

Hydro-mechanical properties of Calcigel-polyacrylamide composites

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ABSTRACT: Calcigel bentonite-polyacrylamide (PAA) composites were investigated for their formation characteristics and their macroscopic hydro-mechanical and microscopic structural properties. The composites prepared were different in terms of the polymer charge, i.e. cationic (PAA⁺), anionic (PAA⁻), non-ionic (PAA⁰) and in terms of the polymer-to-clay ratio. The latter varied according to the individual maximum sorption capacity established from adsorption isotherms. Oedometer and water-retention tests were conducted on composites prepared under initial slurry conditions. The microstructure of the composites was investigated using environmental scanning electron microscopy (ESEM). At low stress, distinctly increased void ratios were found for all types of the composites, whereas under high-stress conditions only the PAA⁺-composite prepared at 100% of the maximum sorption capacity showed an increase in void ratio. Analyses by ESEM on this composite indicated structural changes related to the preferential face-to-face aggregation, which help to explain the macroscopic behaviour and also account for the increased hydraulic permeabilities observed.

KEYWORDS: adsorption isotherms, bentonite, clay-polymer composites, compressibility, soil water characteristic curve.

In recent years, research on clay-polymer composites has developed significantly. In various fields of research, i.e. polymer and colloid science, agriculture and, most recently, geotechnical and geoenvironmental engineering, several beneficial properties of composites have been demonstrated, e.g. enhanced safety and strength properties of the polymeric materials (e.g. Usuki *et al.*, 1995; Fu & Qutubuddin, 2001), stability against erosion of soils (e.g. Wallace & Wallace, 1986; Ben-Hur, 2006) and enhanced barrier performance of clay-based buffer materials (e.g. Razakamanantsoa *et al.*, 2012; Scalia *et al.*, 2014). The characteristics of the composites and composite formation differ significantly in the various research fields. In polymer science a very small amount of exfoliated clay layers are integrated into the polymer matrix, whereas in

agricultural treatment some small portion of the polymer is added to an existing soil structure. In contrast, colloid science usually examines aqueous suspensions with no existing predefined structure of the solids. Regardless of these differences and the varying demands on composite properties, in each case the surface interaction characteristics of the two components, clay and polymer, are the dominant factors controlling the formation and performance of the composite (Theng, 2012).

Research activities in geotechnical and geoenvironmental engineering have yielded several improvements in soil properties due to clay-polymer composite formation. One of the most promising studies to date focused on the modification of bentonite in order to stabilize its sealing capacity even when permeated with chemically aggressive electrolytes. An improvement in bentonite barrier performance caused by anionic polymers was described, e.g. by Di Emidio *et al.* (2011) and Scalia *et al.* (2014). On the other hand,

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failure and limitations in composite barrier performance have been demonstrated using commercial products with unknown composition and composite-formation characteristics (Ashmawy *et al.*, 2002). Similar inconsistencies in composite behaviour can be found in other geotechnical fields, such as soil conditioning in tunnelling (Zumsteg *et al.*, 2013) and expansive soil stabilization (Inyang *et al.*, 2007). The reasons why clay-polymer composites improve the engineering behaviour of soils are not yet understood fundamentally in terms of the mechanisms that determine their macroscopic performance.

In geotechnical engineering, soil behaviour is characterized and evaluated by its macroscopic properties. However, long experience has suggested that the macroscopic properties can be attributed to the microscopic soil characteristics, i.e. the soil structure, which in turn is determined by the external and inter-particle forces (Mitchell & Soga, 2005). In the case of clays with large specific surface areas, particle interaction in particular dominates the influence of gravity on the formation of soil microstructure and is therefore a key issue in understanding the engineering properties of clays. Several quantitative approaches have been used to explain the micro- and macroscopic coupling behaviour in clays, e.g. the cluster model (Olsen, 1960; Mesri & Olson, 1971) and clay aggregation in diffuse double-layer theory (Blackmore & Warkentin, 1960).

Research in colloid science has discovered several relationships between constitutive clay and polymer characteristics, e.g. clay mineralogy, polymer charge and molecular weight and their influence on composite formation, i.e. polymer adsorption on clay surfaces (e.g. Greenland, 1963; Espinasse & Siffert, 1979; Heller & Keren, 2003), as well as the resulting composite microstructure, i.e. clay-particle associations (e.g. Yu *et al.*, 2006; Palomino *et al.*, 2008). Note that these findings on the micro-scale characteristics of composites have rarely been transferred to fields of geotechnical engineering in order to account for the macroscopic behaviour of composites (e.g. McRory & Ashmawy, 2005; Inyang *et al.*, 2007). Furthermore, previous research focused on the characterization of macroscopic material properties with respect to special geotechnical applications, e.g. bentonite barriers and tunnelling, rather than on its fundamental hydro-mechanical behaviour. In the present study bentonite-polymer composites with systematically varied constitutive characteristics were investigated in terms of their macroscopic hydro-mechanical behaviour coupled to their microscopic structural and composite-formation characteristics.

