

# **GEOSYNTHETIC CLAY LINER TECHNOLOGY: Understanding Bentonite**

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## **Abstract**

Geosynthetic Clay Liners (GCLs) are engineered products used extensively in lining and containment operations for the waste management and mining sectors. Bentonite, in particular sodium bentonite, is the most common raw material providing primary sealing action used in geosynthetic clay liners. Frequently, a GCL is installed as a valid alternative to a thick compacted clay liner (CCL). Apart from obvious advantages in field construction and quality control, a GCL can provide benefits in certain aspects of hydraulic performance when compared to a CCL.

Each bentonite source usually has a characteristic suite of surface and chemical properties (e.g., high swell potential, small particle size and high surface area), which are unique to it alone, and which make them suitable as low permeability materials. Consideration of the technical properties of bentonites enables a better understanding of permeability performance of a GCL. From an environmental and social viewpoint, it is evident that the permeability of a GCL is not the only parameter to be considered in any containment system design. As our knowledge of the risks associated with groundwater contamination grows, we should accept that the specification of GCLs in containment applications based purely on permeability is outdated, and that understanding and specifying the clay component is critical to the performance of the system as a whole. This paper will provide further information relating to bentonite technology and how mineralogical properties influence bentonite performance. The intention is to enable designers to specify GCLs with better confidence of the products' expected performance.

## **Bentonite Properties**

The term bentonite is generally used to describe unconsolidated soft rock composed dominantly of the clay mineral montmorillonite. Bentonites are often defined also by their composition and surface properties, such as layer charge or cation exchange capacity and the dominant exchangeable cation present. The key aspects of bentonites which make them suitable as low permeability materials are their high swell potential, small particle size and high specific surface area. These properties are usually bentonite-specific, ie, each bentonite source has a characteristic suite of surface and chemical properties unique to it alone. The sealing performance of bentonite is dependent on the following inter-related properties of bentonites:

- i. montmorillonite content and impurities present;
- ii. chemistry and structural formula;
- iii. layer charge, location of layer charge and cation exchange capacity;
- iv. montmorillonite type;
- v. particle size;
- vi. surface area;
- vii. exchange cation identity;
- viii. swelling and water adsorption;
- ix. clay fabric and;
- x. gel formation and sealing.

These properties enable a systematic differentiation between different bentonites. Properties i–vi are unique to each bentonite deposit (ii–iii define the montmorillonite type, iv). Properties vii–x contribute to the usefulness of the bentonite as a barrier to water flow and each can be modified to some extent by processing, e.g. to remove impurities or to incorporate additives, or by ‘activating’ the bentonite.

Typically particle size refinement can remove most mineral impurities from bentonites, although this is rarely performed for barrier applications, and thus the montmorillonite content (i) is largely taken as indicative of the suitability of a particular bentonite for GCLs. Additives may include dispersants, flocculants or gelling agents and are usually designed to improve performance and manageability of bentonite suspensions. Activation includes exchange activation, grinding or pulverising and is designed primarily to improve dispersion.

Landis and von Maubeuge (2004) suggest that a bentonite having greater than 50% of its CEC occupied by  $\text{Na}^+$  should be termed a “sodium bentonite”, whereas a “calcium bentonite” is one with greater than 50% of its CEC occupied by  $\text{Ca}^{2+}$ . In reality, many natural bentonites are actually bentonites with a mixture of calcium, magnesium and also sodium and potassium on the exchange complex. Magnesium often exceeds calcium and sodium (e.g., Churchman et al, 2002).

As will be discussed in detail, exchangeable  $\text{Na}^+$  imparts many of beneficial properties, including water adsorption, dispersion and sealing – all properties that make sodium bentonites uniquely suited for use in barriers or GCLs. An interesting fact is that essentially only the ‘Wyoming’ bentonites (those sourced from the Bighorn Basin and Black Hills region of Wyoming and South Dakota, U.S.A.) occur naturally in a  $\text{Na}^+$ -saturated. Most economic bentonite deposits throughout the world are  $\text{Ca}^{2+}$ - or  $\text{Ca}^{2+}/\text{Mg}^{2+}$ -bentonites, with perhaps as much as 20-30%  $\text{Na}^+$ . Thus, most bentonites must be processed and sodium activated to improve many of their performance properties.

i. Montmorillonite content and impurities present. As natural rocks, bentonites are not typically composed of one mineral (monomineralic) and various impurities are almost always present in bentonites. The smectite montmorillonite (a swelling 2:1 layer aluminosilicate) typically is the dominant and most reactive constituent of bentonites. The amount of montmorillonite that a bentonite has underpins its usefulness in GCLs.

Most common impurities are clay sized silicas, micas (illites) and feldspars (Table 1). The amount of impurities in most bentonites marketed for industrial and environmental

purposes is generally less than ~30%. It should be stressed that impurities may not always adversely affect the performance properties of bentonite.

Table 1. Mineralogy and component analysis of Miles (L5SA), Queensland (Gates et al., 2002) and Arumpo, New South Wales (Churchman et al., 2002) bentonites.

Miles bentonite	% of oven dried weight
Smectite	69 (3)
Quartz	15 (1)
Cristobalite*	7 (1)
Feldspar	8 (1)
Clinoptilolite	<1
Mica/illite**	<1
Gypsum	<1
Anatase	<1
Arumpo bentonite	Bulk
Smectite	76 – 99 (3 – 5)
Quartz	0 – 7 (1)
Dolomite	0 – 16 (1)
Anatase	<1
Analcime	<<1

Values in brackets are % standard error. \*Indexed as cristobalite, but probably opal cristobalite-tridymite. \*\*clay sized muscovite is commonly termed illite.

Montmorillonite content of bentonites should be assessed using X-ray diffraction and Reitveld refinement techniques (Taylor and Hinczak 2004). It can be performed on the bulk material or separately on size-fractionated materials. Such methodology, while more costly and time consuming, provides quantitative montmorillonite content and is preferable to the traditional methylene blue index (ASTM C837). The methylene blue index is based on the assumption that all montmorillonite has the same layer charge – which in sections ii and iii below will be shown to be a false assumption.

ii. Chemistry and structural formulae. The montmorillonite structure is based on gibbsite-like  $\text{Al}(\text{OH})_3$  octahedral sheets and silica ( $\text{SiO}_2$ ) tetrahedral sheets (Figure 1). The combination of one octahedral and two tetrahedral sheets constitutes a single 2:1 layer, and several tens or even hundreds of layers constitute a crystallite. The mineral surfaces which oppose one another across the interlayer space are the basal or interlayer surfaces. These surfaces are elongated flat plates and constitute the largest surface in the layer silicates. A 2:1 layer with an associated interlayer forms a distinct crystalline unit called a unit cell, which represents the smallest arrangement of the structure that is periodically reproduced throughout the crystal.

