The influence of effective stress on the sorption characteristics of bentonite

L'influence du contrainte effective sur la caracteristiques sorption de bentonite

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ABSTRACT: A series of modified batch tests was carried out on slurry consolidated specimens of bentonite such that the bentonite was confined at a specific effective stress in each test. Zinc chloride solutions up to a concentration of 0.1M were employed and specimens were consolidated up to stresses of 800kPa. Solid:liquid ratios from 1:10 to 1:100 were investigated. The sorption of zinc by the clay was found to be significantly affected by applied effective stress level, and solid:liquid ratio, and was observed to vary by up to factors of 4 over the stress range investigated. The data indicates that several different competing mechanisms are active. A conceptual model of the clay – chemical interaction incorporating the influence of effective stress and soil/liquid ratio is presented and a discussion of the implications of the results in the context of other clay types is given.

RÉSUMÉ: Une série d'essais par lots modifiés a été effectuée sur les spécimens consolidés par boue du bentonite tels que le bentonite a été confiné à un contrainte effective spécifique dans chaque essai. Des solutions de chlorure de zinc jusqu'à une concentration de 0.1M ont été utilisées et des spécimens ont été consolidés jusqu' aux contrainte de 800kPa. Des taux de solid:liquid de 1:10 à 1:100 ont été étudiés. La sorption du zinc par l'argile s'est avérée pour être sensiblement affectée par le niveau appliqué de contrainte effective, et le taux de solid:liquid, et a été observée pour changer par jusqu' à des facteurs de 4 sur l'intervalle de contrainte étudié. Les données indiquent que plusieurs différents mécanismes de concurrence sont en activité. Un modèle conceptuel de l'argile - l'interaction chimique incorporant l'influence du contrainte effective et du taux de soil/liquid est présentée et une discussion des implications des résultats dans le contexte d'autres types d'argile est donnée.

1 INTRODUCTION

Bentonite clay is widely used in the construction of barriers for waste containment due to its low hydraulic conductivity and high cation exchange capacity. Sorption characteristics for geomaterials such as bentonite are typically obtained via batch tests. However the results from such tests are not directly applicable to field conditions because the original structure of the soil and the ambient physical and chemical conditions are not usually replicated accurately. This area has received limited attention. The current work seeks to address the influence of effective stress on sorption characteristics, through a laboratory study of the sorption of zinc by bentonite. Effective stress may influence sorption directly due to the applied mechanical load or indirectly through an alteration to the soil structure.

2 SORPTION PROCESSES IN BENTONITE

In a clay containing little organic matter or carbonate, the dominant sorption mechanisms for heavy metals will be ion exchange, and/or hydroxide precipitation (Yong *et al.* 1992). These mechanisms have been investigated by many researchers in the context of batch (and, to a lesser extent, column) tests. Significant work may also be found in the literature on the influence of pore fluid chemistry and effective stress on clay fabric.

2.1 *Ion exchange properties of clay*

The theory of ion exchange, and concepts of cation exchange capacity (CEC) and diffuse double layer have been extensively covered in the literature (*e.g.* Mitchell 1993). Discussion here will be limited to effects related to heavy metals and montmorillonite (the dominant component of bentonite). Typically, montmorillonites are flat plates. About 80% of their CEC is due to isomorphous substitution within the clay lattice. These exchange sites are found predominantly on the particle faces. The remaining 20% of sites are due to broken bonds on the particle edges, and may be influenced by changes in pH.

Since clay platelets will typically stack together to form tactoids or quasicrystals (Quirk & Aylmore, 1971) any consideration of ion exchange must consider three generic sites: edges, external faces, and interlayers.

Exchange reactions will be quite rapid at the tactoid surfaces or edges, but penetration into the interlayers may take hours or even days, unless significant swelling takes place. Where relatively large ions replace smaller ions (or vice versa), the layers must be moved apart to let the larger ions in or out. The replacement process becomes slower as exchange proceeds. Grim (1968) presents evidence that exchange reactions involving layer contraction may become inhibited; larger ions may become trapped in the centre of the interlayer as the smaller ions move in from the edges.

Studies on swelling of mixed ion Na^+, Ca^{2+} montmorillonite clays (McNeal 1970) indicated that at low ESP (exchangeable sodium percentage) values, the ions demix into separate Na- and Ca-domains and that the interlayer exchange complex is predominately Ca-saturated with Na^+ ions on external sites.

