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Influence of layer charge and charge distribution of smectites on the flow behaviour and swelling of bentonites

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Abstract

The influence of layer charge and charge distribution of dioctahedral smectites on the rheological and swelling properties of bentonites is examined. Layer charge and charge distribution were determined by XRD using the LayerCharge program [Christidis, G.E., Eberl, D.D., 2003. Determination of layer charge characteristics of smectites. Clays Clay Miner. 51, 644–655.]. The rheological properties were determined, after sodium exchange using the optimum amount of Na_2CO_3, from free swelling tests. Rheological properties were determined using 6.42% suspensions according to industrial practice. In smectites with layer charges of -0.425 to -0.470 per half formula unit (phfu), layer charge is inversely correlated with free swelling, viscosity, gel strength, yield strength and thixotropic behaviour. In these smectites, the rheological properties are directly associated with the proportion of low charge layers. By contrast, in low charge and high charge smectites there is no systematic relation between layer charge or the proportion of low charge layers and rheological properties. However, low charge smectites yield more viscous suspensions and swell more than high charge smectites. The rheological properties of bentonites also are affected by the proportion of tetrahedral charge (i.e. beidellitic charge), by the existence of fine-grained minerals having clay size, such as opal-CT and to a lesser degree by the ionic strength and the pH of the suspension. A new method for classification of smectites according to the layer charge based on the XRD characteristics of smecites is proposed, that also is consistent with variations in rheological properties. In this classification scheme the term smectites with intermediate layer charge is proposed.
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Keywords: Smectite; Rheological properties; Layer charge; Low charge layers; Flocculation; Intermediate charge smectites

1. Introduction

Bentonites are used in the drilling industry for their unique colloidal properties, namely swelling and rheology (Güven, 1992). These properties stem from the structural and crystal characteristics of smectite, which include very small particle size and correspondingly high specific surface area, and layer charge which is associated with cation exchange capacity (Odom, 1984; Laird, 1999). Due to the aforementioned characteristics, smectite crystals display a rather complex rheological behaviour when dispersed in an aqueous medium. When present in low concentrations they form suspensions with Newtonian properties (Rand et al., 1980; Kasperski et al., 1986; Brandenburg and Lagaly, 1988; Chen et al., 1990), attributed to hydrodynamic forces, whereas when their concentration increases interactions between the particles induce a non-Newtonian behaviour (Goodeve, 1939; Gillespie, 1960).

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The rheology of a colloidal suspension consisting of uncharged particles normally is controlled by Brownian forces, which resist other forces that may modify its structure and dynamics, and by hydrodynamic forces (Güven, 1992). However, in bentonite suspensions the charge of smectite crystallites enhances the viscosity of the suspension due to the repulsive forces of the electroviscous effect (Adachi et al., 1998). The rheological properties are affected further by attractive forces, which lead to flocculation. The rate of flocculation is determined by energy minima described by the classical DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), although recently certain deviations from the classical DLVO theory have been observed and modified versions of the DLVO theory have been proposed (Israelachvili and McGuiggan, 1988; van Oss et al., 1990; Missana and Adell, 2000; Duran et al., 2000). These deviations are attributed to hydration forces (Israelachvili and McGuiggan, 1988). van Oss et al. (1990) defined these additional forces as polar AB (acid-base) interactions, which include hydrogen bonding on clay surfaces.

So far most studies have focused on the influence of particle concentration and size, type of exchangeable cation, pH, temperature and concentration of electrolytes on the rheological properties of smectites, which include viscosity, thixotropic behaviour, yield stress and shear modulus (van Olphen, 1959; Callaghan and Ottewill, 1974; Rand et al., 1980; Heath and Tadros, 1983; Brandenburg and Lagaly, 1988; Chen et al., 1990; De Kretser et al., 1998; Benna et al., 1999; Abend and Lagaly, 2000; Duran et al., 2000; Tombacz and Szekeres, 2004 among many others). All these studies attempt to explain the rheological properties in terms of the classical DLVO theory and its modifications, and in terms of the type of particle interaction, i.e., face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE). Possible modifications in the chemical composition, and therefore in the structure of smectite also may be important to rheology, as was found during Mg-leaching, especially at higher electrolyte concentrations (Chen et al., 1990).