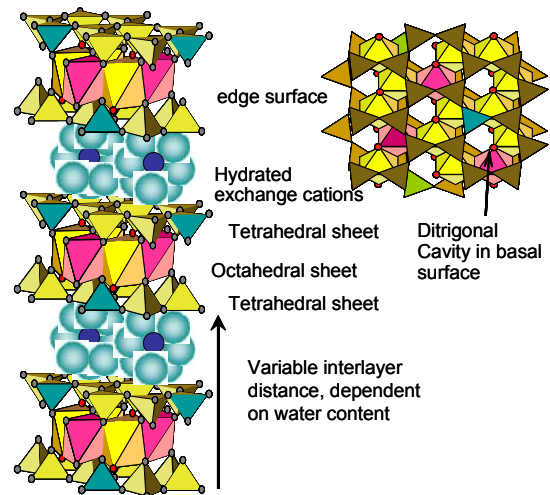
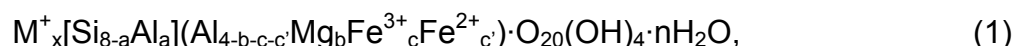


Figure 1. Structure of montmorillonite, a hydrated smectite. Cations commonly occupying tetrahedral sheets are  $\text{Si}^{4+}$  (yellow) and  $\text{Al}^{3+}$  (green) and those occupying the octahedral sheet are  $\text{Al}^{3+}$  (yellow),  $\text{Mg}^{2+}$  (blue),  $\text{Fe}^{3+}$  (pink) and  $\text{Fe}^{2+}$  (not shown). Hydrated exchange cations, which neutralize charge due to isomorphous substitutions occupy the basal or interlayer surface and enable montmorillonite to swell in water.

Montmorillonites typically have complex chemistries. The chemistry of the bulk bentonite is often dominated by the chemistry of the smectite, but usually bentonites have elevated SiO<sub>2</sub> content and depressed Al<sub>2</sub>O<sub>3</sub> content compared to purified montmorillonite. Thus chemical analysis should be performed on the purified material.

In addition to aluminium (Al<sup>3+</sup>), montmorillonites also have ferric iron (Fe<sup>3+</sup>), ferrous iron (Fe<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) in the octahedral sheet, and in addition to silicon (Si<sup>4+</sup>), they also have Al<sup>3+</sup> in the tetrahedral sheets.

The structural formulae – or the chemistry of a unit cell of material – can be expressed as



where M<sup>+</sup> represents a monovalent exchange cation; subscript x is the number of atoms of exchange cation; subscript a the number of Al<sup>3+</sup> atoms substituting in the tetrahedral sheet; subscripts b, c, and c' the number of other atoms (Mg<sup>2+</sup>, Fe<sup>3+</sup>, and Fe<sup>2+</sup> respectively) substituting within the octahedral sheet and n is the number of H<sub>2</sub>O molecules associated with the crystal structure. The cations Si and Al are written within brackets, [ ], to designate them as having tetrahedral coordination, and cations Al, Mg, etc., are written within parentheses, ( ), to designate their octahedral coordination.

Table 2 shows the variability in the chemistries of different montmorillonites. It is important to note that the chemistries can only be determined on a purified fraction of the bentonite containing a known amount of montmorillonite and minimal amount of known impurities. Montmorillonites thus isolated display a range in Al<sup>3+</sup> for Si<sup>4+</sup> substitution in the tetrahedral sheets as well as Fe<sup>3+</sup> and Mg<sup>2+</sup> for Al<sup>3+</sup> substitution in the octahedral sheet. The exchange cation (e.g., Ca<sup>2+</sup>) is neglected in Table 1, and instead the layer charge distribution for each montmorillonite (explained in next section) is shown. Total layer charge, and the distribution of layer charge between the octahedral and tetrahedral sheets provide valuable information regarding the montmorillonite type.

Table 2. Structural formulae of montmorillonites calculated from chemical analysis (by X-ray fluorescence) of ignited samples (after Gates, 2005).

Montmorillonite	Occupancies					Layer Charge		
	Tetrahedral		Octahedral			Total	X	
	Si <sup>4+</sup>	Al <sup>3+</sup>	Al <sup>3+</sup>	Fe <sup>3+</sup>	Mg <sup>2+</sup>		Tet	Oct
	per O <sub>20</sub> (OH) <sub>4</sub> ·nH <sub>2</sub> O					(e <sup>-</sup> )		
JP	7.92	0.08	3.01	0.19	0.79	0.93	0.08	0.85
SCa	7.99	0.01	2.68	0.11	1.29	1.05	0.01	1.04
SWy	7.77	0.23	3.08	0.44	0.45	0.77	0.23	0.54
OB	7.78	0.22	2.92	0.27	0.85	0.94	0.22	0.72
AB	7.92	0.08	2.80	0.37	0.85	0.87	0.08	0.79
JCL	7.94	0.06	3.07	0.41	0.43	0.74	0.06	0.67
MB <sup>+</sup>	7.74	0.26	3.02	0.52	0.45	0.72	0.23	0.46
RB	7.87	0.13	2.50	0.77	0.74	0.83	0.12	0.70

<sup>+</sup>after accounting for SiO<sub>2</sub> as opal-CT.

JP = Jelsový Poltók (Slovakia); Ca = California (United States); Wy=Wyoming (United States); OB=Ossean (South Africa); AB=Arumpo (Australia); JCL=JC Lane (United States); MB=Miles (Australia); RB=Redhill (United Kingdom).

iii. Layer charge, location of layer charge and cation exchange capacity. Substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheet, and  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  for  $\text{Al}^{3+}$  in the octahedral sheet results in a surplus of negative charge, or permanent layer charge. Permanent layer charge is expressed mostly at the basal or interlayer surfaces, and is neutralised by the exchange cations. The permanent layer charge,  $X$ , of montmorillonite may be calculated from its structural by:

$$X = 12 - a - b - c' \quad (2)$$

Layer charge calculated in this way is preferred as a diagnostic analysis because it is based solely on the chemistry of the material and is not influenced by the vagaries of experimental errors such as observed for many of the cation displacement methods (see discussion in Battaglia et al, 2006).

Smectites may develop variable layer charge (also called pH-dependent charge or amphoteric charge) as a result of interaction of the edge surfaces with aqueous solutions. The crystallite edges may contribute to the total negative layer charge at high solution pH, or detract from the total negative layer charge when solution pH is low. Variable charge is negligible for a 1  $\mu\text{m}$  smectite particle, but may contribute significantly to the total layer charge for particles  $<0.2 \mu\text{m}$ .