BACKGROUND

Formation of clay-polymer composites

In this study the formation of clay-polymer composites was examined in aqueous suspensions as this condition is relevant to geotechnical and geo-environmental engineering. Surface interaction between clays and polymers is dominated by their electrostatic properties. For this reason, the formation of composites depends heavily on the charge characteristics of both the polymers (Espinasse & Siffert, 1979) and the clays, i.e. the mineralogy (Schamp & Huylebroeck, 1973; Inyang & Bae, 2005). Additional factors have been identified and characterized in previous studies, e.g. clay-particle size (Heller & Keren, 2003), polymer molecular weight, which accounts for the relevance of entropy effects in adsorption processes (Greenland, 1963), polymer geometry (Beall & Powell, 2011) and the environmental conditions during formation (Heller & Keren, 2003). Special attention has been paid to smectite minerals due to their extensive layer expansion during swelling; thus, leading to significant surface accessibility for polymer adsorption. X-ray diffraction (XRD) measurements by several authors have indicated that polymer chains even intercalate into the interlayer space of highly expandable Na-smectite (e.g. Greenland, 1963; Deng *et al.*, 2006). Similarly, polymers with ionic charge and polar characteristics have been investigated intensively for their adsorption properties rather than non-ionic and non-polar polymers, which are of greater interest in polymeric material science. In addition to clay-polymer interaction, the charge characteristics of polymers also determine polymer conformation. While intramolecular repulsion of identical ionic charges leads to stretched geometries for cationic and anionic polymers, non-ionic polymers can be described as 'randomly coiled' (Theng, 2012). The formation of composites, i.e. polymer adsorption on clay surfaces, can be characterized by several factors.

(1) Amount of polymer adsorbed via adsorption isotherms

According to Greenland (1963) the mass of non-ionic polar polyvinyl alcohols adsorbed on Na-saturated montmorillonite is almost three times greater than on the Ca-saturated version. The same author described decreases of ~85% in the adsorption in the presence of increased electrolyte concentration in solution compared to distilled water. Similar

findings have been demonstrated by Espinasse & Siffert (1979) on acetamide adsorption. The results indicate that surface accessibility plays an important role and this has been confirmed by the limiting effects of polymer geometry on adsorption (Beall & Powell, 2011). The adsorption isotherms of polyacrylamide polymers follow Langmuir-type adsorption (Schamp & Huylebroeck, 1973; Inyang & Bae, 2005). However, based on adsorption kinetics which indicates that practically no equilibration occurs at low polymer concentrations, it has been suggested that in this low polymer concentration region of the adsorption isotherm, adsorption may be better characterized as being of the “high-affinity” type (Cohen Stuart, 1991).

(2) *The type of bonding mechanisms between the clay and polymer during adsorption.*

Cation and anion exchange by the adsorption of ionic polymers on basal surfaces and clay edges, respectively, have been proposed as the dominant mechanisms (Theng, 2012). In addition, significant amounts of clay–polymer interaction with anionic polymers occur due to cation bridging, especially in terms of divalent exchangeable cations (Laird, 1997). This contributes extensively to our understanding of the microstructure of composites, such as clay-particle edge-to-face flocculation due to anionic polymers. In the non-ionic polar polymers, ion-dipole attraction between the polar parts of the polymer and the exchangeable ions on the clay surface, as well as hydrogen bonds to the hydration shell of ions, dominate clay–polymer interaction (Deng *et al.*, 2006). Similar interactions have also been observed for the polar parts of ionic polymers.

(3) *The conformation of polymers on clay surfaces*

The model of adsorption of non-ionic linear polymer in terms of trains (polymer segments adsorbed tightly to the clay surface), loops (polymer segments in solution bound to trains at both sides) and tails (polymer segments in solution bound to trains at one side) (Scheutjens & Fleer, 1980) is accepted widely. With increasing adsorption, the polymer conformation tends to enlarge loops and tails significantly. This behaviour is consistent with the concept of the preferential polymer conformation in solution, i.e. randomly coiled, as well as statistical considerations on segment adsorption in the near range of clay surfaces (Theng, 2012). In contrast, ionic polymers are supposed to stretch out,

even when adsorbed on clay surfaces. For this reason, cationic polymers tend to collapse completely on negatively charged basal surfaces, whereas anionic polymers develop long-range inter-particle bridging.

Micro- and macroscopic coupling in clays

The structure of soils includes the arrangement of particles, i.e. the fabric, as well as the particular bonding mechanisms between them (Mitchell & Soga, 2005). In clays, with inter-particle surface interaction playing a major role in particle arrangement, these properties of the soil structure cannot be separated easily. For this reason, the term ‘structure’ will be used throughout the present study when referring to clay microscale properties, defined as follows (van Olphen, 1991). Preferential face-to-face particle arrangements (FF-flocculation) are formed in aggregated clay structures; whereas edge-to-face and edge-to-edge particle arrangements, EF- and EE-flocculation, respectively, are formed in flocculated clay structures and dispersed and deflocculated clay structures consist of single-particle arrangements. Similar classifications can be found in Lambe (1960). In clay–water systems, the structure depends on the clay mineralogy as well on the environmental conditions. In addition, within the context of unsaturated clays, factors such as the compaction effort and water content have been identified (e.g. Delage *et al.*, 2006).

Clay-particle aggregation and flocculation are very important for micro- and macroscopic coupling in clays, due to the resulting inhomogeneities in the spatial distribution of particles, which yield a double-porosity structure consisting of intra- and inter-aggregate pores (Lloret *et al.*, 2003; Delage *et al.*, 2006; Thom *et al.* 2007). The influence of aggregation and flocculation on the macroscopic hydro-mechanical behaviour of clays has been studied extensively. In oedometric compression paths, aggregated clay structures maintain greater void ratios at the same vertical stress as that of dispersed clay structures (Burton *et al.*, 2014). Similar results have been obtained on flocculated and deflocculated structures (Sachen *et al.*, 2013). During swelling of expansive clays the aggregated clay structures exhibit greater volume change under load conditions and greater swelling pressures in the case of isochoric swelling conditions (Gens & Alonso, 1992; Baille *et al.*, 2010). In addition to alterations in volumetric behaviour, double-porosity structures result in an increased hydraulic permeability (Mesri & Olson, 1971). On this basis, Olsen (1960) proposed a modification on the Kozeny-Carman equation accounting for preferential fluid flow through ‘inter-cluster’ (i.e. inter-aggregate) voids and negligible

involvement of 'intra-cluster' (i.e. intra-aggregate) voids. Another quantitative approach to micro- and macroscopic coupling in clays was proposed by Blackmore & Warkentin (1960), in which aggregation of smectite layers was considered when calculating swelling pressures using diffuse-double layer theory. Note that the stacking of layers also refers to aggregated clay structure, i.e. FF-arrangement (van Olphen, 1991).

