C}$ which would be adequate to vitrify the clay and thereby to tie up the radioactive material in insoluble state. The liquid waste is thus converted into a solid form which can be buried without fear that the radioactive materials will ever be dissolved and mobilized into the ground water resources [13].

(G) Petroleum Industry

Bentonites, halloysite and kaolinite clays are used as catalysts in the thermal cracking of heavy petroleum fractions to gasoline [16].

Bentonite clays are also used as drilling muds in the oil and gas industry. In addition, bentonites and kaolinite are used in compounding rubber to provide desirable reinforcement and stiffening properties in rubber products. Kaolinite clays are extensively used to produce reinforced polyester resins and other reinforced plastics [16].

(H) Clarification of Water

In clarification of portable water, colloidal matter is removed by filtration and/or sedimentation processes. Alum is usually used to flocculate the colloidal materials to enhance its settling and filtration rate. In some cases,



the alum alone is not completely effective, and according to Nordell [18], it may be desirable to add highly colloidal, easily dispersible clay to the water prior to the addition of alum. Alum flocculates the clay which serves to gather up and collect all the colloidal matter in the water that would not have otherwise settle at the base of the water container [20]. Research studies have shown that bentonite clays are best suitable for water clarification purpose because they possess the essential dispersion and adsorptive properties. Weir [28] documented that in water treatment, clays can be used to reduce and remove bad odor and taste in water and for softening of water.

(I) Clarification of Wines, Cider, Beer, etc.

The colloidal impurities in wine have been reported to carry positive charges, and therefore, they can be coagulated and removed by stirring a small amount of negatively charged clay material into the wine, cider or beer for clarification [25]. Bentonites are best suited for this application.

(J) Paint Production

Various kinds of kaolinite clays are used in the manufacture of paints to improve their brushability, body or film surface (glossy or flat) properties [10].

IV. CONCLUSION

Clay minerals are extremely fine-grained, so fine that ordinary microscopes are inadequate for studies of their crystal structures. Clays are best studied and identified using the following: X-ray diffraction, X-ray fluorescence, energy-dispersive X-ray analysis, electron diffraction, differential thermal analysis, infrared spectroscopy, and electron microscopy [30],[10]. Clays have been classified based on origin and structural chemistry, and this classification has fitted satisfactorily to observed properties of clays in the field and laboratories. Clays have several industrial applications in areas such as construction, agricultural, textile, paper, pharmaceutical, ceramic, electrical, nuclear energy, and petroleum industries, etc.

REFERENCES

- [1]. Bailey, S.W., 1980. Summary of recommendations of AIPEA [Assoc. Internationale Pour l'Etude des Argiles] nomenclature committee on clay. *Am. Minerals*, v.65, pp.1-7. Available at http://www.minsocam.org/msa/collectors_corner/arc/nomenclaturecl1.htm.
- [2]. Barr, M., 1958. Activated attapulgite, *J. Am. Pharm. Assoc., Pract Pharm Ed.*, pp. 1985-1987
- [3]. Bogue, R.H., 1955. The chemistry of Portland cement, 2nd Ed., Reinhold Pub. Corp., Inc., New York.
- [4]. Brain, M. and Berry, L.G., 1968. Elements of mineralogy, Freeman and Company, San Francisco.
- [5]. Carlson, L., 2004. Bentonite Mineralogy, Finland Geological Survey Working Report 2004-02, 108 pp.
- [6]. Emmerich, K. and Kahr, G., 2001. The cis- and trans-vacant variety of a montmorillonite: an attempt to create a model smectite. *Applied Clay Miner*, 20, pp. 119-127.
- [7]. Emofurieta, W.O., Kayode, A.A. and Coker, S.A., 1992. Mineralogy, geochemistry and economic evaluation of the kaolin deposits near Ubulu-Uku, Awo-Omama and Buan in Southern Nigeria, *Jour. Min. & Geol.* v. 28, pp. 211-220.
- [8]. Fischer, R. and Iwanoff, W., 1943. The use of various adsorbents for the detection, determination and purification of organic, mainly physiological, active compounds, *Arch. Pharm.* v. 281, pp. 361-377.
- [9]. Goodman, L.S. and Gilman, A., 1955. The pharmacological basis of therapeutics, 2nd Ed., McMillan Co., New York.
- [10]. Grim, R.E., 1962. *Applied clay mineralogy*, McGraw-Hill Book Co., New York.
- [11]. Grim, R.E., 1968. *Applied clay mineralogy*, McGraw-Hill Book Co., New York, 596 pp.
- [12]. Hoffmann, F., 1959. Modern concepts on clay minerals for foundry sands, *Brit. Foundryman*, v. 1, pp. 161-170.
- [13]. Kerr, J. M., 1954. Preliminary tests on clay sinters to retain reactor wastes, *Bull. Am. Ceram. Soc.*, v. 38, pp. 374-376.
- [14]. Krauskopf, K.B., 1989. *Introduction to geochemistry*, McGraw-Hill Book Co., Singapore.
- [15]. LVOV, 1957. *Researches on the uses of clays*, Mir. Publ. House, Moscow.
- [16]. Milliken, T.H., Oblad, A.G. and Mills, G.A., 1955. Use of clays as petroleum cracking catalysts, Clays and clays Technology, *Calif. Div. Mines Bull.* p.169.