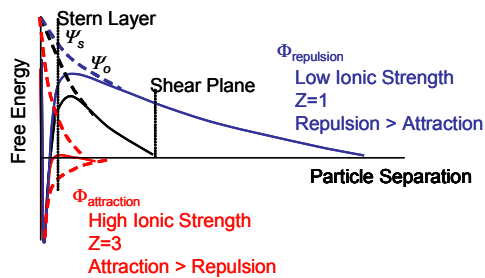


Figure 2. The Net Potential Energy of Particle Interaction. High ionic strength and large counter ion valence ( $Z$ ) promote flocculation. Low ionic strength and small valence promote dispersion.

Particles like smectites have a repulsive surface potential extending a few hundred nanometers into the surrounding aqueous environment that is countered by a concentration of counter ions near the surface, which bridge adjacent surfaces by electrostatic attraction. The interplay between the net potential energy (Laird, 2006)

expressed at the clay surface and chemical properties of the surrounding solution (ionic strength, ion type, viscosity etc) determine whether a given smectite, having given layer charge properties, will swell and disperse or flocculate and aggregate (Figure 2).

The magnitude and behaviour of the net potential energy of particle interaction is dependent on the total layer charge of the clay mineral but also affected by the location of the layer charge. Higher layer charge density increases the total repulsive surface potential, but also attracts a greater concentration of counter-ions close to the surface. Therefore higher layer charge increases the amount of shielding of the surface potential by exchange cations, thereby enabling clay platelets to approach each other more closely. Thus, the net potential energy of particle interaction for high charged clay is actually of lower magnitude at a given distance from the surface compared to a surface with a comparably lower layer charge density.

While net potential energy of particle interaction positively affects the ability of smectites to act as adsorbents, beyond a threshold value clay swelling and gelling capability is negatively affected. In general terms, a montmorillonite having a layer charge  $>0.85 \text{ e-/u.c.}$  (CEC of  $\sim 90 \text{ cmol/kg}$ ) provides good retention of solutes and

adsorption of contaminants, whereas a layer charge  $<0.85$  e-/u.c. typically provides optimal crystalline and bulk swelling properties because it can adsorb more water. Thus, high charged (i.e.  $X > 0.85$  e-) clays generally do not disperse well, but a low charge clay (i.e.  $X < 0.85$  e-) does. In general layer charge located in the octahedral sheet will promote dispersion and gel formation better than similarly charged clay with charge located in the tetrahedral sheet. The effect of layer charge location is more noticeable at layer charges above  $\sim 0.85$  e-, than for lower layer charges.

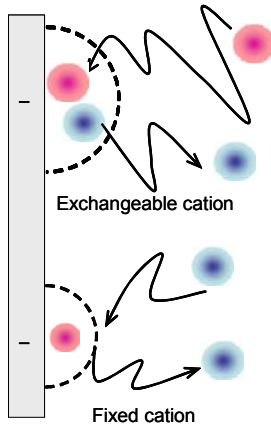


Figure 3. Illustration of cation exchange.

Charge-compensating, exchangeable cations reside within the interlayer space of smectites to neutralise the charge deficit. The cation exchange capacity (CEC) of a bentonite is controlled by the layer charge of the montmorillonite, which as shown above is itself dependent on the clay's chemistry. Layer charges of montmorillonites typically range between 0.7 to 1.1 electron charges per unit cell (u.c.;  $O_{20}(OH)_4 \cdot nH_2O$ ). Equivalent CECs are 75 to 130 milli-equivalents of charge per 100 grams (meq/100g), or centi-moles of charge per kg (cmol/kg) of material.

Conceptually, cations are retained near a surface within a hemisphere of motion (Figure 3), the size of which depends on thermal and kinetic energy, differences in electrostatic affinities of cations for the charged surface, and where within the surface charge originates. A proportion of the "residence time" of exchangeable cations is spent at a distance that is greater than the average distance from the charge site. If at a great enough distance, other cations can displace them by approaching closer to the site. Low charge clays promote a larger hemisphere of motion than clays with greater layer charge.

The cation exchange capacity (CEC) is an operationally defined measure generally determined as the amount of a particular cation that is either (i) displaced from the clay (solution chemistry) or (ii) placed on the clay (solid chemistry). The threshold layer charge value of  $\sim 0.85$  e-.u.c. discussed above is equivalent to a CEC of  $\sim 90$  cmol/kg.

The CEC follows a 1:1 relationship to the layer charge for smectites (Figure 4). For a given smectite, the CEC to layer charge relationship depends on operational factors such as the mass of the exchange cation, its exchange selectivity and pH of the solution. For the reasons described above, the 1:1 relationship between CEC and layer charge for smectites generally breaks down with higher layer charges. With the notable exception of vermiculite, high charge smectites with predominantly tetrahedral layer

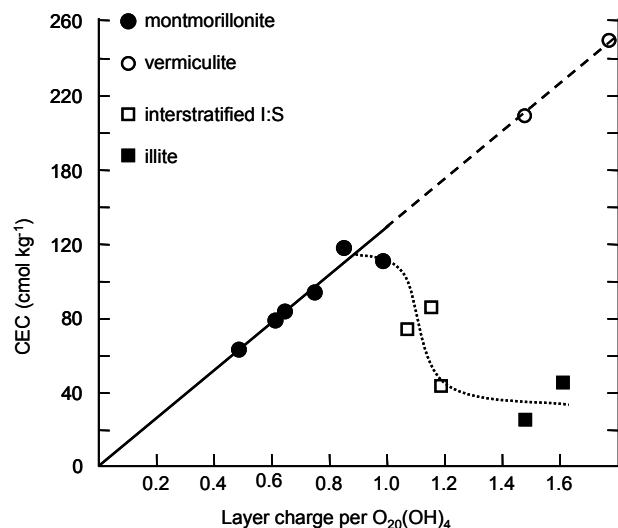


Figure 4. Relationship between layer charge and CEC for some layer silicates. Redrawn from data presented in Tessier and Pedro (1987).

charge may show a considerable deviation of the CEC – layer charge relationship. It also breaks down when non-swelling mineral impurities are present. For example, illite-smectite interstratifications cause a dramatic deviation of the CEC from the 1:1 relationship with layer charge because illites have high layer charge, but low CEC.

CEC is generally determined using the ammonium displacement method, which was developed by soil scientists to analyse agricultural soils. The amount of ammonium retained by the clay is determined either directly using infrared spectroscopy (Petit et al., 2006) or indirectly by measuring the loss of  $\text{NH}_4^+$  from a known concentration reacted with the material of interest (reference). A more appropriate and direct method uses barium saturation (Battaglia et al., 2006) where  $\text{Ba}^{2+}$  is quantified directly on the clay sample using X-ray fluorescence. This method is also robust in that it can be performed on bulk material or size-fractionated material, thereby getting information specific to the montmorillonite. An additional strength is that the entire chemistry of the clay can be determined on the same material enabling structural formulae and layer charge distribution to be determined.

