

# The affect of calcareous permeant on the hydraulic flux of four clay systems used in geosynthetic clay liners.

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**ABSTRACT:** Four different bentonite clay based systems, used in geosynthetic clay liners (GCL's), displayed significantly different flux behaviour when permeated with a calcareous permeant that induced cation exchange in the clays. The flux measurements were made using the ASTM 5887 index flux test with a 500ppm calcium permeant but the hydraulic head pressure was varied to ensure many pore volumes of permeant were passed. The flux data enabled clays to be ranked in their ability to maintain low permeability from best to worst as: polymer fortified Wyoming >Wyoming >European sodium activated>> European calcium bentonite. The ranking reflects the initial exchangeable cation associated with the clay but the small size of the clay silicate layers found in Wyoming bentonite compared to other bentonites seems also to be a likely cause for the different behaviour. The inclusion of polymer promoted swelling of the Wyoming bentonite under a confining force and it was observed that such swell correlated with the ranking from the flux experiments. ASTM 5890 index swell and ASTM 5891 fluid loss tests, often used to assess the suitability of a clay for GCL applications, did not provide the level of discrimination observed in the flux experiments.

## 1 INTRODUCTION

Geosynthetic clay liners (GCL's) are low permeability membranes which are manufactured with smectic clays. Such clays found throughout the world are frequently referred to in industry as Bentonite. The smectic clay mineral component of Bentonite is typically in excess of 80%. Such clays possess the ability to swell upon hydration and display a low hydraulic permeability that decreases with increasing confining pressure applied to it, reaching values of the order of  $10^{-14}$  m.s<sup>-1</sup> (Pusch 1994).

Wyoming Bentonite from the USA together with European calcium and European sodium activated Bentonites are amongst those used in GCL's but their relative performance as low permeability membranes are not identical, particularly against permeants that result in the phenomenon of cation exchange.

In addition to the quantity of smectic clay present in a Bentonite each source displays other differences associated with the clay particles themselves. The clay particles comprise of high aspect ratio alumino-silicate layers, 0.91nm thick but with extensive basal areas and morphology that varies from deposit to deposit. The clay comprise of aggregates of individual alumino-silicate layers that are often stacked in a periodic fashion and thus form quasicrystals. Common to all smectic clays is that associated with the upper and lower basal surface of the individual alumino-silicate layer is a negative electrical charge which is counter balanced, to maintain electrical neutrality, by interlayer cations. The interlayer cations, which are labile, are the dominant influence on the swelling behaviour of the clay.

Upon hydration the water molecules organise themselves around the inter layer cations thereby increasing the effective volume of the cations. This forces the alumino-silicate layers apart with the observable affect of the clay swelling. This disturbs and disrupts the way in which the alumino-silicate layers are aggregated. When sodium is the dominant interlayer cation the swelling is greater than when large monovalent cations or di and tri valent interlayer cations dominate.

In order to create a low hydraulic permeability membrane with Bentonite clay it is necessary for the aggregates of alumino-silicate layers to swell and arrange in a manner that minimises the voids (pores) between them. The pores, which are of three kinds interlamella, interaggregate between primary particles and interaggregate between clusters of clay aggregates (Guven

1992), create pathways through which a permeant can flow. The spacing of these pores ranges from a few tens of nanometres to several microns.

Application of an increasing confining force to the clay reduces the pore size and hydraulic permeability also; enhancing the swelling ability of the clay can also achieve the same. However, inherent features of the clays themselves mean that some are more suited to being low permeability barriers than others.

## 2 CLAY ANALYSES

Three Bentonite clays used in GCLs were studied but one, the Wyoming Bentonite, was studied both alone (Wy) and with the inclusion of a propriety polymer (<1% by weight addition) (WyP). The European sodium activated Bentonite (SAB) had been processed so that the calcium and magnesium interlayer cations had been mainly exchanged for sodium cations, the European calcium Bentonite (CaB) was studied without alteration. All the clays were tested with the same granular particle size distribution - 100% <2mm and 85% lying between 2 and 0.5mm.

The mineralogical composition of the clays, shown in table 1, was determined by X-ray diffraction analysis (XRD).