Due to its direct influence on the electroviscous effect and the thickness of quasicrystals, layer charge is expected to affect the rheological properties of smectites. The same is true for charge heterogeneity, which includes the aspects of charge magnitude (i.e. low or high charge smectites) and charge localization (i.e. octahedral vs tetrahedral) as well as the possibility of order or disorder in Mg-distribution, which influences octahedral charge (Muller et al., 1997). The importance of charge localization on the surface potential of smectite has been modelled by Bleam (1990), who found that the surface potential curves of beidellite show considerably more pronounced maxima and minima compared to montmorillonite. Nevertheless, the influence of layer charge magnitude and heterogeneity on the rheological properties of smectites (and hence bentonites) essentially has not been examined. Brandenburg and Lagaly (1988) observed different rheological behaviour in suspensions of Wyoming (low charge) and Cameron (high charge) smectites, having similar particle size and clay concentration in suspension, but their study focused on the Wyoming montmorillonite. Recently Tombacz and Szekeres (2004) considered charge heterogeneity of montmorillonite in terms of negatively charged surfaces and positively charged edges. In this contribution we present the first report on the influence of layer charge and charge heterogeneity of smectites on the rheological properties of bentonites, and discuss additionally the influence of tetrahedral charge.

2. Materials and methods

Twenty four bentonite samples were used in the present study (Table 1). The materials come from bentonite deposits on Milos, and on the Kimolos Islands, Greece and from, Turkey and the CMS repository. The Miloan bentonites were provided by S&B Industrial Minerals (SB samples), whereas the bentonites from the Kimolos Island and Turkey are from the bentonite collection of G.E. Christidis (GEC samples). The layer charge and charge heterogeneity of the smectites were determined according to the method described by Christidis and Eberl (2003). Briefly, less than 2 μm fractions of the bentonites were separated by settling, saturated twice with K and dried on Si-wafers to make oriented clay mounts. The clay fractions were dried in air and then saturated in ethylene glycol vapour at 60 °C for 16 h. The ethylene glycol solvated clay fractions were examined by X-ray diffraction with a Siemens D500 XRD, using CuKα radiation (40 kV, 30 mA), a graphite monochromator and a step size of 0.02 degrees two theta, with 4 s count time per step. The layer charge and charge distribution of the smectites were determined using the LayerCharge program (Eberl and Christidis, 2002). The LayerCharge program have been described in detail by Christidis and Eberl (2003). The layer charge distribution is presented in terms of proportion of low charge, intermediate charge and high charge layers. Inasmuch as the rheological properties of the bentonite suspensions are dictated only by smectite, it was necessary to determine the smectite content of the bentonites. This was done by means of two methods: by PVP adsorption (Blum and Eberl, 2004) and by random powder XRD using the RockJock computer code. The Rockjock has been tested successfully in an international quantitative analysis competition, and in artificial mixtures it generally gives results that are within 1–2% of actual values (Eberl, 2004). The program compares integrated XRD intensities for minerals present in the sample with that of an internal sample (zincite), and weight percents are calculated from previously measured mineral intensity ratios (Eberl, 2004).

Table 1
Origin, smectite content determined from RockJock, layer charge and charge distribution of the smectites present in the bentonites used in this study