MATERIALS AND METHODS

Clay

The microstructural properties and the macroscopic hydro-mechanical behaviour of Calcigel bentonite (Süd Chemie, now Clariant, Bavaria, Germany), a smectite-rich clay, were investigated and compared to clay-polymer composites. The basic properties and soil-mechanical classification test results of Calcigel bentonite are summarized in Table 1.

Polymer

The polymer used was polyacrylamide (SNF Floerger, Andrézieux-Bouthéon, France), which is polar and non-ionic (PAA⁰), in a homopolymer form and cationic (PAA⁺) and anionic (PAA⁻) in a copolymer form. For cationic and anionic polymers the ionicity, i.e. the ratio of charged monomers in the polymer chain, amounts to 40%. The polymer structures are linear with molecular weights ranging from 7,500,000 (PAA⁺) to 16,000,000 (PAA⁻) g/mol.

Composites

In order to enable distinct interaction between clay surfaces and polymers, Calcigel-polyacrylamide composites were prepared by the solution-intercalation method. Detailed information about the preparation conditions is given below. The adsorption characteristics were analysed by the determination of adsorption isotherms. Thereafter, composites were prepared at the maximum adsorption capacity, q_{\max} (mg/g), detected for polymer adsorption as well as at 10% of q_{\max} . The soil-mechanical classification test results of composites are summarized in Table 1.

Adsorption isotherms

Polymer adsorption was performed in a constant laboratory environment under a controlled temperature of 20°C. The clay and polymer were suspended

separately in deionized water. After 2 h, the two suspensions were mixed and stirred at room temperature for 24 h as the adsorption process was almost completed within this period (Greenland, 1963; Schamp & Huylebroeck, 1973). For each test, the suspension strength (clay concentration) during adsorption was 100 g/L, which corresponds to a water content of $\sim 10\times$ the liquid limit. The polymer concentration was varied between 0.2–10 g/L (non-ionic PAA), 0.1–6 g/L (cationic PAA) and 0.05–0.5 g/L (anionic PAA). After adsorption, the clay-polymer suspensions were centrifuged at $4000\times g$ for 30 min. The supernatant was analysed for total organic carbon (TOC) to determine polymer concentration in solution after adsorption and the amount of polymer adsorbed on the sedimented clay.

For hydro-mechanical testing, pure clay and clay-polymer composites were prepared to initial slurry conditions that correspond to water contents of 1.1 times the liquid limit. In doing so, the initial specimen microstructures developed at approximately zero hydraulic and mechanical-loading conditions. Under these conditions it is assumed that the microstructure formation is most sensitive to particle-surface interactions and, thus, to small-scale alterations due to polymer adsorption.

Oedometer tests

Oedometer tests involved investigation of the samples in terms of their compressibility and hydraulic permeability. The initial samples were 70 mm in diameter and 19 mm in height. Vertical loads were applied including a loading path up to 800 kPa followed by an unloading path. Compression and decompression indices, C_c - and C_s - respectively, were determined along $e-\log(p')$ relationships, where e is the void ratio and p (kPa) is the applied pressure, the coefficients of consolidation, c_v (m²/s), were calculated according to the Casagrande $\log(t)$ -method for each stress increment along the loading path. Subsequently, hydraulic permeability, k (m/s), was computed from the corresponding value of c_v and the coefficient of volume compressibility, m_v (kPa⁻¹).

Soil water characteristic curve (SWCC) – first drying path

Clay and clay-polymer composites were investigated with respect to their water retention and volumetric behaviour at unconfined conditions along the first drying path. Application of suction to the samples was achieved using the osmotic method and

TABLE 1. Basic properties and soil mechanical classification test results of Calcigel bentonite and Calcigel-polyacrylamide composites.

Material	CEC (meq/100 g)	ρ_s (g/cm ³)	w_l (%)	w_p (%)	w_s (%)
Calcigel	65 (35 Ca ²⁺)	2.60	109.0	32.9	13.1
100% PAA ⁺			149.2	—*	16.1
10% PAA ⁺			139.0	33.6	14.0
100% PAA ⁻			170.7	37.9	11.9
10% PAA ⁻			138.2	30.4	12.4
100% PAA ^o			161.7	—*	10.9
10% PAA ^o			162.4	52.7	12.2

*determination failed, standard test method unsuitable.

the vapour equilibrium technique. The former method was applied in the low-suction range between 0.1 and 10 MPa using polyethylene glycol (PEG)-water mixtures of 20,000 g/mol molecular weight (mw.) of PEG. Suctions, which depended on the PEG concentration were calculated according to the relationship given by Tripathy & Rees (2013). Specimen conditions in the osmotic method as applied in this study were constrained to the saturated state, i.e. no air was allowed to enter the system. In the high-suction range, i.e. 20–360 MPa, the vapour equilibrium technique was adopted using saturated salt solutions. Details of both methods can be found in Delage *et al.* (1998). After equilibration of the specimens the water contents and, in the case of the vapour equilibrium technique, the volumes of the specimens were determined.

Volume measurement was conducted by fluid displacement using kerosene following the method of Péron *et al.* (2007). For the osmotic method, the volumes of specimens were calculated based on their saturated conditions.

Microstructure

The microstructures of pure clay and clay-polymer composites were investigated qualitatively using ESEM. Materials were placed in the microscope pressure chamber at initial slurry conditions and equilibrated subsequently at relative humidities of 90–95%, which correspond to suctions of ~7 MPa.