Table 1 XRD Mineralogical description of Bentonites

Mineral	Wy	SAB	CaB
Smectic clay %	85	87	74-78
Illite/mica %	1	-	-
Quartz %	4	4	6-8
Opal CT %	-	-	12-13
Feldspar %	4	-	2-3
Barytes %	6	-	-
Calcite %	-	6	1
Dolomite %	-	6	-

The major elements present in the Bentonites were determined by X-ray Fluorescence analysis (XRF) and are shown in Table 2. The XRF gives a measure of the cations present but does not indicate where they reside in the Bentonite.

Table 2 X-ray fluorescence analysis data given as % by weight.

ANALYTE	Wy	SAB	CaB
Na <sub>2</sub> O	2.5	4.25	1.49
MgO	2.5	5.1	3.5
Al <sub>2</sub> O <sub>3</sub>	20.2	17.7	12.1
SiO <sub>2</sub>	62.4	50.8	53.2
Fe <sub>2</sub> O <sub>3</sub>	5.1	8.4	8.2
SO <sub>3</sub>	0.7	0.6	0.5
K <sub>2</sub> O	0.4	0.8	1.6
CaO	1.2	9.5	12.5
TiO <sub>2</sub>	0.2	0.9	0.8

Exchangeable interlayer cations associated with each of the clays can be determined using a method that displaces these cations from the clay using Benzyl triammonium chloride. The displaced exchangeable interlayer sodium, calcium and magnesium cations were determined with background corrections made for soluble non interlayer cations, results are given in Table 3.

Table 3 Exchangeable Interlayer cations associated with the Bentonites before and after flux experiments

Clay	Exchangeable cations milliequivalents/100g clay					
	SODIUM		CALCIUM		MAGNESIUM	
	Start	Finish	Start	Finish	Start	Finish
Wy	46	0	21	86	6	6
SAB	74	10	3	49	11	24
CaB	15	4	17	26	12	10

The particle size distributions were determined from Bentonites, dispersed under non forcing conditions by hand shaking with no dispersing aids, as 4% solids in deionised water. A Coulter LS 5250 laser light scattering apparatus was used and applying a Fraunhofer analysis the mean, median and % volume fractions <10% and <90% were determined, given in Table 4.

Table 4 Particle Size Distribution of Bentonites

Clay	Particle size in $\mu\text{m}$			
	Mean	Median	<10%	<90%
Wy	5.5	3.6	1.2	11.6
SAB	18.4	8.1	1.8	43.5
CaB	15.6	8.8	1.9	38

### 3 METHODS

The hydraulic barrier performance of the clays was determined using flexible wall triaxial permeameters (Trautwein Soil Testing Equipment) with 500ppm calcium solution (calcium nitrate) for hydration and permeation. Flux (volume of permeant passing a defined surface area in a given time) was measured using the starting conditions of ASTM 5887 but in order to ensure many pore volumes of permeant passed through the clays the hydraulic head was varied. The clays were contained between a woven and non-woven geotextiles such as those used in GCLs, these are porous and are not hydraulic barriers under the experimental conditions. The test pieces were 10.16cm in diameter containing clay with a dry mass per unit area of 4.4kg/m<sup>2</sup>.

The swell of the clays was measured without a confining force according to the swell index test ASTM 5890 using both de-ionised water and a 500ppm calcium solution. The swell induced in clay samples at 4.4kg clay/m<sup>2</sup> under a 20kPa confining force with a 500ppm calcium solutions was determined using a one dimensional consolidation apparatus (ELE oedometer). The concentration gradient was maintained essentially constant by replenishing the calcium solution every two or three days.

The fluid loss values were determined according ASTM 5891 Fluid loss of clay component of GCLs.

### 4 RESULTS

Fluid loss and swell index data are given in table 5 and flux data is given in table 6. The extent of one-dimensional swell against time is given in Figure 1.

Table 5 Fluid loss and index swell of CaB, SAB, Wy and WyP with De-ionised (DI) water and 500ppm calcium solution (Ca soln.)

CLAY	FILTRATE LOSS (mls.)		SWELL INDEX (mls.)	
	DI water	500ppm Ca soln.	DI water	500ppm Ca soln.
CaB	36	118	12	6
SAB	20.6	34	26	14
Wy	22	50	38	16
WyP	11.2	19.8	34	20

Table 6 Flux measured under different hydraulic head pressures (HH) also showing cumulative time of experiments