Shainberg *et al.* (1971) present evidence that a Ca-saturated montmorillonite consists of tactoids, within which several (4-9) clay platelets are in parallel array with interplatelet distances of 0.9nm. The interlayers may consist of 2 sheets of water coordinated with a single layer of non-hydrated cations. If a diffuse layer is present it acts on the outside of these tactoids only, and dominates the volume change behaviour of the clay. Tactoids may be broken down by increasing the ESP, while an increase of pressure may increase the number of platelets in a tactoid.

2.2 *Influence of the pore fluid chemistry*

The replacing power of cations is dependent on a number of factors. A high replacing power may be associated with a high concentration in the external solution (due to the law of mass action), a high valency and high ionic size, or low hydrated size (small ions tend to be more highly hydrated).

In the case of heavy metals, the issue of metal complexes (*e.g.* $ZnCl^+$ and $ZnOH^+$) becomes important. These complexes may participate in exchange reactions, potentially allowing exchange of the metal in excess of the CEC (when based on the divalent form). A number of authors, *e.g.* Bar-Tal *et al.* (1988), Ma & Uren (1998), Elgabaly & Jenny (1943) present evidence that for montmorillonite, $ZnOH^+$ has a higher affinity for the clay surface than Zn^{2+}. Ma & Uren (1998) and Elgabaly & Jenny (1943) state that montmorillonite preferentially exchanges $ZnOH^+$ over Zn^{2+}, K^+, Na^+ and Mg^{2+}, while other authors (see below) focus on precipitation as the mechanism of loss of zinc and hydroxyls from solution. The argument for preferential exchange derives from the significantly lower degree of hydration of the $ZnOH^+$ compared to the other cations present. In circumstances such as these, even if trace concentrations of $ZnOH^+$ are present in equilibrium with Zn^{2+} and other complexes, clays can remove significant quantities. Since the equilibrium is destroyed as the ion is sorbed, then more $ZnOH^+$ must form if equilibrium is to be maintained. However in all cases the sorption of the ion must be accompanied by a stoichometric release of another ion.

2.3 *Precipitation*

Farrah & Pickering (1976a, 1976b, 1976c, 1978) report that as the pH increases, the amount of heavy metal ion adsorbed by a clay increases. This is, in part, attributed to decreased competition from protons for adsorption sites, but also to precipitation of hydroxy species. The precipitation of the metal ions occurs at pH values which can be several units lower than those predicted from tabulated solubility product values. The implications are that hydroxyl concentrations near the clay surfaces are much higher than their bulk values, and that the sorption is not to do with ion exchange but that both zinc ions and hydroxl ions are sorbed by the clay surface. This interaction then yields a chemisorbed species which serves as a nucleus for further growth. Evidence for direct bonding rather than loose coprecipitation is that the zinc hydroxide was shown to be stable at high pH, when in the absence of clay it would be expected to dissolve. This process will not result in the appearance of exchanged ions.

2.4 *Influence of soil fabric and density*

Soil density has been observed to have significant influence on the sorption capacity of soils (*e.g.* Celorie *et al.* 1989, and Oscarson *et al.* 1994). Typically the denser the soil, the lower the sorption. This was attributed to small and occluded pores that restrict diffusion of the adsorbate.

This statement requires more detailed consideration in the context of soil fabric. Clay soils will possess a macro, meso and microfabric (Mitchell 1993). Excepting very large molecules, diffusion through macro and meso pores should be unrestricted. However at the microfabric level where the clay plates form aggregates or tactoids, then the interlayer void space may prove less accessible to smaller metal ions as discussed above.

Mitchell (1993) states that the chemical environment is critical during initial stages of fabric formation. After this, chemistry is less important and mechanical energy dominates. For example, as an initially flocculated but dispersed soil is consolidated, it is likely to become increasingly (irreversibly) aggregated with increasingly parallel orientation of the aggregates. As clay plates are brought together they overcome an energy barrier and form stable units. Unloading does not necessarily cause the plates to overcome that barrier in reverse.

The implications are that, at high stresses, the clay is likely to have an aggregated structure accompanied by possible demixing. In these circumstance small ions may not be able to fully access interlayers occupied by larger ions; this could, in effect, give rise to the reduced sorption observed due to reduced surface availability.

3 MATERIALS AND METHODS

The materials and methods employed have been described by Smith & Pearce (1999) and in more detail by Pearce (2000). A commercially available bentonite was investigated using batch tests based on those that might typically be conducted in industry. Thus the bentonite was not homoionised and the pH of the experiments was not directly controlled. The main aspects are summarized below.