RESULTS AND DISCUSSION

Adsorption isotherms

The adsorption isotherms of PAA^o, PAA⁺ and PAA⁻ on Calcigel bentonite are given in Fig. 1. In accordance with previous findings (Schamp & Huylebroeck 1973), adsorption isotherms can be characterized as of Langmuir type following the equation:

$$q = \frac{K \cdot q_{\max} \cdot c_{\text{eq}}}{1 + K \cdot c_{\text{eq}}}$$

Where, q (mg/g) is the amount of polymer adsorbed per gram of bentonite; K (–) is the Langmuir sorption coefficient; q_{\max} (mg/g) is the maximum sorption capacity and c_{eq} (mg/L) is the equilibrium concentration of the polymer in solution. The parameters K and q_{\max} describing the adsorption isotherms of all three types of polymers on Calcigel bentonite are summarized in Table 2.

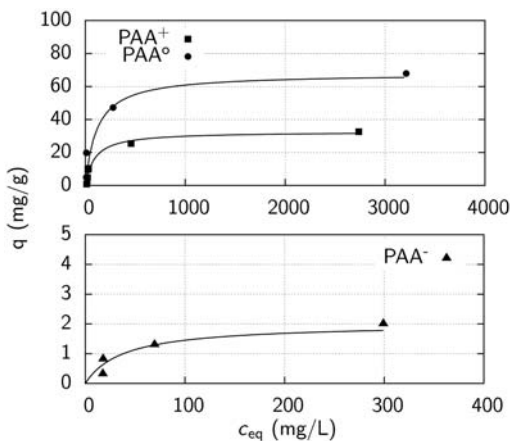


FIG. 1. Adsorption isotherms of polyacrylamides on Calcigel bentonite.

TABLE 2. Parameters of polymer adsorption according to Langmuir type.

Polymer	K (-)*	q_{\max} (mg/g)
PAA ⁺	0.011	32.6
PAA ⁻	0.026	2.0
PAA ^o	0.009	67.9

*(-) represents a dimensionless parameter.

The polymer charge has significant influence on the maximum sorption capacity. The largest degree of polymer adsorption was observed for PAA^o (67.9 mg/g), whereas the maximum sorption capacity of PAA⁺ amounts to approximately half as much (32.6 mg/g). This behaviour is in accordance with previous studies (e.g. Denoyel *et al.*, 1990) on the influence of polymer cationicity on adsorption characteristics and can be explained by the geometrical conformation of polymers in the adsorbed state. The randomly coiled PAA^o chains are adsorbed as large loops and tails, whereas the stretched geometries of PAA⁺ result in a large proportion of train segments, leading to reduced adsorbed volumes even if surface coverage of the clay surfaces is equal. Additional information can be obtained when taking into account the PAA⁺ ionicity in the results on maximum sorption capacity. The q_{\max} of 32.6 mg/g corresponds to 12.3 meq/100 g. As the CEC of Calcigel bentonite is 65 meq/100 g it can be concluded that the PAA⁺ chains do not intercalate completely into the clay layers replacing exchangeable cations. Therefore, on average, the inner surfaces of five stacked layers remain inaccessible for polymer adsorption; this is in agreement with previous studies that reported restricted access of polymers to the inner surfaces of smectites containing divalent exchangeable cations (e.g. Greenland, 1963).

In the case of PAA⁻, a maximum sorption capacity of 2.0 mg/g was detected, which is considerably lower than comparable values for PAA^o and PAA⁺. The results indicate that anion exchange and cation bridging are significantly less important than cation exchange. In addition, ion-dipole and hydrogen bonding to polar parts of the polymer (e.g. Deng *et al.*, 2006) are of minor significance for PAA⁺ and PAA⁻ compared to PAA^o.

Oedometer tests

The compression and decompression paths of pure Calcigel and the Calcigel-polyacrylamide composites

are shown in Fig. 2a–c. The void ratio is presented in terms of the clay structure only (e_{clay}), by considering the volume of polymer as voids between the clay platelets. In this manner, changes in clay-particle association as a consequence of composite formation can be identified directly. In accordance with their individual liquid limits and, thus, initial water content under slurry conditions in the low vertical stress range, the compression curves of the composites remain distinctly above that of Calcigel bentonite. With increasing stress the compression paths for composites

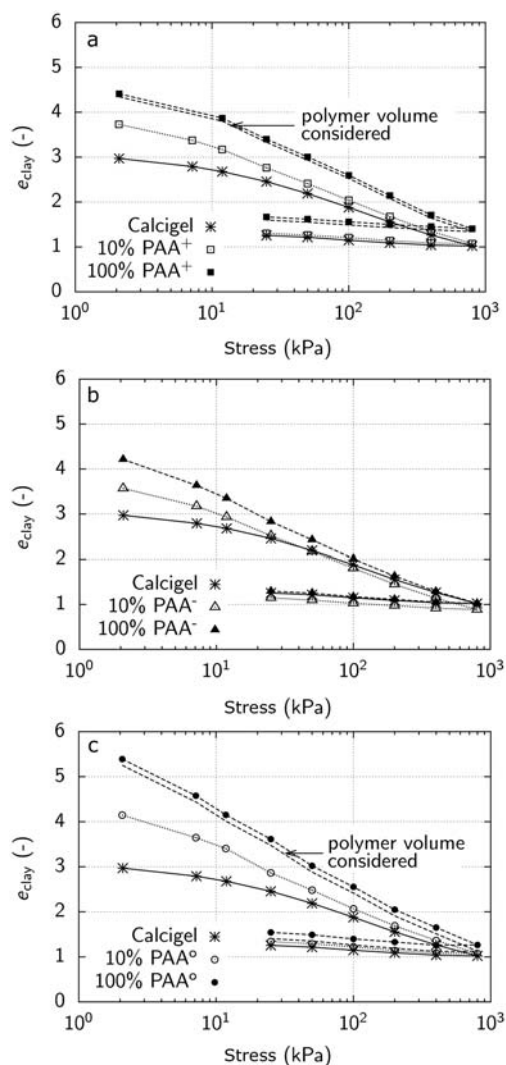


FIG. 2. Compressibility of Calcigel bentonite and: (a) Calcigel–PAA⁺ composites; (b) Calcigel–PAA⁻ composites; and (c) Calcigel–PAA^o composites.