*iv. Montmorillonite type.* Bentonites can differ markedly in their performance because they are natural products. As shown in Table 3 the different montmorillonite types can be differentiated based on chemical composition and layer charge characteristics (Schultz, 1969). The Otay (or Cheto) montmorillonite type represents the ideal end member composition for montmorillonite, represented by high octahedral  $\text{Mg}^{2+}$ , low octahedral  $\text{Fe}^{3+}$ , and high layer charge ( $X > 0.85$ ) located predominantly in the octahedral sheet. The Wyoming, Tatilla (also called Chambers) and Beidellitic types all represent deviations from ideal montmorillonite character. The total layer charge of  $X = 0.85$  (equivalent to methylene blue index (MBI)  $\sim 90$  meq/100g or cation exchange capacity (CEC)  $\sim 100$  cmol/kg) used for division is indicative, as borderline analyses are common. As indicated above, sufficient evidence exists to support that this layer charge threshold is real (e.g., Tessier and Pedro, 1987; Laird, 1996; Laird, 2006; Gates et al., 1998; Gates, 2005).

Table 3. Montmorillonite type discriminations modified after Schultz (1969), Brigatti and Poppi (1981), Brigatti (1983), Güven (1988), Schoonheydt (1995) and Gates (2005).

Montmorillonite type	Octahedral occupancy		Layer Charge (X)	
	$\text{Mg}^{2+}$	$\text{Fe}^{3+}$	Total	% tetrahedral
Wyoming	0.40 – 0.80	0.36 – 0.60	< 0.85	< 50
Otay (or Cheto)	0.80 – 1.2	0 – 0.42	> 0.85	< 15
Tatilla (or Chambers)	0.50 – 0.90	0 – 0.22	> 0.85	15 – 50
Beidellitic	< 0.40	0.60 – 1.2	> 0.85	50 – 85

Of particular interest is that the Wyoming type montmorillonites have lower total layer charge ( $X < 0.85$ ) and generally lower octahedral  $\text{Mg}^{2+}$  contents than the other montmorillonite types. The Wyoming type is also generally more dispersible in water and has better swelling characteristics than the other types. Several of the montmorillonites displayed in Table 2 are Wyoming type montmorillonites.

*v. Particle size.* The particle size of bentonites is generally discerned by dispersion or suspension (e.g., Australian Standard 1289-3.6.2). The fundamental particle size influences many surface and physico-chemical properties of bentonites, and the particle size distribution of a bentonite is usually indicative of its smectite content

(Table 4). Bentonite used in GCLs should have a predominance of fundamental particles at  $<0.5 \mu\text{m}$  size. The clay size fraction of bentonites is often present as aggregates larger than clay size and physical grinding or pulverisation and/or chemical dispersion is needed to release the fundamental particles. However, if significant proportion of the sample has particles  $>2 \mu\text{m}$ , there is good probability that other minerals are present as impurities. Thus, chemical analyses enabling layer charge determination should be only performed on size-fractionated and purified materials. The smectite component of bentonites suitable for environmental barriers often dominates the mineralogy of particles  $<0.5 \mu\text{m}$ .

Table 4. Fundamental particle size of the montmorillonite component of a bentonite from Miles (L5SA), Queensland. From Gates et al. (2002).

Mineral	Size Fraction			
	0.5-2 $\mu\text{m}$	0.2-0.5 $\mu\text{m}$	$<0.2\mu\text{m}$	$<<0.1\mu\text{m}$
	% by mass			
Smectite	26(1)	70(2)	97(1)	99(1)

Values in brackets are % standard error.

Many colloidal characteristics for which bentonites are known are increased or improved with decreasing particle size, including specific surface area, swelling, plasticity, gelling and dispersion. Decreasing mean particle size generally means increased reactivity of the particles with their surroundings due to the larger surface areas exposed. On a unit mass basis, a barrier composed of smaller particles will have a greater reactive surface area, and the pore sizes will be smaller, than one composed of larger particles. Thus smaller particle sizes enhance sealing and result in decreased permeability. Dry screening (e.g. 75  $\mu\text{m}$  mesh) provides a measure of aggregate particle size.

As shown recently by Bouazza et al. (2006), the aggregate particle size of a bentonite also impacts initial hydration characteristics. Powdered bentonites generally hydrate uniformly from the outer surfaces of the GCL toward the centre (Figure 5a), resulting in rapid sealing against advective and diffusive water movement. On the other hand, the outer surfaces of each individual granule in granulated bentonites wets first (Figure 5b), and the interior of aggregates are wet more slowly. Thus, initial advective and diffusive water movement is higher in granulated forms because of the larger flow paths between aggregates.

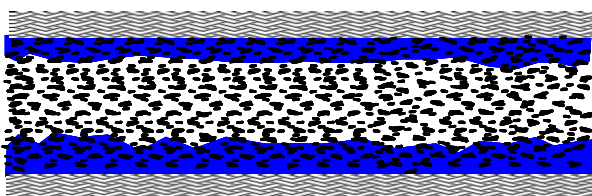


Figure 5a. Wetting of powdered bentonite – water slowly wets the bentonite particles across the entire wetting front forming a thin uniform layer of hydrated bentonite.

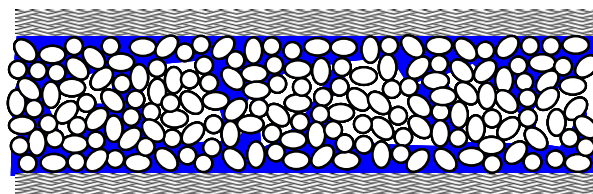


Figure 5b Wetting of granular bentonite – water quickly wets the external surfaces of aggregates initially then more slowly penetrates aggregate interior potentially forming an unevenly hydrated bentonite

*vi. Surface Area.* Smectites have two main surfaces: the interlayer or internal surface ( $S_i$ ) and the interparticle (inter-aggregate) or external surface ( $S_E$ ) (Table 5). Together

these represent the total specific surface area,  $S_o$ . With appropriate crystallographic data, the specific surface areas of smectites can be determined directly.

Table 5. Crystallographic specific surface areas of montmorillonites purified from some reference bentonites calculated based on chemical and mineralogical analysis (Gates, 2005).

Montmorillonite*	m u.c.† g	$S_c$	$S_i$ $m^2 g^{-1}$	$S_E$
JP	745	844	807	37.2
SCa	747	867	830	37.2
SWy	748	865	828	37.1
OB	749	825	788	37.1
AB	750	847	810	37.1
JCL	750	873	835	37.0
MB	751	829	792	37.0
RB	760	816	779	36.6

\*JP = Jelsovy Poltok (Slovakia); SCa =California (United States); SWy=Wyoming (United States); OB=Ossean (South Africa); AB=Arumpo (Australia); JCL=JC Lane (United States); MB=Miles (Australia); RB=Redhill (United Kingdom).