3.1 *Soil properties*

The bentonite used in this study was imported from Colony, Wyoming and supplied by Redland Minerals, Milton Keynes, UK as a milled and air classified constant fine powder, with 85% by weight passing 75 microns. The bentonite consisted mainly of the clay mineral montmorillonite and the principal exchangeable ion was sodium. The liquid and plastic limits were 416% and 47% respectively in distilled water and the clay had a specific gravity of 2.58. The CEC of the clay was measured as 0.89 meq/g.

3.2 *Batch test characterisation*

Initial batch tests of 1:10 mixtures of bentonite and a range of zinc chloride solution concentrations were conducted. Samples of the fluid taken after 4 weeks were analysed by inductively coupled plasma atomic emission spectrometry. The results (previously reported in Smith & Pearce 1999) are replotted in Fig. 1 in terms of ionic fractions. The *y*-axis represents the ionic fraction of the Zn^{2+} cation in the adsorbed phase, Y_{Zn}:

$$Y_{Zn} = \text{amount of cation adsorbed (meq/g) / CEC (meq/g)} \qquad (1)$$

Also plotted on the *y*-axis is the ionic fraction Y_o of desorbed other ions.

3.3 *Oedometer and permeameter test apparatus*

Oedometers and flexible wall permeameter cells were employed to apply mechanical stress to the samples, and were modified to allow fluid circulation around the top and bottom of the samples. Assuming that the fluid external to the clay was in equilibrium with that internal to the clay, then circulation of fluid from a reservoir around the edges of the specimens allowed continuous monitoring of changes in the pore fluid concentration. The tests were intended to simulate conventional batch tests except that the clay samples were kept under a known stress state.

3.4 *Test methodology*

Samples of saturated and homogeneous bentonite were produced from a consolidated slurry of 1:10 bentonite powder to water or zinc chloride solution. These were matured for two days and then de-aired in a vacuum desiccator for several hours. The slurry was then poured into a 100 mm diameter consolidation pot, and consolidated under a load of 60 kPa. The expelled solution was retained and sampled to establish initial conditions.

Bentonite samples were extruded from the consolidation pot and trimmed to provide a sample of a suitable thickness, not more than 20 mm. The porous discs were saturated in the same concentration of fluid as that in the specimen. To maintain a bentonite to fluid ratio of 1:10 the moisture content of the sample was ascertained from the trimmings and the required volume of fluid was added to the reservoir. At a load of 60 kPa in the test apparatus, the sample should be in chemical equilibrium with the circulating solution, with no ion exchange occurring. In the oedometer, consolidation was monitored by measuring the specimen height using a LVDT. In the flexible wall permeameter apparatus, the expelled fluid that flowed into the reservoir was weighed periodically.

Samples were taken through a variety of test pathways (com-

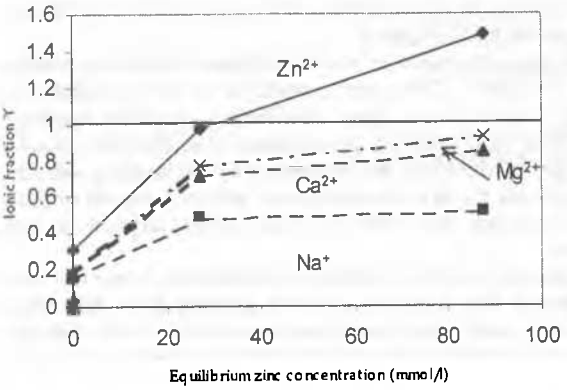

Figure 1. Ionic fraction of sorbed zinc and cumulative desorbed sodium. calcium ~~and magnesium plotted against equilibrium zinc~~ concentration for 1:10 batch tests. Zinc is assumed to be sorbed only as Zn^{2+}

bination of mechanical loading stages and changes in zinc chloride concentration in the reservoir). It is beyond the scope of this paper to discuss the details of all pathways. Results from the final stages of oedometer tests O1 to O3 and triaxial tests T1 to T3 are reported. In these stages the clay is initially at a confining stress of 800 kPa in equilibrium with a certain reservoir solution. The changes in equilibrium zinc concentration and zinc sorption were then monitored as the sample was first unloaded to 100kPa and then, in the ultimate stage, the pressure was fully released. At this point half the bentonite sample was placed in half the fluid from the reservoir to investigate the complete removal of mechanical stress on zinc sorption. Test T3 was designed to examine the influence of bentonite to fluid ratio (maintained at 1:30 rather than 1:10). In test O3 due to the nature of the test path, only the final 100kPa - 0kPa stage could be shown.

