Environmental characteristics of clay and clay-based minerals

Suzanne Christine Aboudi Mana, Marlia Mohd Hanafiah and Ahmed Jalal Khan Chowdhury

Department of Geology, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia; Faculty of Science and Technology, School of Environmental and Natural Resources Sciences, National University of Malaysia, UKM, Bangi, Malaysia; Kulliyah of Science, International Islamic University, Kuantan, Malaysia

ABSTRACT
Clay is an inherently occurring material constituted with fine-grained mineral. The minerals are generally less than 2 microns and occur to be plastic in water content which solidify when dried. In the earth surface, clay represents the most available mineral and forms rocks known as shale and is the major component of sedimentary rocks. The small size of the particles and their unique crystal structures give clay minerals special properties. These properties include: cation exchange capabilities, plastic behaviour when wet, catalytic abilities, swelling behaviour, and low permeability. They give to clay and clay-based minerals higher application in many industries and processes. To acknowledge all the features of clay and clay-based minerals, the understanding of their properties especially the cation exchange capability which affects the mechanical and physical properties of the clay is important, and also to acquire information about the crystal structure of clay mineral in general and montmorillonite especially. The purpose of this laboratory is to illustrate the importance of chemistry on the physical properties of montmorillonite, the clay mineral most often used to isolate dangerous waste materials from the environment.

1. Introduction

Among the world’s most important and useful industrial minerals, clay minerals are of great significance. They are used in a number of geological applications such as stratigraphic correlations, indicators of environments of deposition and temperature for generation of hydrocarbons. In agriculture, the clay minerals are a major component of soils and determinants of soil properties. The clay minerals are important in construction where they are a major constituent in brick and tile. The physical and chemical properties of clay minerals determine their utilization in the process industries (Table 1).

Up to date, clay and clay-based minerals need improvement due to their utilization and demand. Processing techniques need to be improved and new equipment needs to be available so that improved clay mineral products are available. Pillared clays and nanocomposites will become important. Further developments in organoclay technology and surface treatments will provide new usage for these special clays.

Clays and clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. The cycle of formation of clay and clay-based mineral varies dependently of the environment. Weathering of rocks and soil is the primary way that clays and clay minerals form at the Earth’s surface today. The weathering process involves physical disaggregation and chemical decomposition that change original minerals to clay minerals. Clay and clay-based minerals can be formed by the alteration of pre-existing mineral by weathering: for example, weathering boulders on a hillside, sediments on sea or lake bottoms, deeply buried sediments containing pore water, and rocks in contact with water heated by magma (molten rock) are to form relatively pure clay deposits that are of economic interest known as bentonites and primarily montmorillonite.

Immediately after their formation, processes of transport and deposition through gradual mechanisms of diagenesis excluding surficial alteration (which is weathering) also favour in-place alteration of clay and clay-based mineral to more stable forms, which occurs, for example, when minerals stable in one depositional environment are exposed to another by burial and compaction. Common silicate materials such as quartz, feldspars, and volcanic glasses, as well as carbonates, non-crystalline iron oxides, and primary clay minerals, are transformed during diagenesis into more stable clay minerals mainly by dissolution and recrystallization.
Undoubtedly, clays and clay minerals are critical components of both ancient and modern sedimentary environments.

So the initial type of rock, factors governing rock weathering and soil formation, the ratio of water to rock, the temperature, the presence of organisms and organic material, and the amount of time play an important role in the types of clay minerals found in weathering rocks, and thus strongly control how the properties of the weathered rock will abound under various climatic conditions (such as humid-tropical, dry-tropical, and temperate conditions).

In order to outline a simple but efficient classification, Grim classification is the most useful. This classification gives a rough idea of the differences between various clay minerals and proposes their nomenclature. In this classification, clay minerals are divided into four main groups: kaolinite group, illite group, smectite group, and vermiculite.

Geologic and geochemical information is necessary to establish environmental characteristics that affect the use of clays and clay minerals. Since clay minerals play important roles in environment protection, their environmental characteristics allow them to be a barrier in the nature of inorganic contaminants distribution, such as metals and metalloids like arsenic, iron, and lead, in clay-bearing rocks. These minerals have been used in the disposal and storage of hazardous chemicals as well as for remediation of polluted water. The use of clay minerals as the adsorbents for the adsorption of various hazardous substances (heavy metals, dyes, antibiotics, biocide compounds, and other organic chemicals) has been widely studied by a large number of researchers. So there is a need to reinforce information about current studies and discuss improvements that are to be made to expand the knowledge of clay minerals and clay-based minerals. Certain clay minerals have the ability to catalyse the polymerization of some unsaturated organic compounds and yet to inhibit polymer formation from other closely related monomers. This apparently contradictory behaviour of clay minerals is known as electron-accepting and electron-donating sites in the silicate layers.