† m.u.c. = mass of the unit cell considering  $Ca^{2+}$  as the exchange cation.

Higher specific surface areas tend to enhance the important properties of bentonites such as greater swelling, adsorption and viscosities, and lower permeability. Values of  $S_c$  greater than  $\sim 840 m^2 g^{-1}$ , or  $S_i$  greater than  $\sim 800 m^2 g^{-1}$ , tend to yield better swell indices, although particle size and layer charge characteristics influence this as well.

The specific surface areas are often determined from measurement of the mass of some substance adsorbed to a unit mass of clay. For example  $N_2$  gas is a selective adsorbate and only penetrates the external surfaces of particles; thus the  $N_2$  specific surface ( $S_N$ ) provides an estimate of  $S_E$ , and really has little relation to inherent ability to of a clay to swell. Water, methylene blue or ethyleneglycolmonoethylether, adsorb generally onto the interlayer surfaces, therefore providing estimates of  $S_i$  ( $S_W$ ,  $S_{MB}$ , and  $S_{EGME}$ , respectively), which may provide a better indication of surface reactivity.

*vii. Exchange cation identity.* The identity of the predominant charge-balancing cation exerts a large influence on clay performance as a barrier. A  $Na^+$  form bentonite generally provides better swelling and permeability characteristics than  $Ca^{2+}$  or  $Mg^{2+}$  forms. Most natural bentonites are mixtures of the  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  forms and pure  $Na^+$  forms of bentonites are generally rare (except for Wyoming bentonites). Most Australian bentonites are of the  $Ca^{2+}$  or  $Mg^{2+}$  (or mixtures of  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$ ) forms, thus processing is generally required to enhance sealing and barrier properties.

Intrinsic properties (Table 6) of cations govern their exchangeability and thus their interaction with the clay. Ions with small ionic radii have a high charge potential and therefore interact strongly with solvents such as water (Teppen and Miller, 2005). Smaller ions tend to have greater hydration energies, and thus within the interlayer of clays can attract more water than larger ions. While the hydrated size of  $Mg^{2+}$  and  $Ca^{2+}$  is larger than either  $Li^+$  or  $Na^+$ , their higher valency enables a greater attraction between them and the clay surface. Greater attraction energy enables cations like  $Ca^{2+}$  and  $Mg^{2+}$  to interact strongly with both surfaces of adjacent clay layers, therefore

they are retained more strongly than  $\text{Na}^+$ . The ratio of the difference in ionic and hydrated radii to the cation valence ( $\Delta\text{radius}/\text{valence}$ ) provides a measure of this interaction. Cations with larger  $\Delta\text{radius}/\text{valence} > \sim 200$  have lower affinity for the clay surface.

Table 6. Properties of common exchange cations.

Element	Symbol & valence	Ionic radius (pm)	Hydrated radius (pm)	$\Delta\text{radius} / \text{valence}$ ratio	Number of hydration shells
Sodium	$\text{Na}^+$	102	358	263	3+
Potassium	$\text{K}^+$	138	331	198	1
Magnesium	$\text{Mg}^{2+}$	58	428	182	2
Calcium	$\text{Ca}^{2+}$	100	412	157	2

The degree of attraction to the clay surface of  $\text{Na}^+$  is less, so a  $\text{Na}^+$  is more conducive to swelling when present at the clay surface, because adjacent negatively-charged layers can be made to repel one another during the absorption of water into the interlayer. On the other hand,  $\text{Ca}^{2+}$  saturation results in only limited swelling because the attraction of the cation for adjacent surfaces is stronger.

From a practical viewpoint, the competition between cations for the clay surface influences bentonite processing. If  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  predominates on the exchange complex, a large excess ( $>10x$ ) of  $\text{Na}^+$  will be required to efficiently displace these cations. Cation exchange competition also influences barrier performance. If solutions bearing  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  permeate a  $\text{Na}^+$ -saturated bentonite liner, an exchange of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  for  $\text{Na}^+$  will take place, potentially resulting in increased permeability of the liner (Dobras and Elzea, 1993; Shackelford et al., 2000; Egloffstein, 2001; Shackelford and Lee, 2003).

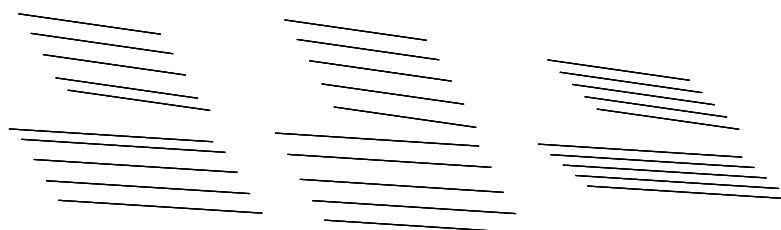


Figure 6. Schematic of crystalline and bulk swelling. Crystalline swelling results in increased volume of crystallites due to increased distance between adjacent layers of clay (left). Bulk swelling results in increased distance between adjacent crystallites, or collections of clay layers (right). For hydrated gels, both mechanisms occur simultaneously (middle).

*vii. Swelling and water adsorption.* Montmorillonite is one of the few minerals which undergoes volume change during the uptake of water. They do this by imbibing water between individual clay layers within crystallites – called crystalline swelling – and between crystallites – called bulk swelling (Figure 6). The high hydration energy of exchange sodium enables  $\text{Na}^+$  montmorillonite to absorb large amounts of water and swell. Crystalline swelling is the result of a balance between forces of attraction and repulsion operating between adjacent interlayer faces. Recall that the net potential energy of particle interaction is dominated by electrostatic attraction between the exchange cations and the negative basal surfaces of the clay, and the cations may act as bridges between adjacent clay layers. Repulsion is initiated by the hydration energy of the exchange cations - the exchange cations exist within the interlayer in

partially hydrated states, thus they will attract waters of hydration that will force the interlayer apart to a point at which the net potential energies of attraction and repulsion are balanced. Unsaturated conditions or saturated conditions with high electrolyte concentrations favour the dominance of net forces of attraction; while fully saturated conditions of low electrolyte concentration favour the dominance of net forces of repulsion (see Figure 3).

The “crystalline” hydrates of  $\text{Na}^+$  smectites can contain zero, one, two, three or four discrete layers of water molecules, distinguished by specific separation distances between adjacent layers – called d-spacings (Figure 7). Not all smectites exhibit all these spacings and not all exchange cations give rise to all these d-spacings during hydration of the smectite. The different layer hydrates can be viewed as phases with different thermodynamic properties where any change in d-spacing is a phase change (Laird, 1996; Laird and Shang, 1997).