Sample	Origin	Smectite content	Layer charge	Proportion of 17 Å layers	Proportion of 13.5 Å layers	Proportion of 9.98 Å layers
SB2	S&B Industrial Minerals	56	0.43	0.6	0.2	0.2
SB3	S&B Industrial Minerals	86	0.45	0.4	0.25	0.35
SB4	S&B Industrial Minerals	66	0.47	0.35	0.20	0.45
SB5	S&B Industrial Minerals	86	0.59	0.20	0.20	0.60
SB9	S&B Industrial Minerals	75	0.43	0.75	0.10	0.15
SB10	S&B Industrial Minerals	63	0.49	0.30	0.45	0.25
SB12	S&B Industrial Minerals	84	0.45	0.40	0.30	0.30
SB14	S&B Industrial Minerals	80	0.45	0.40	0.25	0.35
SB17	S&B Industrial Minerals	87	0.61	0.20	0.25	0.55
SB18	S&B Industrial Minerals	87	0.43	0.70	0.10	0.20
GEC1	G.E. Christidis	n.d.	0.55	0.10	0.50	0.40
GEC2	G.E. Christidis	70	0.43	0.65	0.10	0.25
GEC3	G.E. Christidis	51	0.40	0.95	0	0.05
GEC4	G.E. Christidis	38	0.41	0.85	0	0.15
K–Y	G.E. Christidis	43	0.42	0.75	0.1	0.15
K–G	G.E. Christidis	55	0.46	0.40	0.20	0.40
K–W	G.E. Christidis	86	0.47	0.30	0.20	0.50
Turkey	G.E. Christidis	80	0.45	0.40	0.30	0.30
SWy-1*	CMS repository	88	0.36	1.00	0	0
Hectorite*	CMS repository	89	0.41	0.90	0.05	0.05
Belle Fourche*	D.D. Eberl	87	0.40	0.85	0.15	0
Kinney*	D.D. Eberl	96	0.49	0.20	0.45	0.35
SAz-1*	CMS repository	88	0.55	0.10	0.50	0.40
Otay*	CMS repository	94	0.60	0.05	0.40	0.55

*Data from Christidis and Eberl (2003). Samples GEC3 and GEC4 (Rema and Garyfalakena deposits, Milos respectively), contain beidellite (Christidis and Dunham, 1997) n.d. = not determined.

The two methods yield comparable results. In order to calibrate the two techniques at low smectite contents, we used a volcanic glass, which displayed incipient alteration to smectite. For most samples the RockJock program gave smectite contents, which are greater by 7% compared to the PVP results. However, for some bentonites containing smectites with layer charge >0.425 (high charge smectites according to Newman and Brown, 1987) the PVP technique yielded considerably lower smectite contents compared to RockJock, due to inadequate dispersion of smectite flakes in PVP suspensions. The non-smectitic fraction in these samples is small in general, suggesting that the RockJock results are reliable. Although the PVP technique yielded comparable results for most of the bentonites for consistency we used the smectite contents determined by RockJock.

Free swelling indices of the bentonites were determined according to Christidis and Scott (1996). The samples were treated (activated) with 1, 2, 3, 4, 5 and 6 wt.% Na_2CO_3 and then 1 g of clay was added in 10 ml volumetric cylinders. The concentration of Na_2CO_3, which caused maximum free swelling volume in bentonites, considered to be the optimum concentration, was then used to determine the free swelling index and to serve as a guide for determination of the rheological properties. The free swelling index obtained was converted to volume of gel per 10 g of bentonite. The swelling index provides a direct indication of bentonite quality, i.e. the anticipated performance in industrial applications, and an indirect indication of the bentonite grade (Inglethorpe et al., 1993; Christidis and Scott, 1996). This is because smectite is the only swelling mineral in bentonites, since vermiculite either is absent or, more rarely, is present in trace amounts. The rheological properties of the bentonites were determined in all samples except for sample CEC 1 with a Fann 35 S, Couette-type viscometer at 20 ± 1 °C. The viscometer operates at six