HH (m)	Cumulative Time (Days)				Flux (cm <sup>3</sup> .cm <sup>-2</sup> .s <sup>-1</sup> )			
	CaB	SAB	Wy	WyP	CaB	SAB	Wy	WyP
1.4	0.22	39.1	42	48.5	1.2x 10 <sup>-3</sup>	8.7x 10 <sup>-7</sup>	1.0x 10 <sup>-6</sup>	2.1x 10 <sup>-7</sup>
7		57.2	55.6			3.3x 10 <sup>-6</sup>	3.1x 10 <sup>-6</sup>	
7		60.1	73.5	67.2		1.8x 10 <sup>-5</sup>	3.9x 10 <sup>-6</sup>	5.1x 10 <sup>-7</sup>
14		60.5	169.6	179.8		3.3x 10 <sup>-5</sup>	5.1x 10 <sup>-6</sup>	6.9x 10 <sup>-7</sup>
21				222.8				1.2x 10 <sup>-6</sup>
21			282.1	261.4			4.9x 10 <sup>-6</sup>	3.1x 10 <sup>-6</sup>
28			319	466.2			4.6x 10 <sup>-6</sup>	2.9x 10 <sup>-6</sup>
21			327.2	593.9			3.7x 10 <sup>-6</sup>	2.2x 10 <sup>-6</sup>
14			335.7	602.9			2.7x 10 <sup>-6</sup>	1.7x 10 <sup>-6</sup>
7			342.4	623.5			1.5x 10 <sup>-6</sup>	9.9x 10 <sup>-7</sup>
1.4			412.8	637.2			4.6x 10 <sup>-7</sup>	2.9x 10 <sup>-7</sup>

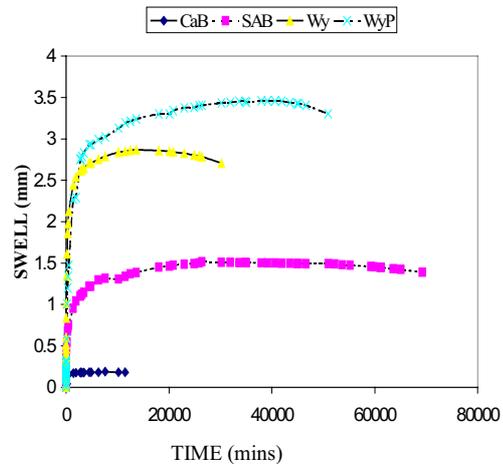


Figure 1 One-dimensional (oedometer) swell under a 20 kPa load

## 5 DISCUSSION

### 5.1 Evidence for cation exchange

The flux experiments demonstrate that those bentonites with sodium as the dominant interlayer cation experienced a change in their hydraulic barrier performance. The volume of permeant outflow versus time graphs for each of the sodium bentonites displayed a distinct increase in the rate of flow after several pore volumes of permeant had passed through the clay (Figure 2).

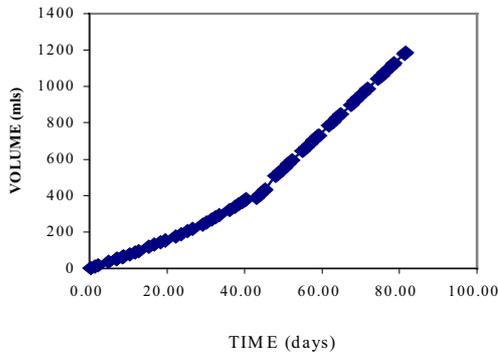


Figure 2 Cumulative volume of permeant passed through Wy under a 21m hydraulic head

These changes were not attributable to destruction of the Bentonite clay as XRD diffractograms after the flux experiments were the same as those obtained at the start except for changes which occur due to changing the exchangeable cation from sodium to calcium.

The flow of permeant through the calcium Bentonite (CaB) had to be terminated after a short period as the flux was too high, even under the least forcing ASTM 5887 conditions. It would in any case be unlikely that such an obvious change in flux would have been observed as this clay was initially predominantly in the calcium form.

When these changes in flow rate occurred there had been no disturbance of the experiments, no change in dielectric constant, pH, temperature or applied confining force. The flexible wall membrane precluded sidewall leakage and there were no observable faults or abnormalities noted in the test pieces on disassembling them. The change in flux was therefore interpreted as a direct result of interlayer cation exchange where calcium has replaced a large portion of the interlayer sodium cations. Analysis of exchangeable cations after the flux test is consistent with this conclusion.

With SAB the change in flow rate was observed after 7 pore volumes had passed, with Wy after 8.8 pore volumes and WyP after 10.3 pore volumes. Changes in flux were relatively discrete, occurring over a few days and the rate of flow of permeant moving from one steady state to a new higher steady state as also observed by Egloffstein (Egloffstein 2001).