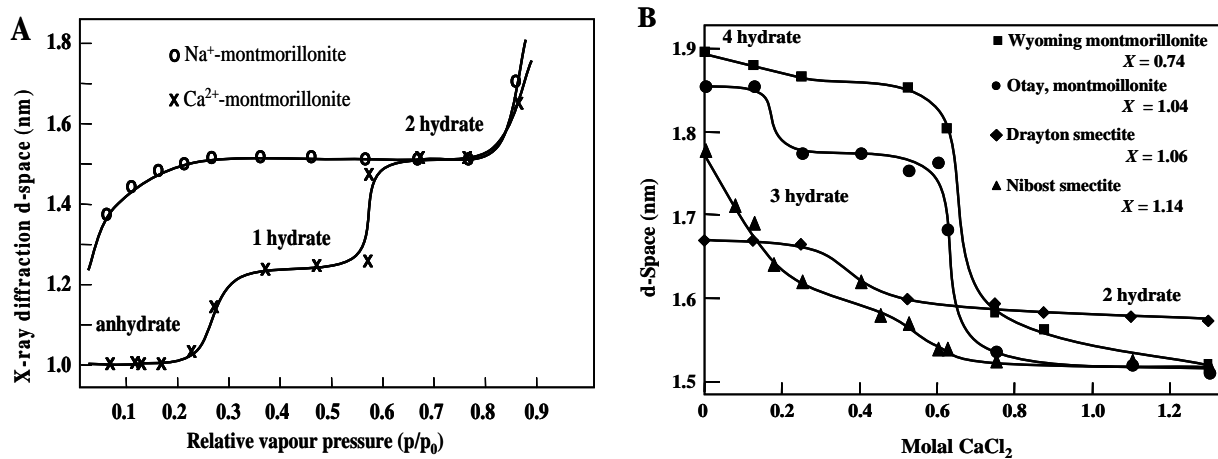


Figure 7. Crystalline swelling of montmorillonite A) as a function of relative humidity in the unsaturated state (data from Mooney et al., 1952) and B) as a function of ionic strength in the saturated state (data from Slade et al., 1991).

As crystalline swelling proceeds, more and more of the basal surface area becomes exposed, and is therefore available to react with the surrounding solution (Figure 8 – following page). Swelling is critical to the reactivity of clay minerals in various processes, such as adsorption of heavy metals, catalysis reactions and colloidal behaviour. Even the exchange processes necessary for converting a  $\text{Ca}^{2+}$ -montmorillonite to a  $\text{Na}^+$ -montmorillonite requires crystalline swelling to proceed efficiently.

The swellability of a bentonite is affected by many factors that are inherent to the bentonite in its natural state. These include: layer charge (CEC), location of layer charge, exchange cation identity, the clay fabric in its natural state and impurities present. The amount of crystalline swelling is dependent on the layer charge characteristics of the smectite (see Figure 7B). For a given layer charge, dioctahedral smectites with most of the charge originating in the octahedral sheet (i.e., montmorillonites) have greater swelling than those with most of the layer charge originating in the tetrahedral sheet (i.e., beidellites). Because swelling of smectites underpins their performance in GCLs, it follows that those GCLs containing bentonites with moderate to low CEC, such as the Wyoming type bentonites, will most likely have greater swelling indices than those with higher CEC.

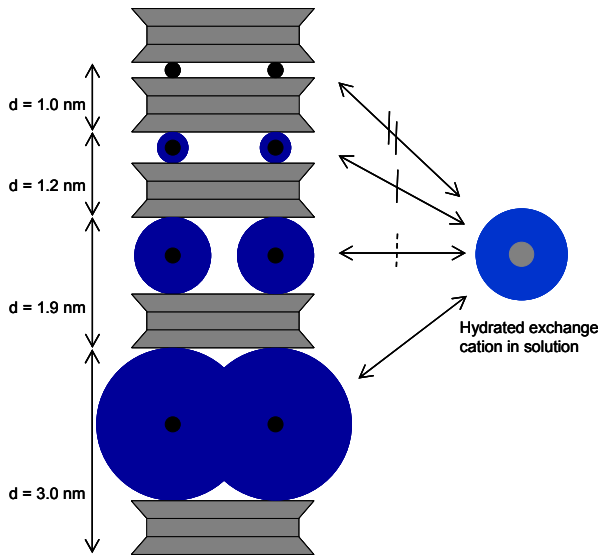


Figure 8. Clay swelling and surface reactivity. Absorption of water increases the spacing between adjacent layers exposing more interlayer surface area to reacting fluids, which increases the ability of the smectite to react with other exchange cations. Hydrated cation on right can readily exchange with highly hydrated clays, but is limited in its efficiency of exchange with less hydrated or non-hydrated clays.

Swelling is commonly measured by the Swelling Index (ASTM D-5890) where a quantity of clay is added to a known volume of water the volume occupied by the clay is recorded. In general, for GCLs, a Swell Index exceeding 24 is indicative of a material with good swelling and therefore good sealing capabilities. A related measure of bentonite-water interaction is Fluid Loss (ASTM D-5891) that evaluates the amount of water lost by a bentonite under an applied pressure for a specific period of time. Lower volumes (<15 ml) lost are indicative of a bentonite with adequate water-retention characteristics. Modification of this index test, where the fluid is expressed until equilibrium is achieved, provides a measure of the clay's swelling pressure.

In this case, greater water contents of the clay gel subjected to this modified test are indicative of good clay-water relations.

Processing such as changing the exchange cation to sodium is commonly used to improve bentonite swellability, in part through rearrangement of clay fabric. Other processing such as grinding or pulverising can increase swellability by increasing the reactive surface area. Removal of impurities can also improve bentonite swelling properties. Bentonites with strong particle interactions will require processing in the form of pulverising or mechanical shearing to yield a material with adequate Swell Index and therefore expected sealing and barrier performance.

*ix. Clay fabric.* The 3-dimensional organisation of montmorillonite, called clay fabric (also referred to as texture or microstructure) influences bentonite swelling and sealing behaviour. In the gel state, clay fabric enables the effective translation of properties, such as swelling, from the individual layer or crystallite level to the macro-scale level (Egloffstein, 2001; Likos and Lu, 2006).