different speeds, from 3 to 600 rpm yielding shear rates 5.1–1021 s^{-1}. The materials were dried at 105 °C, and ground to pass through a 75-μm sieve. The suspensions were prepared according to the specifications of the American Petroleum Institute (API 13A, 1993) by adding 6.42% of ground bentonite and the optimum amount of Na$_2$CO$_3$ in distilled water. The concentration of Na$_2$CO$_3$ in the suspensions varied from 0.006 M to 0.03 M (6–30 mmol dm^{-3}) according to the amount of Na$_2$CO$_3$ added (Table 2). The suspensions were stirred for 20 min and then aged for 16 h. Therefore the bentonites used for rheological tests were Na-saturated. The properties determined were apparent viscosity (shear stress/ shear rate ratio at shear rate 1021 s^{-1}) plastic viscosity (the slope of the flow curve), yield stress and 10 min gel strength (stress applied to break the bentonite gel after 10 min rest). For all samples we constructed complete flow curves (rheograms) and thixotropic loops. The thixotropic behaviour of the bentonites was evaluated from the area of the thixotropic loops. Since all bentonites contain a wide range of impurities according to the XRD (3–50% wt.%) the rheological properties determined were recalculated to 100% smectite content considering that the other minerals present in the bentonites (quartz, opal-CT, feldspars, carbonates, kaolinite, Ti- and Fe-oxides and gypsum) do not contribute to the rheological and swelling properties of bentonite suspensions. Although this assumption is valid it does not take into account the fact that

Table 2

Free swelling indices and concentration of of Na$_2$CO$_3$ in the suspensions of the bentonites studied

Sample	Concentration of Na$_2$CO$_3$ in suspension (mmol dm^{-3})	Swelling index
SB 2	18	181 [3]
SB 3	30	171 [5]
SB 4	18	129 [3]
SB 5	30	126 [5]
SB 9	24	173 [4]
SB 10	30	150 [5]
SB 12	24	184 [4]
SB 14	24	187 [4]
SB 17	30	116 [5]
SB 18	24	211 [4]
GEC 1	24	134 [4]
GEC 2	24	191 [4]
GEC 3	18	257 [3]
GEC 4	18	215 [3]
K–Y	30	215 [5]
K–G	24	165 [4]
K–W	18	150 [3]
Turkey	24	139 [4]
SAz-1	30	111 [5]
Hectorite	6	209 [1]
Swy-1	6	205 [1]
Kinney	30	121 [5]
Belle Fourche	6	191 [1]
Otay	24	98 [4]

Values in brackets indicate the concentration of Na$_2$CO$_3$ (wt.%) which yielded maximum swelling volume.
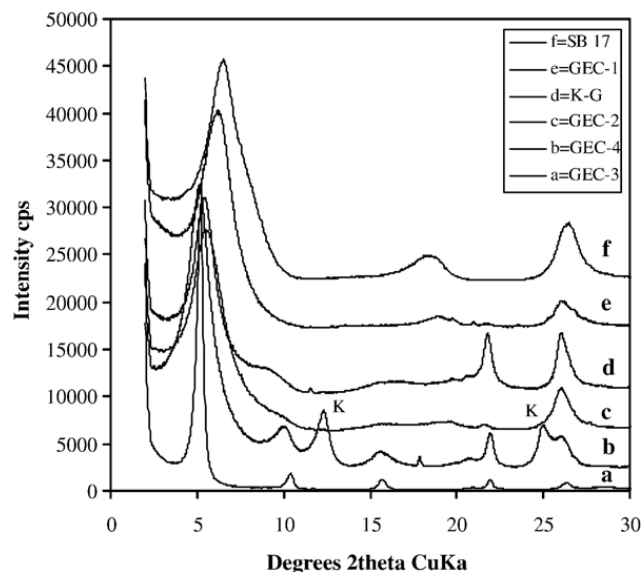

Fig. 1. Representative XRD traces of oriented clay fractions of the bentonites studied. K = kaolinite.

clay size minerals such as opal-CT, quartz and/or kaolinite often abundant in bentonites, may disrupt the network of smectite particles and affect viscosity, when present in close association with smectite (see Discussion section below). Finally the pH of the suspensions was measured with an Inolab pH electrode. The pH of the bentonite suspensions varied between 7.6 and 8.9. Except for samples GEC3 and GEC4, which yielded pH 7.6 and 7.7 respectively, the pH of the remaining samples varied between narrow limits (8.3–8.9).

The significance of the linear regressions, which were observed between the rheological properties and/or between the rheological and swelling properties and layer charge, was tested with ANOVA using a 5% level of significance ($\alpha = 0.05$). It will be shown that in all cases the *F* test values fall well in the critical region indicating that the linear equations, which fit to the data, are true models of the regressions.