The composition of clay is affected by the mineralogical and chemical compositions of the parent material. This may be the solid bedrock or a non-lithified superficial layer such as boulder clay resting on bedrock. The clay mineral deposit is geochemically and biochemically controlled in the environment in which it exists naturally. Hence, deposit of a given type of clay has similar geologic characteristics which also have similar environmental signature that can be quantified by pertinent field and laboratory data and summarized in geoenvironmental models for clay deposit type (Du Bray, 1995).

### Table 1. Physical properties of original clay in a native land of Tanjung Beringin Langkat by Panjaitan (2014).

| No | Nature of soil | Unit | The original clay |
|----|----------------|------|------------------|
| 1  | Specific gravity (Gs) | – | 2.66 |
| 2  | Plastic limit (PL) | % | 20.78 |
| 3  | Shrinkage limit (SL) | % | 54.47 |
| 4  | Liquid limit (LL) | % | 40.23 |
| 5  | Plastic index (PI) | % | 19.43 |
| 6  | Sieve analysis | % | 52.30 |
| 7  | Dry weight contents (yd maks) | gr/cm³ | 1.363 |
| 8  | Optimum moisture content (Wopt) | % | 21.00 |

2. Clay and clay-based minerals properties

#### 2.1. Clay minerals as electron acceptors and/or donors in organic reactions

The electron-accepting and the electron-donating sites of clay can be explained by the fact the electron acceptor sites are aluminium at crystal edges and transition metals in the lower valency state. The catalysed polymerizations involve the conversion of the organic molecule to a reactive intermediate; hence, the clay mineral accepts an electron from the vinyl monomer and a radical cation is formed, where the organic compound gains an electron and forms a radical anion.

The inhibition of polymerization processes involves the conversion of reactive organic intermediate, such as free radicals, which has been formed by heat or radical initiators, to non-reactive entities. An example of a thermal polymerization is illustrated by the loss of an electron from the free radical which gives a carbionium ion.

In predicting the electron-accepting or electron-donating behaviour, colour reactions on clay minerals are useful for the reason that it similarly proceeds with mechanisms of polymerization reactions. For example, a blue reaction of benzidine: here there is one electron transfer from the organic molecule to the electron-accepting sites in the mineral (aluminium edges, transition metals in the higher valency state).

In order to understand the many abilities of electron exchange of clay minerals, masking the crystal edge with polyphosphate destroys the electron-accepting properties of the crystal edges. This method is used to assess the control of the reactivity of the mineral and distinguish the crystal edge from the transition metal sites as electron-acceptor sites in the clay minerals. (Solomon, 1968)

#### 2.1.1. Ion exchange and cation exchange capacity

When erosion, transport, and deposition take place, clay minerals react to change in the environment. Ion exchange, reconstruction of degraded mineral, and formation of one type clay-based mineral from another or simpler substance appear as a result of those processes. Exchange reactions are dominated by physicochemical laws and depend upon the clay mineral, the nature, and ion population of the exchange sites and on the concentration and the composition of the solution in which the clay mineral is found. However, the increase in salinity when in a marine environment results in a decrease in the total
exchange capacities of clay mineral when clay enters the sea. So the crystal chemistry of clay mineral is considered when exchange of cations takes place. Interlayer water cations and layer charge appear to be particularly important in the understanding of selective adsorption and fixation in the process of cation and ion exchange (Gillott, 2012).

2.1.2. Swelling behaviour
Clay mineral swelling is dependent on clay mineral type, the electrolyte concentration, and the nature of the cations in the solution. The swelling mechanism can be divided into mechanical and physicochemical processes. Through burial diagenesis, expandable layers are removed in the clay mineral structure such that inter and intralayer swelling of expandable clay mineral types can be expected to be at a minimum in older rocks than in younger rocks. Mechanical swelling occurs in response to elastic and time-dependent stress unloading, which can be brought by man in digging excavations or by nature in tectonic uplift and erosion because the clay is free to expand in the vertical direction but not in the horizontal direction. On the other side, physicochemical swelling is governed by intrinsic effective stress which commands the size disparity between larger, inter-aggregate voids and smaller intra-aggregate voids within clay mineral domains and between clay minerals themselves, all those forces which exist in a clay–electrolyte system subject to unloading after water had entered the system in response to mechanical cause (Taylor & Smith, 1986).