and clays tend to become similar. Starting from vertical pressures of 200 kPa, the PAA⁺- and PAA^o-composites prepared at 10% of q_{max} and PAA⁻-composite prepared at 100% of q_{max} follow comparable compression paths, equal to that of pure Calcigel bentonite. On the other hand, the PAA⁺- and PAA^o-composites prepared at 100% q_{max} remain considerably above, while the PAA⁻-composite prepared at 10% of q_{max} even crosses the compression path of Calcigel bentonite and remains slightly below it. The differences observed in the case of the PAA⁺- and PAA^o-composites, i.e. the additional volume of the voids existing in the composite structures, cannot be attributed to the volume of polymer, which had been considered as voids in calculating the bentonite void ratio. This is illustrated by the lower dashed line in the $e \log(p')$ relationship (Fig. 2a,c), in which the additional volume of polymer is considered and subtracted from the pore volume. For PAA^o-composites this conclusion is valid, at least for vertical stresses of <800 kPa. Generally, it can be concluded that, due to composite formation, the clay structures underwent significant changes that were sensitive to an increase in stress level. The structural changes in PAA⁺- and PAA^o-composites prepared at 100% of q_{max} lead to increased global bentonite void ratios that persist even at high stresses.

The compression (C_c) and decompression (C_s) indices obtained by linearization of the $e \log(p')$ relationships between 25 and 800 kPa vertical stress are listed in Table 3.

For Calcigel bentonite the C_c value determined was 0.97, which is slightly below the range given by Mitchell & Soga (2005) for montmorillonite, i.e. 1–2.6. The difference can be attributed to the fact that Calcigel bentonite is not composed exclusively of montmorillonite and additional minerals exist in the

TABLE 3. Compression and decompression indices of Calcigel bentonite and Calcigel–polyacrylamide composites.

Material	C_c (-)	C_s (-)
Calcigel	0.97	0.17
100% PAA ⁺	1.33	0.15
10% PAA ⁺	1.14	0.16
100% PAA ⁻	1.22	0.19
10% PAA ⁻	1.10	0.18
100% PAA ^o	1.55	0.21
10% PAA ^o	1.20	0.19

clay mixture. Generally, the C_c values of pure Calcigel and composites prepared at 10% of q_{max} tend to increase with increasing liquid limit of the materials. In the composites prepared at 100% q_{max} , irregularities in this tendency may be observed with high C_c values obtained for the PAA^o-composite and low values

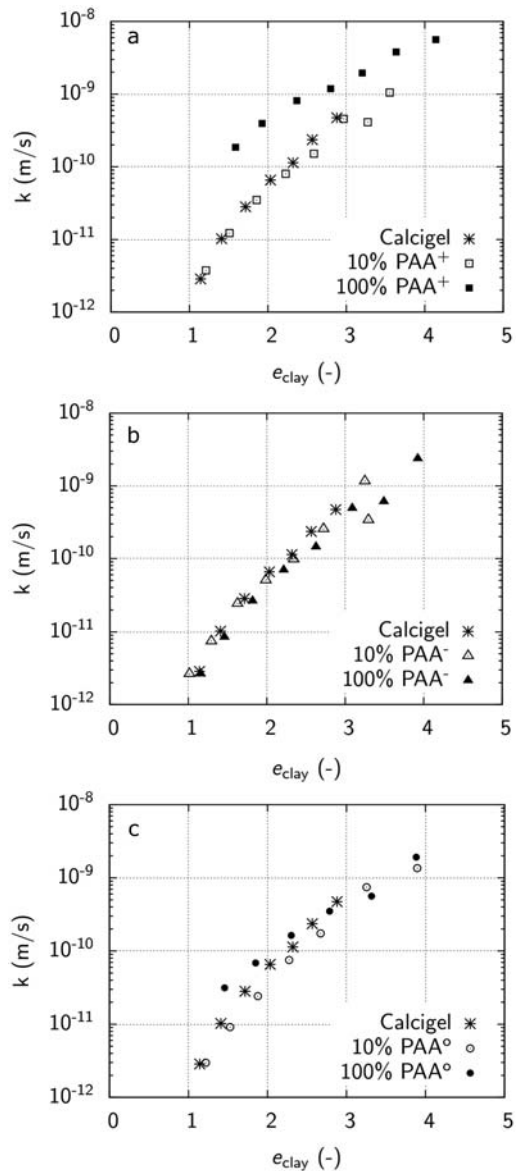


FIG. 3. Hydraulic permeability of Calcigel bentonite and: (a) Calcigel–PAA⁺ composites; (b) Calcigel–PAA⁻ composites and (c) Calcigel–PAA^o composites.

obtained for the PAA⁻-composite. The C_s values are consistently equal to 10–20% of the corresponding C_c values.

The relationship between hydraulic permeability and void ratio is shown in Fig. 3a–c. With decreasing void ratio the hydraulic permeability decreases exponentially in agreement with Baille *et al.* (2010). In general, composites prepared at 10% q_{max} exhibit similar behaviour to that of Calcigel bentonite, as do the PAA^{o-} and PAA⁻-composites prepared at 100% of q_{max} . In contrast, the hydraulic permeability calculated for the PAA⁺-composites prepared at 100% of q_{max} is distinctly higher than those of Calcigel bentonite by up to one order of magnitude along the whole range of void ratios tested. Taking into account the compression path, which remains above that of the Calcigel bentonite and the distinct increase in hydraulic permeability, the authors conclude that microstructural changes according to preferential face-to-face aggregation occurred as a consequence of PAA⁺ adsorption on the basal surfaces of clay particles. As a result, an increased amount of macropores developed leading to: (1) interferences in loading-induced particle rearrangement and (2) preferential fluid flow. In the PAA^{o-}-composites prepared at 100% of q_{max} , the hydraulic permeability did not change. This is attributed to the fact that particle aggregation is not the only mechanism controlling the behaviour in the compression path, which is similar to that of the PAA⁺-composites.