Individual layers (crystallites) of smectites interact in face-face and overlapping face-face, edge-face and edge-edge associations (Figure 9) to form quasi-crystals (Aylmore and Quirk, 1960; Tessier, 1991, Hetzel et al., 1994). A quasi-crystal is a heterogeneous smectite particle composed of more-or-less coherently stacked crystallites, which themselves are composed of hydrated clay

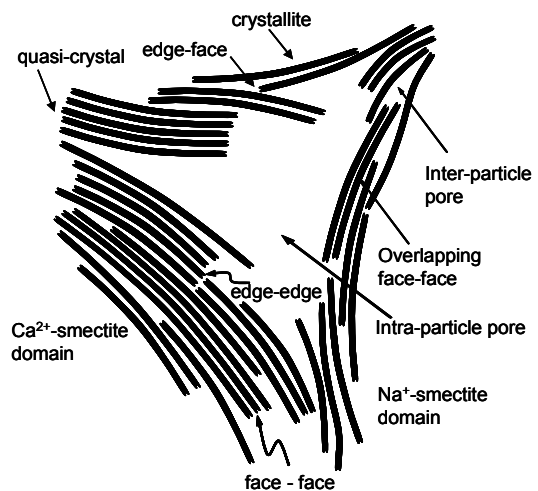


Figure 9. Idealized clay fabric showing particle associations (edge-edge, edge-face, face-face and overlapping face-face) that enable crystallites to form quasi-crystals and at the next size scale, quasi-crystals to form larger clay domains. Face-face associations dominate  $\text{Ca}^{2+}$ -smectite domains and overlapping face-face associations dominate  $\text{Na}^{+}$ -smectite domains.

layers (platelets). It is thus an equilibrium structure that smectites adopt which reduces the net potential energy of particle interaction (Laird, 2006). The number of layers that constitute a quasi-crystal, its size, shape and interaction with other quasi-crystals is generally dependent on the layer charge characteristics of the clay, electrolyte concentration and identity of the exchange cation.

Attractive van der Waals forces enable interactions between quasi-crystals forming larger interconnected clay domains. A clay domain is a group of quasi-crystals that are mostly in parallel alignment, but individual domains are randomly arranged with a larger bentonite particle. Clay domains can have various size and durability, depending on the surrounding external environment (Aylmore and Quirk, 1960; Lagaly, 2006). Typically the thickness of  $\text{Na}^+$ -bentonite clay domains is <100 individual layers, but the aspect ratio is large (Tessier, 1991). The resulting micro-structure has a distribution of inter-particle pore sizes which optimise water retention and inhibit water flow (Egloffstein, 2001). On the other hand,  $\text{Ca}^{2+}$ -bentonite clay domains are composed of several hundred individual layers, which result in a pore size distribution and fabric more conducive to water permeability (Egloffstein, 2001). The highly flexible nature of clay platelets enables overlapping face-face associations to dominate the fabric of  $\text{Na}^+$  saturated smectite gels, but these are relatively unimportant in  $\text{Ca}^{2+}$ -smectite gels.

Total layer charges of  $<0.8 e^-$  favour the formation of overlapping face-face interactions, whereas layer charges  $>0.8 e^-$  favour face-face interactions. Octahedral layer charge promotes overlapping face-face interactions, but tetrahedral promotes face-face interactions. Low ( $<10^{-4}$  M) ionic strength solutions enable the hydration (repulsive) energies of the interlayer cation to dominate, thus allowing the uptake of water and expansion of the interlayer (crystalline swelling). However, high ( $>1\text{M}$ ) ionic strength solutions remove water from the interlayer, causing the interlayer to collapse. Then, face-face associations will dominate over overlapping face-face associations and preferentially large quasi-crystals will form, substantially restricting swelling.

Processing or beneficiation of bentonites changes the clay fabric, thereby improving the swelling and permeability performance of bentonites. The initial fabric state is an often overlooked aspect of marketed natural bentonites – especially those provided in the granulated form. In the natural state, the fabric is largely controlled by conditions that existed during bentonite formation and subsequent weathering (Likos and Lu, 2006), which may not be best for efficient hydration and swelling. The fabric of a processed bentonite is largely controlled by the clay type, its layer charge (and location) as well as the identity of the exchange cation. A sodium activated bentonite is often fabricated by mixing unprocessed bentonite with ~2 -3% soluble sodium salt (Guyonnet et al., 2005; Harvey and Lagaly, 2006), enabling  $\text{Na}^+$  cations to displace exchangeable  $\text{Ca}^{2+}$  (and  $\text{Mg}^{2+}$  and  $\text{K}^+$ ). The most commonly used sodium salts are sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ). Sodium activated bentonites are also referred to as sodium activated calcium bentonite, calcium bentonite activated with sodium or activated sodium bentonites.

The influx of  $\text{Ca}^{2+}$ , present in permeating fluids, into a  $\text{Na}^+$  bentonite barrier will cause exchange of  $\text{Ca}^{2+}$  for  $\text{Na}^+$  that will eventually result in a change in the microfabric from one with a high proportion of interlayer voids to one with a high proportion of interparticle voids. The bottom portion of Figure 9, where a  $\text{Na}^+$ -smectite clay domain

and a  $\text{Ca}^{2+}$ - clay domain meet may be very common, especially where partial  $\text{Ca}^{2+}$  for  $\text{Na}^+$  exchange has taken place. Such partial exchange will generally follow the larger voids between clay domains initially, causing changes to clay fabric resulting in regions with higher permeability interspersed within the mass of lower permeability.

If this occurs under minimum confining pressure, the permeability will increase by at least 2 orders of magnitude. Under sufficient confining stress, such a condition may result in consolidation of the barrier concurrent with the change in the relative amounts of interparticle and interlayer voids (Lee et al., 2005), and thus attenuate the permeability increase to about 1 order of magnitude. It should be noted that a typical final cover soil of 1-2 m depth is probably insufficient to minimise large permeability increases induced by cation exchange and desiccation in GCLs used as capping liners for landfill tombs (Meer and Benson, 2007).

x. *Gel Formation and Sealing.* Swelling clays can absorb 200% or more of their mass in water and increase their original volume many fold. In order to effectively seal under confinement, domains of quasi-crystals must be able to re-arrange and expand into the available inter-particle pore space during wetting. Thus, the formation of a stable gel state is of paramount importance as these materials form the most effective seals.

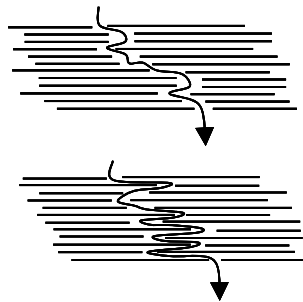


Figure 10. Tortuosity of flow path (indicated by arrows) is dependent on the size and degree of dis-connectivity of pores. The lower scheme will have lower permeability due to greater tortuosity than the upper scheme.

A clay gel is a transitional hydrous (saturated) phase that exists between the condensed (plastic) phase and the dispersed (fluid) phase. It is a borderline equilibrium state where unlimited crystalline swelling and passive particulate dispersion may occur during further uptake of water on the one hand, and shrinking, flocculation and fabric rearrangement occur during water loss on the other hand. Typically clay gels represent a material with reduced void sizes and minimal inter-connectivity of pores, and therefore increased tortuosity of flow path (Figure 10).