2.1.3. Adsorptive and low permeability properties
As absorptive material, there are three ways clay minerals and clay-based minerals can exert non-covalent adsorptive power on various molecules from liquid to gaseous states. Firstly, physical adsorption: there is non-ionic adsorption onto the surfaces of finely divided material (large surface areas of clay minerals are comprised in small volumes), secondly ion exchange adsorption through electrostatic interaction and exchange, and finally, the inclusion of small molecules in pore or cavities, and partial or complete exclusion of larger molecules by those cavities through the zeolitic adsorption action. (Giese & van Oss, 2002). Permeability properties of clay minerals can be explained by the type and distribution of the clay minerals within the pore system. Generally, in rocks which are predominantly argillaceous, permeability is low. The mineralogy of different types of rocks semi-permeable to unloading after water had entered the system in response to mechanical cause (Taylor & Smith, 1986).

3. Clay mineral classified by its structure and layer type
The interaction between clay minerals depends on their structure. This structure controls the behaviour of clay minerals’ double layer which is the primary generator of repulsive pressure in the double layer model. The forces controlling the repulsive pressure are governed by physicochemical swelling in clay minerals since the attractive forces by comparison are small within the range of the external forces involved in the clay structure. Cations are attracted to external surfaces of clay minerals which are negatively charged and can also be drawn to internal surfaces of expandable minerals, so that clay mineral properties and structure can be changed. The sequence of replacement in clay minerals sites in nature of some principal cations is the same as their abundance (Ca²⁺ > Mg²⁺ > K⁺ > Na⁺).

3.1. Clay minerals classified by layer
Clay minerals can be described very simply by the stacking of two kinds of layers: 1:1 layers and 2:1 layers. They are layered by silicate in which each layer in the structure in reality consists of two sublayers. The sublayer consists of octahedral coordinates and structural water in the form of hydroxyl groups.

Anionic clays also known as layered double hydroxides (LDHs) show a great example of the influence of clay layers on their cation–anion exchange capabilities. The intercalated structure and isomorphous replacement of trivalent cations for a fraction of divalent cations leads to positively charged host layers, where oxygen atoms coordinate each metal cation, forming an octahedron. Octahedra are composed of two-dimensional sheets formed by a wide range of interlayer anions, which then can constitute various kinds of anionic clay materials. The computation model of anionic clay minerals by Yan et al., 2008 in their layered double hydroxides (LDHs) formula corroborated with previous work that the value of the stoichiometry coefficient (X), the identities of the interlayer anion (Aⁿ⁻), and the intra-layer cation when they vary enable to produce a wide range of specific tailor-made materials. To understand the electronic structure inside the LDHs is important for the stability formula of clay-based minerals. The electronic structure of LDH materials is often firstly focused on properties related with the whole bulk of the LDHs crystal in its entire extension in the periodicity coupled with ab initio plane-wave density functional theory or linear combination of atomic orbitals methods and secondly to predict the geometry of layer structure and the structural and chemical properties are investigated through semi-empirical molecular orbital method. So Hong Yan et al. (2008) concluded in their work that the distortion angle of an octahedral coordinated hexahydrated cation plays a significant role in the formation of anionic clay layers. Also, the structural properties of the hexahydrated cations such as metal–oxygen bond length, O–M–O bond angle distortion, binding energy, and valence electronic configuration ligand field are in great agreement with the construction of anionic clay layers. Therefore, metal cations with similar ion size to Mg²⁺ are able to form the canonical hexahydrated structure...
3.2. Clay minerals classified by the structure

3.2.1. Adsorption
Weathering and precipitation at the mineral–water interface are of interest in mineral structure separation processes such as flotation, sedimentation, adsorption, scavenging of trace element, and transport of nuclear or other materials in groundwater (Batley, 1988). Chemical reactivity of the mineral–water interface is influenced by properties which can be electrically charged at the surface of the mineral leading to the formation of an electrical double layer, less mobility of ions and water molecules. However, effects of the perturbed layer of water and the electrical double layer on chemical reactions at the interface play an important role. Understanding mechanism reactions of sorption is valuable and their kinetic interpretation explains the rate of attachment between an ion and the surface mineral. So the arrangement of group sites on mineral surface may influence the adsorption; however, under certain conditions, the formation of a monolayer of adsorbing ions may be less favourable than the formation of multi-layers or precipitated material; such a process plays a critical role in accelerating the rate of redox reactions, polymerization, hydrolysis, and other transformations taking place in the surface structure of clay minerals.