SWCC - first drying path

For the specimens equilibrated using the vapour equilibrium technique, the degree of saturation, $S_r (-)$, was calculated from experimental determination of the equilibrium water content and the corresponding volume of specimens. Calculations are based on adopted water densities, which depend on the clay-water content as proposed by Martin (1960). In the osmotic method, specimen drying was restricted to $S_r = 1$. Results are shown in Fig. 4a–c. The fitting curves follow the relationship given by Fredlund & Xing (1994):

$$S_r = C(s) \frac{1}{\left\{ \ln \left[\exp(1) + \left(\frac{s}{a} \right)^n \right] \right\}^m}$$

where $C(s)$ is a correction function assumed to be unity (Leong & Rahardjo, 1997); s (MPa) is the suction and n , m and a are fitting parameters. The SWCC drying curves of the composites are quite similar to that of pure Calcigel bentonite. Slight differences were

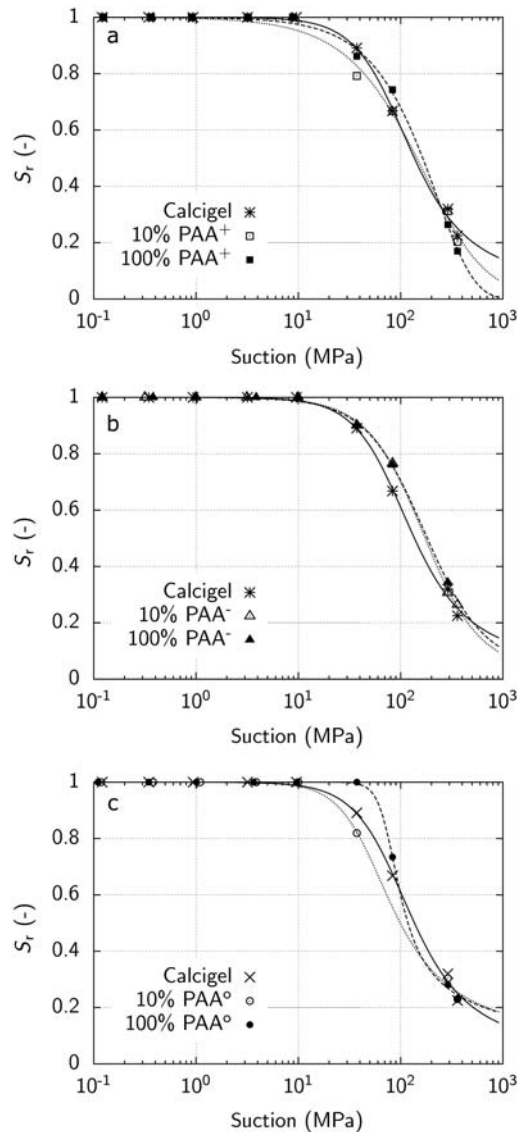


FIG. 4. SWCC – first drying path of Calcigel bentonite and: (a) Calcigel–PAA⁺ composites; (b) Calcigel–PAA⁻ composites and (c) Calcigel–PAA^o composites.

observed in the PAA^o-composites prepared at 100% of q_{max} , where desaturation initiates at greater suctions than for the Calcigel bentonite.

The volumetric behaviour of the materials tested after equilibrium was reached for each suction step is shown in Fig. 5a–c. Similar to the oedometer test results, the composites exhibit greater void ratios at low suctions with a tendency to approach the values of

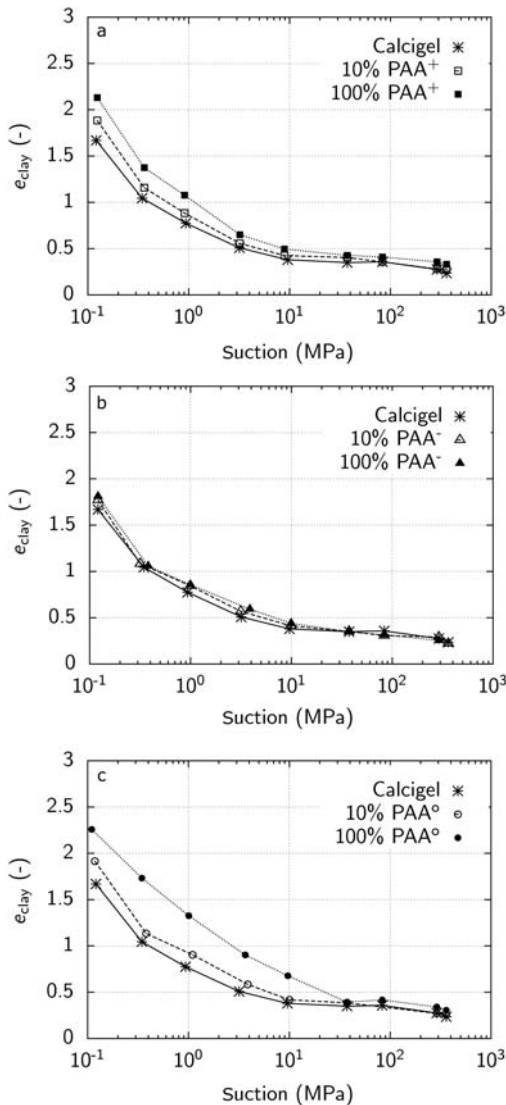


FIG. 5. Volumetric behaviour in the first drying path of Calcigel bentonite and: (a) Calcigel-PAA⁺ composites; (b) Calcigel-PAA⁻ composites; and (c) Calcigel-PAA⁰ composites.