- [17]. Murray, H.H., 1960. Clay industrial materials and rocks, 3rd Ed., *Publ. Am. Inst. Of Min., Metall. And Petrol. Eng., New York*, Seeley, W. Mudd Series, pp. 259-284.
- [18]. Nordell, E., 1951. *Water treatment for industrial and other uses*, Reinhold Pub. Corp., Inc., New York.
- [19]. Obaje, S.O., 2008. Geotechnical and industrial properties of Naraguta clays on the Jos Plateau, Nigeria, *Records of Nigerian Geological Survey Agency v. 11*, pp. 23-37.
- [20]. Olin, H.L. and Peterson, H.W., 1937. The use of bentonite as a coagulant in water treatment, *J. Am. Water Works Assoc.*, v. 29, pp. 513-517.
- [21]. Packer, E.R., 1967. *Materials data book for engineers and scientists*, Publ. McGraw-Hill Book Co., New York, 283 pp.
- [22]. Pauling, L., 1930. The structure of chlorites, *Proc. Nat. Acad. Sci.*, v. 16, pp. 578-582.
- [23]. Pusch, R. and Karnland, O., 1996. Physicochemical stability of smectite clays, *Engineering Geology 41*, pp. 73-85.
- [24]. Reider, M., Cavazzini, G., D'yakonov, Y.S., Frank-Kamenetskii, V.A., Gottardi, G., Guggenheim, S., Koval, P.V., Müller, G., Neiva, A.M.R., Radoslovich, E.W., Robert, J.L., Sassi, F.P., Takeda, H., Weiss, Z., and Wones, D.R., 1998. Nomenclature of micas, *Clays Miner*, v.46, pp. 586-595.
- [25]. Saywell, L.G., 1935. The bentonite process of clarifying wine, *Calif. Wine Rev.*
- [26]. Singer, F. and Sonja, S.S., 1971. *Industrial ceramics*, Publ. Chap and Hall, London, 56 pp.
- [27]. van Straaten, P., 2002. *Rocks for crops: Agrominerals of sub-Saharan Africa*, ICRAF, Nairobi, Kenya, 338 pp.
- [28]. Weir, P., 1938. The use of clay in coagulation, taste and odor control, *J. Am. Water Works Assoc. V. 30*, pp. 1528-1539.
- [29]. Woolman, M.S. and McGowon, E.B., 1926. *Textiles*, McMillan Co., New York.
- [30]. WHO, 2005. Bentonite, Kaolin, and Selected Clay Minerals (Environmental Health Criteria 231), World Health Organization, Geneva, 196 pp.