### 5.2 Affect of cation exchange on clay and water structure

A probable explanation for the increase in flux induced by ion exchange is that the proportion of bulk, relatively mobile water in the pore volume of the clay body has increased and some pathways through the clay body have opened up.

Upon cation exchange where calcium displaces those sodium cations associated with the clay particles shrinkage in the volume the clay occurs. This phenomenon that can be readily observed on the macro scale and is illustrated in figure 1. where swell has passed through a maximum. The likely explanation for this behaviour is that as a result of calcium cations displacing sodium cations the immediate surface of the clay particles have been significantly changed and it is the nature of the surface of clay

particles that influences the structure sensitive properties of water. The surface structure of the clay affects the orientation of water molecules and these affects can extend to an appreciable distance from the clay surface >5nm (Low 1992). Thus this volume of clay surface orientated water can represent a large fraction of the pore volume and when highly structured the water molecules are of low mobility.

Calcium and multivalent exchangeable cations associated with the clay surface reduce the extent of the structured layer of water relative to sodium exchangeable cations. Thus the effective volume of hydrated low mobility cations close to the clay particle surface is less with bentonite in the calcium form than in the sodium form. Consequently that proportion of pore volume occupied by mobile bulk water must increase and this can be considered to mean that pathways capable of conducting water through the GCL have increased.

Calcium cations can also cause formation of quasicrystals (Kjellander 1988) where adjacent alumino - silicate layers are drawn together in close proximity to each other face to face. This can open up pores between clusters of clay layers through which water can flow and the close association of clay particles results in a reduction in swell observed. The limited ability to swell of Bentonites with calcium or magnesium as the predominant cations is illustrated by comparing the low swell index value in deionised water of CaB compared to Wy or which have a predominance of sodium exchangeable cations. When dominated by calcium exchangeable cations the clay particles are unable to dissociate significantly from each other leaving pathways through the body of clay through which water may pass relatively easily.

### 5.3 Clay factors affecting hydraulic flux

In these experiments cation exchange led to an increase by a factor of 5.5 in flux associated with SAB whereas the flux of the Wyoming bentonites increased by factors of 1.3 for Wy and 1.7 for WyP. Although WyP displayed a greater increase in flux than Wy it must be recalled that WyP had an initial flux value five times less than Wy thus in absolute terms WyP is a better hydraulic barrier material.

From the flux data in table 7 it is possible to give a ranking of the ability of the clays to maintain their hydraulic barrier performance when cation exchanged. From best to worst:

polymer fortified Wyoming (WyP) > Wyoming (Wy) >  
European sodium activated (SAB) > European calcium  
Bentonite (CAB)

The extent to which a pathway or channel through which permeant can flow will depend on the swelling ability, morphology, and particle size and percentage of clay component in Bentonite. Given that the clay content of the three sodium bentonites studied is very similar it is unlikely that the percentage of clay present is in this case a factor responsible for the differences seen between the flux behaviours. The ranking of hydraulic performance matches that predicted from the one-dimensional swell experiments, figure 1, where CaB barely became swollen and SAB was swollen to a considerably lesser extent than the two Wyoming Bentonite systems. This data also shows the swell of Wyoming clay is enhanced by the addition of polymer.

The particle size distributions given in table 5 for the three clay types, whilst must not be considered to be absolute values, does give an indication of the relative size of clay aggregates. Clearly the Wyoming bentonite is smaller than the two European clays.

The small particle size and ability to swell indicates the Wyoming bentonites have a greater likelihood of dissociating to individual alumino - silicate platelets or small groups of platelets than do the other two clays. Dissociated platelets under the applied consolidating force will be able to pack and organise in a

manner that will minimise the pore volume and this may account for their superior ability to resist the effects of cation exchange..

The calcium bentonite never established a good barrier with high flux and so the long term behaviour could not be assessed. The flux experiments of the other clays continued beyond the point where the flux increased to determine if further changes occurred. A plot of flux versus hydraulic head, figure 3, illustrates that when ion exchange has occurred there is an increase in flux shown by a vertical transition. The sodium activated clay once the cation exchange had occurred became far more permeable than the Wyoming based clays and this experiment had to be terminated as the outflow from the permeameter was too fast.