Calcigel bentonite at increased suction. For the PAA⁺- and PAA⁰-composites prepared at 100% of the q_{max} , even in the high-suction range, the void ratios are greater than that of the Calcigel bentonite. This behaviour is in agreement with the bentonite void ratios determined at the shrinkage limit (Table 4), which are distinctly greater for both types of composites.

The SWCC, as well as the oedometer test results, suggest that the formation of the composites causes

TABLE 4. Void ratios e_{clay} and $e_{equivalent}$ of Calcigel bentonite and Calcigel-polyacrylamide composites at the shrinkage limit.

Material	e_{clay} (-)	$e_{equivalent}$ (-)
Calcigel	0.24	0.24
100% PAA ⁺	0.38	0.31
10% PAA ⁺	0.27	0.26
100% PAA ⁻	0.23	0.22
10% PAA ⁻	0.23	0.23
100% PAA ⁰	0.36	0.22
10% PAA ⁰	0.24	0.23

changes in the clay microstructure, which influence the macroscopic volumetric behaviour and are sensitive to the stress level, i.e. the mechanical stress in case of the oedometer tests and the hydraulic stress in the SWCC tests. At very low stresses, <100 kPa in the oedometer compression path, distinct void ratio increase is observed for all types of composites tested. It is assumed that in this condition, long-range inter-particle bridging plays an important role, which is in accordance with the lack of influence of polymer concentration on the macroscopic behaviour, e.g. 32.6 mg/g PAA⁺ vs. 2.0 mg/g PAA⁻, as well as with its sensitivity to the stress level. This assumption is also confirmed by the significantly increased liquid limit, even in the case of the PAA⁻-composites with small polymer-to-clay ratios. In order to obtain further information on the controlling mechanisms at high stresses, the residual structure in the drying process, i.e. the structure at shrinkage limit, might be analysed as follows. Table 4 summarizes the bentonite void ratios at the shrinkage limit obtained when: (1) the volume of polymer was added to voids in order to characterize only the clay-particle separation (e_{clay}); and (2) the volume of polymer was considered as an additional phase in order to account for its contribution to clay-particle separation ($e_{equivalent}$). For the PAA⁺-composite prepared at 100% of q_{max} the void ratio calculated according to the $e_{equivalent}$, remains above that of Calcigel bentonite. On the other hand, the $e_{equivalent}$ calculated in the case of the PAA⁰-composite prepared at 100% of q_{max} became equal to the Calcigel bentonite. Both composites exhibit distinctly increased void ratios in terms of e_{clay} . For this reason, it is concluded that in the case of the PAA⁰-composite the polymer volume only accounts for increased clay-particle separation, which confirms the oedometer test results on this composite at maximum mechanical stress of 800 kPa. In the case of

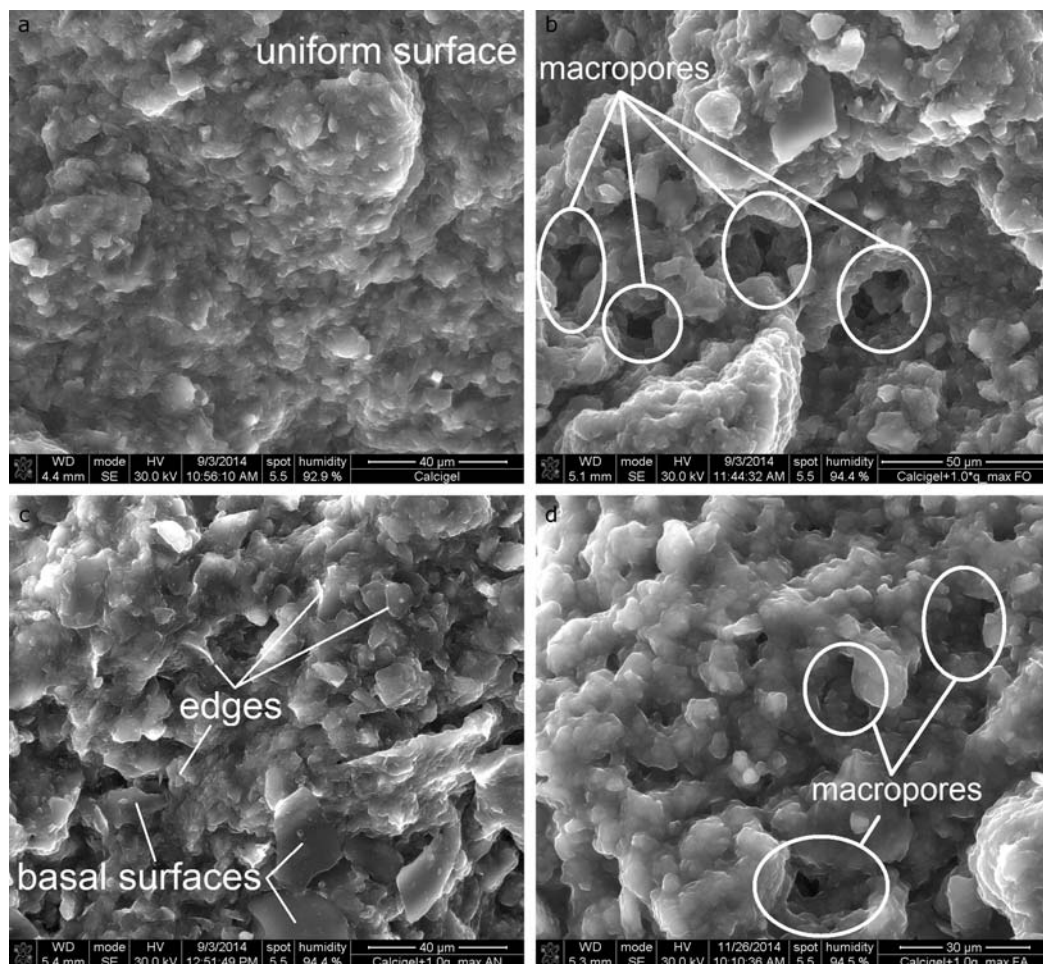


FIG. 6. ESEM images of: (a) Calcigel bentonite; (b) Calcigel-PAA⁺ composites; (c) Calcigel-PAA⁻ composites; and (d) Calcigel-PAA⁰ composites.