If a large concentration of counter ions exists in solution, they will tend to shield the repulsive forces that operate between adjacent clay layers and result in attractive forces becoming dominant (see Figure 3). Conversely, lower concentrations of counter ions in solution fail to fully shield the repulsive forces, thus enabling repulsive forces to override the attractive forces. For good gel formation, low ionic strength solutions are needed to hydrate the bentonite.

Full hydration will provide better protection against thermodynamically driven cation exchange and resulting changes to clay fabric by slowing the process down and ensuring that the entire clay CEC is utilised in the exchange. If the entire CEC is involved in cation exchange under full hydration, then the clay fabric will change gradually from an expanded (Figure 8, bottom) to a collapsed (Figure 8, upper). Gradual re-arrangement of the clay fabric can allow confining pressures to consolidate the resulting structures (Egloffstein, 2001), maintaining highly tortuous flow paths (Figure 10, lower). Conversely, if partially hydrated, only a portion of the CEC is involved in the exchange – relegated to the hydrated regions (e.g. Figure 8, middle) – thus resulting rather quickly in a fabric that is unevenly consolidated, resulting in less tortuous flow paths (Figure 10, upper).

## Compatibility Issues with GCLs

Because only a few mm of bentonite in GCLs are called upon to withstand ion diffusion and advection for generally decades or longer, it must be stressed that not all cover materials, base materials or materials used in drainage layers are compatible with GCLs. This is because leachates, as they pass through these materials, will present fluids having chemical composition at equilibrium with these materials.

All potential materials need to be subject to thorough testing and analyses during the early planning stages of landfill design in order to minimise such effects. Mineralogical and chemical analyses as well as leachate tests should be performed on the materials to determine the possible risks associated with any detrimental reactions. This is especially important if soluble and/or exchangeable calcium (or any other divalent cation) is expected to be produced in the leachates from potential materials used in lining systems.

Potential materials that are calcareous should be avoided, especially where their

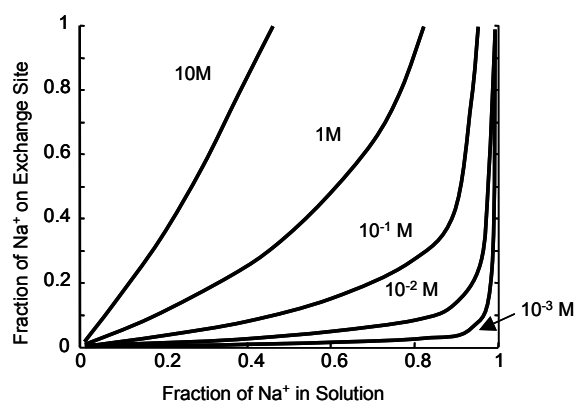


Figure 11. Typical exchange dynamics for the binary  $\text{Ca}^{2+}$  -  $\text{Na}^{+}$  exchange system. Low total concentrations require a very high  $\text{Na}^{+}:\text{Ca}^{2+}$  ratio in solution to effectively maintain  $\text{Na}^{+}$  on the exchange complex.

leachates are expected to come into direct contact with the GCL. These include crushed concrete, certain building rubble and calccrete fill. In order to minimise  $\text{Ca}^{2+}$  for  $\text{Na}^{+}$  exchange under conditions most likely to be encountered in a landfill leachate (i.e., within the range  $10^{-4}$  to  $10^{-1}\text{M}$ ), solution  $\text{Ca}^{2+}$  needs to be of very low concentration ( $<10^{-3}\text{M}$ ), and the  $\text{Na}^{+}$  concentration needs to be at least a magnitude greater ( $\sim 10^{-2}\text{M}$ ) (Figure 11). This is because  $\text{Ca}^{2+}$  has an increased competitive affinity for the charged clay surface over  $\text{Na}^{+}$

under low total ionic strength. Thus, the concentration of  $\text{Na}^{+}$  in solution needs to be  $>10\times$  that of  $\text{Ca}^{2+}$  under typical conditions.

Under more saline conditions, where the high ionic strength will induce flocculation of clays, greater  $\text{Ca}^{2+}$  concentrations can be acceptable, because  $\text{Na}^{+}$  can more effectively out-compete  $\text{Ca}^{2+}$  for positions within the collapsed interlayer space of the clay (review Figures 3, 6, 9 & 10 and accompanying text). Typically, however, if the total ionic strength exceeds  $\sim 5 \times 10^{-1}\text{M}$ , the effect of ionic strength essentially overrides the effect of  $\text{Ca}^{2+}$  for  $\text{Na}^{+}$  exchange and the resulting changes to clay fabric will result in increased hydraulic conductivity (Shackelford et al., 2000; Egloffstein, 2001).

Other physical-chemical properties of the leachate fluids, including viscosity, surface tension, density, permittivity and pH, can have a large impact on the behaviour of GCLs. For example, the interaction of petrochemicals (which have low density and surface tension) with the clay can result in large changes in the void ratio and porosity thereby detrimentally impacting on permeability (Shackelford, 1994). Leachates of

high pH tend to enhance dispersion of clay particles, but if in excess of pH 9, can cause dissolution of smectite structures. Leachates with pH below 4.5 usually favour dissolution of clay structures as well, but also generally cause flocculation. Obviously, dissolution of the reactive component of a GCL would be detrimental to its performance as a hydraulic barrier. Often the onset of such effects will depend on whether the bentonite is pre-hydrated prior to contact with incompatible leachates – pre-hydrated GCLs have been shown to retained lower permeability for a greater number of pore volumes (longer time) than non-pre-hydrated GCLs when exposed to mock solutions of up to 1M concentration (Petrov et al., 1997; Petrov and Rowe, 1996; Sangam and Rowe, 2001; Shackelford and Lee, 2003).

## **Summary**

The properties of bentonites which make them attractive as barriers to waste waters are small particle size, large surface area, chemistry, montmorillonite content, the amount and type of non smectite minerals present, their swelling and gelling characteristics and amount and type of processing, including Na-activation, polymer beneficiation, pulverising or grinding.

Bentonites are not all the same, and the montmorillonite type largely determines the relative usefulness of a particular bentonite for various purposes. This document has detailed certain aspects of montmorillonite properties with the aim of increasing the general awareness amongst engineers of how differences in chemistry, mineralogy and processing may impact performance to enable science-based decision-making in regards to the application of bentonites as barriers.

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## Standard Methods

- ASTM D-5890. Standard test method for swell index of clay mineral component of geosynthetic clay liners.
- ASTM D-5891-02. Standard test method for fluid loss of clay mineral component of geosynthetic clay liners.
- ASTM C-837-99. Standard test method for methylene blue index of clay.
- AS 1289-3.6.2. Methods of testing soils for engineering purposes – Soil classification tests – Determination of the particle size distribution of a soil – Analysis by sieving in combination with hydrometer analysis (subsidiary method).