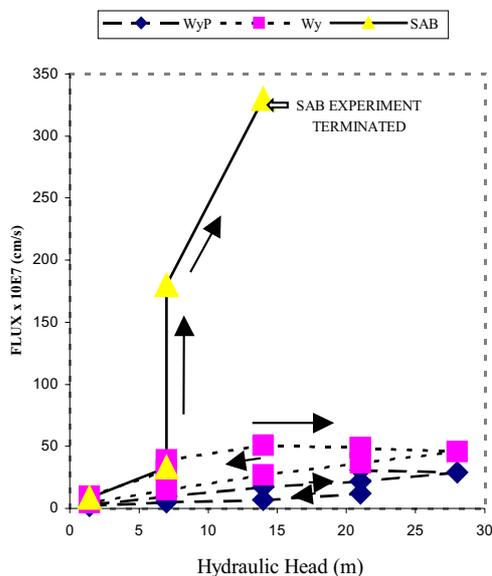


Figure 3 Flux of SAB, Wy and WyP as a function of Hydraulic head

The better performance of the polymer fortified Wyoming Bentonite over the straight Wyoming bentonite is illustrated more clearly in figure 4. Increasing the hydraulic head from 14 to 28 metres produced a slight reduction in flux for Wyoming (Wy) and similarly for polymer fortified Wyoming clay (WyP) going from 21 to 28 metres.

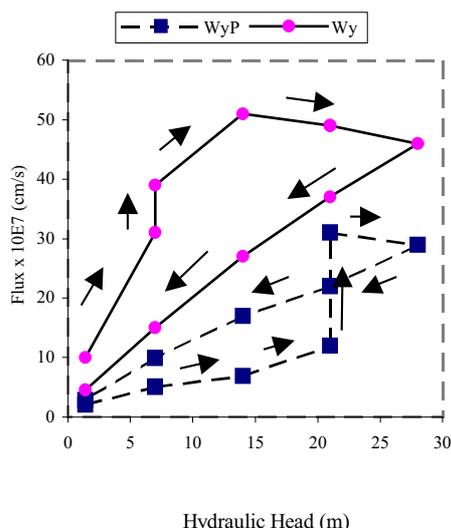


Figure 4 Flux of Wy and WyP as a function of Hydraulic head

These data are interpreted as being the result of clay being compressed under the high hydraulic head applied as this will act as an additional confining force in the vertical direction. The small clay particles that have more readily swollen and probably thereby dissociated can be orientated under a directional confin-

ing load becoming compressed compressed to minimise the inter and intraagglomerate pores as the confining load increases. Once cation exchanged to the calcium form however there is no internal force to increase these pore dimensions so they remain compressed even as the hydraulic head was reduced, incrementally, to the initial ASTM 5887 conditions. Indeed when the triaxial cell experimental conditions returned to the starting conditions the flux values are the same or slightly improved despite the clays now being in the calcium form.

#### 5.4 Correlation of flux behaviour to index tests

Other tests are frequently employed to evaluate clays for use in GCL's however it seems unlikely that these accurately measure the affect of cation exchange on hydraulic barrier performance and are at best index tests. The ASTM 5891 filtrate loss and ASTM 5890 swell index experiments are often used but these present the clay in a form not experienced in GCL's. The clay in practice in a GCL is not mechanically dispersed in a fluid as in ASTM 5891 nor is it able to keep taking in water as in ASTM 5890 as water uptake is proportional to confining pressure applied. ASTM 5890 using 500ppm calcium solution did correlate with the flux experiments in predicting the clay flux performance ranking. Whilst qualitatively correct this test however did not demonstrate the size of the difference in the initial flux measured nor the extent of change in flux following ion exchange. The clay was presented in the oedometer swell experiment in the same form as in the flux experiments and does seem to correlate quite well with the flux experiments.

## 6 CONCLUSIONS

Index tests are only capable of giving a broad indication of the ability of a clay to withstand cation exchange and retain a low permeability.

The Wyoming bentonite gives the best hydraulic barrier performance of the clays studied maintaining the lowest flux when subjected to ion exchange. The activated sodium clay does give good initial performance and is considerably better than the calcium bentonite that was a very poor hydraulic barrier.

The ability to generate a large swell against a confining load together with consisting of smaller sized aluminosilicate particles appear to be features of a smectic clay that help maintain a low flux even after cation exchange. Such features are displayed by Wyoming Bentonites but it is most probable that other morphological features not yet studied are also important in determining a clay's performance in GCLs.

## 7 REFERENCES

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