the PAA⁺-composite, additional changes in the clay structure occurred caused by clay-particle aggregation, as had already been indicated by the increase in hydraulic permeability.

Microstructure

Microscopic images of the Calcigel bentonite and Calcigel-polyacrylamide composites prepared at 100% of q_{\max} are shown in Fig. 6a–d. The clay structure in the PAA⁺-composite is affected by macropores that are tens of μm in size. In contrast, surface images obtained on Calcigel bentonite illustrate homogeneous distribution of particles and pores. This finding confirms the interpretation of macroscopic composite behaviour in

terms of clay-particle face-to-face aggregation due to PAA⁺ adsorption. The surfaces of the PAA⁻-composite were rough and angular as compared to the smooth surfaces of the Calcigel bentonite. In fact, clay particles with varying orientations were identified, indicating that clay particle EF and EE flocculation dominates the composite structure. Macroscopically, flocculation in the PAA⁻-composites is obvious only at low stresses of <100 kPa, i.e. caused by increased global void ratio. The flocculated structure is therefore assumed to be most sensitive to the application of stress and may be completely reorganized from a certain stress level upwards. This finding may also account for the reduced C_c value, which was determined at vertical stress of >25 kPa and by ignoring the composite

behaviour at vertical stresses of <25 kPa. The microscopic images of the PAA⁰-composite illustrate surface characteristics that are comparable with those of the PAA⁺-composites, i.e. macropores in the range of several tens of μm and preferential FF particle orientation. At high mechanical and suction stresses it was calculated that increased global void ratios could be attributed to polymer volume only. For this reason, aggregated structures as observed microscopically at ~ 7 MPa suction, are obviously sensitive to the stress level. With reference to the macroscopic behaviour of the PAA⁰-composites prepared at 100% of q_{max} (i.e. hydraulic permeability equal to that of Calcigel bentonite and increase in air entry value), clay-particle aggregation is not the mechanism that controls the macroscopic behaviour of the composite.

SUMMARY AND CONCLUSIONS

Calcigel bentonite and Calcigel-polyacrylamide composites were investigated experimentally for their adsorption characteristics and hydro-mechanical and microscopic structural properties. Polymer charge and mass were varied systematically. The latter was adjusted considering the maximum sorption capacity established by means of adsorption isotherms. The behaviour of the material was investigated following a mechanical loading and unloading path up to 800 kPa at oedometer conditions. In addition, hydraulic loading at unconfined conditions was conducted up to 360 MPa. Microstructural material properties were determined using ESEM. The results can be summarized as follows:

(1) Adsorption isotherms are of Langmuir type with increasing maximum sorption capacity in the following order PAA⁰ > PAA⁺ >> PAA⁻. The maximum polymer masses adsorbed indicate that clay layers were not intercalated completely by the polymer chains.

(2) At low stresses the global void ratio, e_{clays} was increased significantly due to composite formation. As this behaviour was observed even at low polymer concentrations and was independent of the polymer charge it is concluded that long-range inter-particle bridging is important in clay-structure formation at low stresses. This conclusion also accounts for the distinctly increased values of the liquid limit.

(3) With increasing stress the composites prepared at low polymer concentration approach the void ratio-stress relationship of pure Calcigel bentonite, whereas the PAA⁺- and PAA⁰-composites prepared at 100% of q_{max} remain above this relationship. At the shrinkage

limit, i.e. at structures resulting from the greatest suction stress conditions, as well as at maximum mechanical stress, only the PAA⁺-composite retains an increase in the global void ratio, which cannot be attributed to the polymer volume only. Therefore, structural changes due to long-range inter-particle bridging in the low-stress range are highly sensitive to the stress level.

(4) Hydraulic permeabilities determined from oedometer time-compression curves are equal to that of Calcigel bentonite, except for the PAA⁺-composites prepared at 100% of q_{max} . The latter exhibits permeability values approximately one order of magnitude greater than that of Calcigel bentonite and the remaining composites.

(5) Microscopic investigations conducted at 7 MPa revealed that changes in clay structure occur due to the formation of composite – FF aggregates in the case of the PAA⁻- and PAA⁰-composites and EF and EE flocculation in the case of the PAA⁻-composite. In contrast, the structure of the Calcigel bentonite was homogenous, i.e. deflocculated and dispersed.

(6) The microscopic and macroscopic properties of the PAA⁺-composite prepared at 100% q_{max} were consistent, i.e. the volumetric properties even at high stresses and the hydraulic permeability increased due to clay particle aggregation. On the other hand, the PAA⁰-composite prepared at 100% q_{max} also exhibited aggregated structures, which did not influence the hydraulic permeability and had limited influence on the volumetric properties up to a certain stress level. Therefore, the microscopic observations do not account for the governing mechanism of the coupling between microscopic and macroscopic properties. Clay-particle flocculation due to PAA⁻-composite formation was most sensitive to the stress level. Macroscopically, composite behaviour was approximately equal to that of Calcigel bentonite at high stresses.

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