3.2.2. Layer charge
Either electrically neutral or negatively charged structure of clay mineral may occur as a result of the tetrahedral and octahedral sheets’ junction in clay. The electrical neutral charge exists if the octahedral sheet contains trivalent cations in two octahedral sites, with a vacancy in the third octahedron, or with the divalent cation occupying all the octahedral sites, secondly in the lower charge cation where all the octahedral sites Al$^{3+}$ and Mg$^{2+}$ are substituted, and thirdly when there is presence of vacancies. This aspect of the layer charge is the most important feature of 2:1 clay minerals because it influences occupancy of the interlayer space by exchangeable cations (Figure 2).

3.2.3. Polytypism
This feature of clay minerals structure is mentioned in several diverse structural modifications in which layers of identical structure and composition are stacked in different ways. The normal periodicity to layers varies with stacking sequence between polytypes according to the number of layers involved.

3.2.4. Mixed layers structures
Mixed layer structures or inter-stratified layers can be built by two or more than two different components. This clay minerals can have ordered or regular-mixed layer structures if different layers alternate along the...
minerals’ surface bound for example to organic matter compounds determines the organo–clay interaction and influence of the sorption capacity at the solid aqueous interface (Baldock & Skjemstad, 2000).

Many mechanisms of biological protection in environment containing clay minerals and clay-based mineral particles operating from the smallest to the largest scale depend on the chemical properties and the dimensional arrangement of layers in the mineral. As a result, diverse mechanisms of protection can be attributed to clay minerals in some matrix-like soil for example. Due to firstly the physical nature of the mineral fraction, especially the presence of surfaces capable of adsorbing organic materials, and secondly the architecture of layers in the clay surface, there are multiple applications of clay minerals because of their versatile arrangements (Baldock & Skjemstad, 2000). Surface reactive phases of clay minerals and clay-based minerals also play an important role in the regulation of contaminant fate and transport in surface and subsurface of the environment because these surfaces are the primary controllers of sorption processes in soils, thus acting as important regulators of contaminant transport. The modification of surface charge of clay minerals by organic constituents is responsible for dispersion/flocculation mechanisms of clay assemblage in the surface as well as the transport of mineral colloidal phases through soil. This surface charge is manifested by a significant retention of anions which assure that complex chemical properties have a number of important implications for solute and contaminant transport (Bertsch & Seaman, 1999).

Mutations and transformations of clays and clay-based minerals respond to their chemical and thermal environments, their properties and species change at each step from the origin, weathering, through their transportation, sedimentation, burial diagenesis, and metamorphism.

Another transformation through the bounding mechanism between the organic cation and the charged clay layers is essentially electrostatic. Through ion exchange
clays with quaternary ammonium salts producing organophilic solids which can be used as paint thickeners and for other industrial uses and similar applications. These transformations make organo-clay formulations suitable for environmental applications since they are generally based on the (i) substrate: due to its unique mineralogical structure, it offers several binding sites to different types of molecules, (ii) the modifier: the organic molecule bound to the clay mineral allows the modification of the substrate surface to increase the affinity of the hybrid nanomaterial obtained, and (iii) the molecule of interest: the organoclay is prepared either to remove contaminants by adsorption, to avoid the leaching or decomposition, or to enhance the activity of an organic molecule. So organophylic clay minerals as mentioned above like clay modifiers have the capability to efficiently sorb organic compounds and remove them from water or effluents, reaching high capacity of reactions, the inorganic exchangeable cation of layered silicates belonging to clay minerals can be replaced by organic cations (Figure 3).

The ions used for this purpose result in the formation of organophilic clay minerals which may greatly adsorb a wide variety of organic compounds. These materials are known as organoclays. Their properties and applications strongly depend on the nano and micro-structural arrangement of hybrid materials and from the mechanisms involved in the clay–organic interactions. Hence, diverse applications can be derived from the characteristics of organoclay minerals. For example in the preparation of polymer-clay nano composites, organophilic polymers and clays acting as nanofillers are also used to develop inorganic heterostructures and inorganic polymer clay nano-composites that generates porous silica acting as pillared materials. Another use of organoclay is the preparation of sepiolite or palygorskite microfibrous clays with quaternary ammonium salts producing organophilic solids which can be used as paint thickeners and for other industrial uses and similar applications. These transformations make organo-clay prepared formulations suitable for environmental applications since they are generally based on the (i) substrate: due to its unique mineralogical structure, it offers several binding sites to different types of molecules, (ii) the modifier: the organic molecule bound to the clay mineral allows the modification of the substrate surface to increase the affinity of the hybrid nanomaterial obtained, and (iii) the molecule of interest: the organoclay is prepared either to remove contaminants by adsorption, to avoid the leaching or decomposition, or to enhance the activity of an organic molecule. So organophylic clay minerals as mentioned above like clay modifiers have the capability to efficiently sorb organic compounds and remove them from water or effluents, reaching high capacity of
adsorption at high pollutant concentrations allowing the use or reuse of water that before treatment would be considered unusable (Ruiz-Hitzky, Aranda, Darder, & Rytwo, 2010) (Figure 4).

