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## Research paper

## Review of the fundamental geochemical and physical behaviors of organoclays in barrier applications

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## ABSTRACT

Organoclays are organic-rich clay minerals, synthesized under controlled laboratory conditions, with engineering properties enhanced for use in containment applications. Organoclays can be formed using a variety of clay minerals as the base material; however, montmorillonite is used most commonly due to its high cation exchange capacity. The cationic organic phase is exchanged onto the mineral surface through ion exchange, with the organic cations displacing the clay's naturally occurring inorganic cations (e.g., Na<sup>+</sup>, Ca<sup>2+</sup>). Most commonly, quaternary ammonium cations are used as the organic phase, and organoclay behavior can be engineered through careful selection of the organic cation structure, size, and density of loading.

Organoclays are promising materials for geoenvironmental applications due to their high sorption affinity for nonpolar organic contaminants. Sorption mechanisms can be engineered to be competitive or non-competitive, linear or non-linear, depending on the organic cation that is exchanged into the clay interlayer. Exchange of an organic phase for the naturally occurring inorganic interlayer cations also allows control of engineering properties, and clays can be synthesized with increased strength and decreased compressibility. This review of organoclays examines the fundamental behavior of organoclays, with an emphasis on geochemical properties including electrokinetic potential, hydrophobicity, sorptivity, attenuation of nonpolar compounds and electrical conductivity; physical properties including hydraulic conductivity, strength, dynamic properties and thermal stability and thermal conductivity. Relevance of organoclays to different barriers is discussed. Emerging polymer-clay hybrid barrier materials are also summarized.

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## 1. Introduction

An ever-increasing world-wide need for the containment and remediation of contaminants from municipal, industrial, and nuclear resources emerges in recent decades due to many factors in different regions, including the growing populations (expected growth of ~70 million by 2045 in the United States), the increasing trend of population moving into megaregions (representing over 75% of the population and employment in the United States; similar situation in China), the need for remediation of brownfield and the rising planned nuclear power plants around the world (USDOT, 2015). Traditional excavation and replacement strategy is often too cost prohibitive to be widely utilized. Alternatively, risk-based analysis has been proposed recently (Sarkar et

al., 2012; Reddy, 2014). Risk-based analysis evaluates the risk of the bio-availability of the contaminants to the public, and uses barrier system, sometimes accompanied by other long-term remediation means (e.g. phytoremediation), to reduce such risk to an acceptable level. This approach potentially reduces the remediation cost significantly. As a result, various barrier systems have gained growing popularity in recent decades. To date, however, barrier system still faces limitations in the field application due to limited knowledge on the operating mechanisms, lack of complete set of properties and long term performance (Bohnhoff and Shackelford, 2014; Sarkar et al., 2012).

Organoclay, an artificially synthesized engineering material, has increasing usages in a variety of barrier systems, such as landfill clay liner, vertical cutoff wall, slurry wall, and cover system (Sharma and Reddy, 2004). Compared to unmodified natural clays, organoclay has enhanced physical and physicochemical properties, including hydraulic conductivity, sorptive capacity, swelling index, suspension stability, strength and stiffness. In spite of its growing popularity, previous studies on organoclays are limited to one or a few particular properties. As an integrated component of a physical structure (e.g. a barrier), the

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complete set of knowledge on organoclay behaviors, both geochemical-ly and physically, is required. Furthermore, the fundamental mechanisms on those behaviors of organoclays are yet to be made clear, so as to bring confidence to the owners and the practitioners. This review paper strides to address above two issues.

The outline of this review paper is as follows. Part 1 introduces the organoclay by its definition, composition, synthesis, microstructure and characterization techniques. Part 2 presents geochemical (electrokinetic potential, hydrophobicity, sorption and attenuation of nonpolar compounds and electrical conductivity) and physical (hydraulic conductivity, strength, dynamic properties and thermal stability and thermal conductivity) properties of organoclays, accompanied by the fundamental mechanisms for such properties. Part 3 discusses the relevant organoclay properties to the requirements of each type of barriers. Part 4 reveals recently developed polymer-modified bentonites so as to embrace the state-of-the-art knowledge and identify the future development trends. Part 5 gives the summary.

## 2. Part 1. Introduction to organoclays

### 2.1. Definition, composition and synthesis

Organoclays are organic-rich clay minerals, synthesized under controlled laboratory conditions, with engineering properties enhanced for use in containment applications. Organoclay is composed of two components: the base clay and the organic matter. Montmorillonite, which is the major components of bentonite, is the most often used base clay. Other clay minerals, such as hectorite, synthetic fluorohectorite, synthetic micas, sepiolite, illite, muscovite, clinoptilolite, kaolinite and vermiculite were also used (Soule and Burns, 2001; de Paiva et al., 2008). The organic matters used in organoclay include quaternary ammonium cations (QACs; a type of surfactants), many other organic compounds (i.e. polymeric quaternary alkylammonium salts and copolymers, alcohols, and aldehydes), biomolecules (i.e. proteins, enzymes, amino acids and peptides) and proprietary agents in commercial products (de Paiva et al., 2008; Bate et al., 2014; Lee et al., 2012). Among them, QACs are the most used organic compounds for organoclays (de Paiva et al., 2008; Sarkar et al., 2012), and the properties of QAC-modified organoclays are the major components of this review paper.