4 RESULTS AND DISCUSSION

Ca^{2+}

$Mg \rightarrow (Na^{+})$

4.1 *Initial batch tests*

It may be seen from the initial batch test results that initially almost all the zinc (~0.2 CEC) is adsorbed by the bentonite. Beyond that as more zinc is adsorbed more remains in solution. It is also seen that the quantity of adsorbed zinc exceeds the quantity of desorbed ions by about 25-50%. This may be attributed to adsorption of zinc complexes such as $ZnOH^+$ and/or precipitation particularly at the higher concentrations where the CEC is significantly exceeded. The pH values (see Table 1) are consistent with literature values for precipitation.

4.2 *Oedometer and triaxial test results*

The results of the oedometer and triaxial tests are presented in Fig. 2 in the form of adsorbed ionic fraction vs. concentration of zinc. The variation in starting position for each of the tests is a result of the individual test paths followed. Additional data on equilibrium pH and inferred interparticle spacing, *d*, is given in Table 1. Individual test results should lie on a straight line. Projection of this line onto the x axis gives the amount of zinc in the system (solid + liquid), per litre of liquid in the test. The slight deviation from a single straight line for some of the oedometer tests was due to leakage problems in the apparatus.

4.3 *Discussion*

It may be observed that some data points in tests T1 and T3 exceed twice the CEC implying that some precipitation must be occurring. It is reasonable therefore to propose that in all experiments a combination of ion exchange involving Zn^{2+} and $ZnOH^+$ (and possibly $ZnCl^+$) and precipitation is occurring. The relative proportions are difficult to determine, but based on concentration of other ions in solution, the changes in Zn concentrations far exceed the corresponding changes in competing ion concentrations, thus indicating both non stoichometric (precipitation) and stioichometric processes (ion exchange). In three of the tests path reversal is seen through 100kPa. It is reasonable to infer that there are at least two significant sorption processes, one being enhanced, the other diminished by increased stress. The effect of clay/solution ration can be clearly seen - the 30:1 test shows a roughly 3 fold greater change at each stage than any of the 1:10 tests. Three mechanisms are proposed to explain the results:

4.3.1 *Altered diffuse double layer equilibrium*

At high mechanical stress, it is reasonable to assume that the balance of exchange between sodium, calcium and zinc ions and associated complexes *e.g.* $ZnOH^+$ is altered in favour of exchanges resulting in volume contraction *i.e.* divalent over monovalent and smaller hydrated over larger hydrated, and therefore ions of larger ionic radius over smaller. It is expected that this would favour $Zn(OH)^+$ (ionic radius 0.21nm) over Na^+ (0.095nm) but Ca^{2+} (0.099nm) over Zn^{2+} (0.074nm). If $ZnOH^+$ exchange is preferred, as suggested by some authors, then this could lead to enhanced sorption at high stress, as seen in tests T2, O1 and O2 at 800kPa when compared to sorption at 100kPa. This mechanism would require a relatively large double layer. However, despite the small voids ratios of the samples, if an aggregated clay structure with approximately 6 plates / tactoid is assumed then, following the method of Shainberg *et al.* (1971), large double layer thicknesses on the outside faces of the tactoids are still indicated (Table 1).

4.3.2 *Modified Interlayer accessibility*

In circumstances where tactoids are formed in the absence of zinc *i.e.* where tactoid interlayers contain calcium, it may be difficult for smaller zinc ions to replace them. This will be particularly so at high stresses at which aggregation may be at a higher level, and the interlayers are more tightly compressed. At low stresses the interlayers will be more accessible and more able to open up, thus increasing the sorption capacity for zinc. This may in part explain why, in all tests, but in particular T2, O1, O2, and O3 there is more zinc sorption at zero stress than at 100kPa.

4.3.3 *Inhibited precipitation*

At high stresses, precipitation may initially fill unstressed voids. Further growth must push particles apart. According to Correns (1949), crystal growth pressure P_c can be expressed as a function of the degree of solution supersaturation (S), and the molar volume of the crystal (V) as follows:

$$P_c = \frac{RT}{V} \ln S \qquad (2)$$

where R is the gas constant and T the temperature (K). Reduced sorption at high stresses may thus be attributed to higher equilibrium concentrations in the pore fluid. It can be seen from Fig. 2 that even a 5% change in equilibrium solution concentration has a significant influence on the resulting sorption. Proceeding on the assumption that $Zn(OH)_2$ is being precipated (V = 32.6 cm^3/mol) and that the solution is saturated with respect to precipitation at 0kPa, a value of S =1.05 gives a crystal growth pressure of 3.6 MPa at 293K. This is reasonably close to the maximum effective stress applied in the experiments (0.8 MPa) particularly since the interparticle contact stresses may be higher than the effective stress. The presence of nucleation sites may also be influenced by the clay fabric and density, which, in turn, are controlled by the stress level. This would explain the bulk of the continued increase in sorption in tests T1 and T3, and part of the increased sorption in other tests as stresses are reduced.