5. Conclusion

Clay is abundant and the clay-based minerals are derived from versatile raw materials from a small to a wide range of composites which make it suitable for environmental applications and purposes. Nanostructured hybrid materials resulting from ion exchange to covalent bonding explain organoclays’ preparation and its feasible environmentally friendly use, like removal of pollutants and pesticides formulations. Although there is improvement in the use of clay minerals and hybrid materials based on clay minerals and organic molecules for the removal of pollutants, several problems remain unsolved. The regeneration of the polluted sorbent and the low hydraulic conductivity are some of the issues among others in the removal of contaminants which are still unresolved and may be of great interest for future research aiming to improve the mechanical behaviour in order to enhance structural features of organoclay as far better functionally useful materials for environment among others applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

Bailey, S. W. (1980). Structures of layer silicates. In G. W. Brindley & G. Brown (Eds.), Crystal structures of clay minerals and their x-ray identification, 5 (pp. 1–123). London: The Mineralogical Society.

Bailey, S. W. (1988). Hydrous phyllosilicates. Washington, DC: American Mineralogical Society.

Balducci, J. A., & Skjærumstad, J. O. (2000). Role of the soil matrix and minerals in protecting natural organic materials against biological attack. Organic Geochemistry, 31, 697–710.

Bertsch, P. M., & Seaman, J. C. (1999). Characterization of complex mineral assemblages: Implications for contaminant transport and environmental remediation. Proceedings of the National Academy of Sciences, 96, 3350–3357.

Brigatti, M. E., Poppi, L., & Medici, L. (2002). Effect of ionic solutions on clay mineral crystal chemistry. In C. Di Maio, T. Hueckel, & B. Loret (Eds.), Chemo-mechanical coupling in clays (pp. 29–46). Lisse: Balkema Publishers.

Du Bray, E. A. (1995). Preliminary compilation of descriptive geoenvironmental mineral deposit models. Denver, CO: US Geological Survey.

Giese, R. F., & van Oss, C. J. (2002). Colloid and surface properties of clays and related minerals (Vol. 105). Boca Raton, FL: CRC Press.

Gillott, J. E. (2012). Clay in engineering geology. Amsterdam: Elsevier.

Nadeau, P. H., Wilson, M. J., McHardy, W. J., & Tait, J. M. (1984). Interparticle diffraction: A new concept for interstratified clays. Clay Minerals, 19(5), 757.

Panjaitan, S. R. N. (2014). The effect of lime content on the bearing capacity and swelling potential of expansive soil. Journal of Civil Engineering Research, 4, 89–95.

Ruiz-Hitzky, E., Aranda, P., Darder, M., & Rytwo, G. (2010). Hybrid materials based on clays for environmental and biomedical applications. Journal of Materials Chemistry, 20, 9306–9321.

Solomon, D. H. (1968). Clay minerals as electron acceptors and/or electron donors in organic reactions. Clays and Clay Minerals, 16, 31–39.

Taylor, R. K., & Smith, T. J. (1986). The engineering geology of clay minerals: Swelling, shrinking and mudrock breakdown. Clay Minerals, 21, 235–260.

Whitney, G. E. N. E. (1990). Role of water in the smectite-to-illite reaction. Clays and Clay Minerals, 38, 343–350.

Yan, H., Lu, J., Wei, M., Ma, J., Li, H., He, J., … Duan, X. (2008). Theoretical study of the hexahydrated metal cations for the understanding of their template effects in the construction of layered double hydroxides. Journal of Molecular Structure: THEOCHEM, 866, 34–45.

Yan, H., Wei, M., Ma, J., Evans, D. G., & Duan, X. (2010). Plane-wave density functional theory study on the structural and energetic properties of cation-disordered Mg–Al layered double hydroxides. The Journal of Physical Chemistry A, 114, 7369–7376.