Organoclays were most often synthesized by cation exchange reactions in aqueous solution, although neutral organic compounds can also be adsorbed by other driving forces as summarized in Section 2.2.2. Alternatively, solid-state reaction was also used in several studies (de Paiva et al., 2008), where dry organics and clay minerals were mixed mechanically, sometimes with elevated temperature (Breakwell et al., 1995). For organic molecules with polar groups, the negative parts of the polar groups attract cations on the surface of clay mineral and displace surrounding water molecules. This reaction is named ion-dipole interaction (de Paiva et al., 2008). Solid-state reaction has the advantages of environmental friendly and suitability for industry production (de Paiva et al., 2008).

### 2.2. Microstructural changes of organically modified clays

Essentially the interlayer species controls the sorption and osmosis potential in the organoclays while the surface species controls the inter-particle forces, stability of suspended particles, electrokinetics and fluid conduction. Therefore, the surface properties and interlayer microstructure of the clayey barrier material are highly relevant to its physical and chemical properties and ultimately, the barrier performance. In this section, the fundamentals of organic surfactant morphology and organoclay surface characteristics will be discussed, followed by their relevance and impact to the organoclay barrier performance. Due to the availability of data and simplicity of discussion, quaternary ammonium cations were chosen as representative organic surfactants,

#### 2.2.1. Alternation of clay surface species and characteristics

Montmorillonite is often used as the base clay for a barrier material because of its high net surface charge, high surface area, and sub-micron size. Numerous models on the ions (charges) distribution near the surface of a often negatively charged clay mineral in aqueous environment have been proposed as elaborated in Stumm and Morgan (1996) and Israelachvili (2011). The general features of those models are as follows. (1). Immediately next to the clay mineral surface is a thin layer (about a few molecules thick) of ions and water molecules, both with limited mobility. The majority, if not all, of the ions are positively charged. The water molecules are called surface-bound water (more details in Bate and Burns, 2014). This layer is often termed Stern layer (or Helmholtz plane). (2). Outside of the Stern layer and inside of the bulk fluid, charge-balancing ions accumulate and render a cloud consisting of predominant positively charged ions (cations) and fewer negatively charged ions (anions) (Stumm and Morgan, 1996). This cloud is termed the electrical diffuse layer (EDL), which can be quantified by Guoy-Chapman theory. The arrangement of Stern layer and electrical diffuse layer is referred to as the electrical double layer, as illustrated in Fig. 1a (Stumm and Morgan, 1996). Interactions among clay particles occur primarily through electrical double layer.

In classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the thickness of the diffuse layer ( $\phi$ ) is governed by Eq. (1):

$$\phi = \sqrt{\frac{\epsilon_0 k}{2e_0^2 N_{av}}} \cdot \sqrt{\frac{\kappa T}{cz^2}} \quad (1)$$

where  $\epsilon_0 = 8.85 \times 10^{-12}$  F/m is the permittivity of free space,  $k = 1.38 \times 10^{-23}$  J/K is Boltzmann's constant,  $e_0 = 1.602 \times 10^{-19}$  C is the electron charge,  $N_{av} = 6.022 \times 10^{23} \text{ mol}^{-1}$  is Avogadro's number,  $\kappa$  is the real relative permittivity of the fluid (Bate and Burns, 2014),  $T$  is the absolute temperature (K),  $c$  is the bulk fluid concentration (mol/L), and  $z$  is the ionic valence. As dictated by Eq. (1), both higher concentration and higher valence reduce the thickness of the diffuse layer, and bring montmorillonite particles closer to each other. In macroscopic point of view, higher concentration or higher valence induced large void spaces (only filled with aqueous solution), higher hydraulic conductivity and lower swelling index.

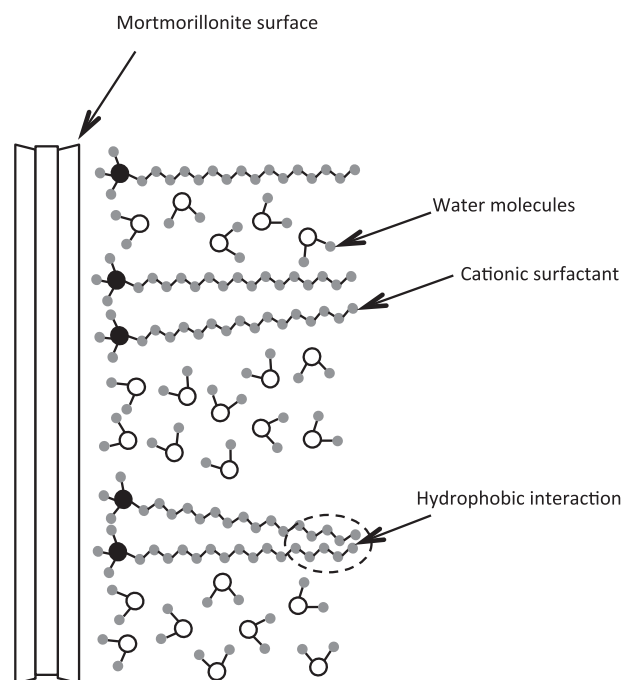


Fig. 1. Conceptual sketch of species around surfactant coated clay surface.

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