In test T3, most of the additional sorption can only be attributed to precipitation. A larger reservoir means that pH will change more slowly as Zn^{2+} and OH^- ions precipitate out of solution and thus more precipitate can form before the system comes to equilibrium.

Table 1: pH and void ratios for batch, triaxial and oedometer tests. *d'* gives half spacing between tactoids assuming 6 plates/tactoid (Shainberg *et al.* 1971)

Test	Stage	pH	*e*	*d* (nm)	*d'* (N=6) (nm)
B1	0.001M	8.3			
	0.01M	6.8			
	0.05M	5.9			
	0.1M	5.7			
T1	800kPa	5.6	0.51*	0.26	-0.69
	100kPa	5.6	1.86	0.95	3.44
	reservoir	5.7			
T2	800kPa	5.6	1.58	0.81	2.58
	100kPa	6.0	1.63	0.83	2.74
	reservoir	5.8			
T3	800kPa	5.8	1.53	0.78	2.43
	100kPa	5.9	1.7	0.87	2.95
	reservoir	5.6			
O1	800kPa	5.3	1.37	0.70	1.94
	100kPa	5.5	1.76	0.90	3.14
	reservoir	5.6			
O2	800kPa	5.0	1.38	0.70	1.97
	100kPa	5.0	1.82	0.93	3.32
	reservoir	5.0			
O3	100kPa	5.6	2.06	1.05	4.05
	reservoir	5.3			

*This value appears anomalously low, though the authors could find no errors in its determination.

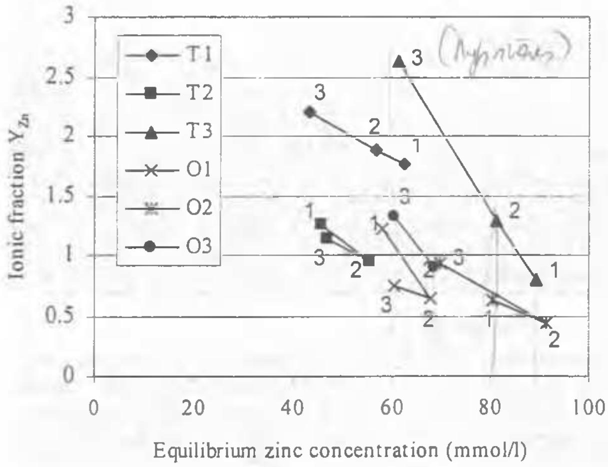

Figure 2. Triaxial test and oedometer test sorption data showing variation in sorption as stress is reduced from 800kPa (1) to 100kPa (2) and finally to zero (3).

4.4 *Applicability to other clays and heavy metals*

The double layer mechanism should be applicable to other common clay types, though it will clearly be influenced by CEC, type of exchange site, and relative hydrated sizes of the exchanging ions. Interlayer accessibility will be specific to smectites only, and will be dependent on the relative ionic sizes of the ions involved. The mechanism of inhibited precipitation may be expected to have general applicability; the precipitation process has be shown to be significant in illites and kaolinites (Farrah & Pickering 1976a, 1976b). Carbonate precipitation may also be important for other clays (Yong *et al.* 1992).

In general the concentrations used here were relatively high - however the results of Oscarson *et al.* (1994) do indicate that a density effects may also be observed at low (nM) concentrations.

5 CONCLUSIONS

The sorption of zinc by bentonite clay was found to be significantly affected by applied effective stress level and solid:liquid ratio. Sorption was observed to vary by up to factors of 4 over the stress range investigated.

The data indicates that several different competing mechanisms are active. Three mechanisms have been proposed involving: altered double layer equilibrium, modified interlayer accessibility and inhibited precipitation. The first two involve exchange reactions and are influenced by exchanging ion size. However only the first mechanism can lead to increased sorption at high stresses, the latter two will inhibit sorption at high stresses.

Depending on which mechanism dominates, it may therefore be expected that sorption isotherms gleaned from zero stress batch tests could significantly over or possibly under estimate the sorption characteristics of a soil possessing fabric and stress.

It must be emphasized that the proposed mechanisms are tentative at this stage. Work is in progress to apply detailed quantitative double layer and thermodynamic theory to the processes involved. Further experimental work is also warranted.

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