3. Results

3.1. Layer charge characteristics of the smectites

Representative XRD traces of the clay fractions of the K-saturated samples are shown in Fig. 1. The XRD profiles of the various smectites vary between broad limits, reflecting the different layer charge and charge distribution (Table 1). Characterization of the smectites according to their XRD traces follows Christidis and Eberl (2003). According to this scheme, typical low charge smectites (group 1a smectites) with layer charge lower than −0.425 per half formula unit (phfu), are characterized by first order reflection between 16.6 and 17.1 Å, and well defined rational higher order basal reflections (Fig. 1a–b). They contain a large fraction of
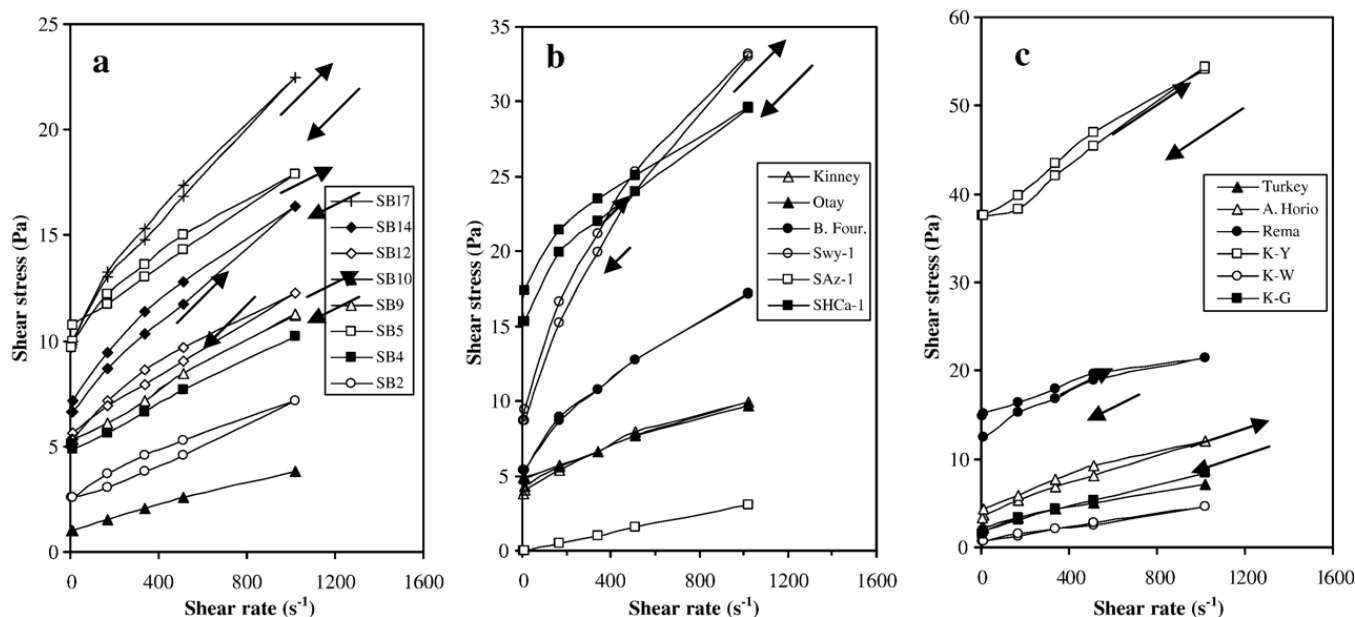
Fig. 2. Flow curves with an increased (upward) and then decreasing (downward) shear rate indicated by the arrows.

low charge fully swelling (17 Å) layers and (with K saturation) a small fraction of non-swelling (10 Å) layers. The non-swelling layers are not true illite layers because they swell when saturated with a cation with high hydration energy such as Na, Ca and Mg (Christidis and Eberl, 2003). High charge smectites (group 2 smectites) have first order reflections between 15.5 Å and 13.5 Å, a 003 reflection at 4.65–4.70 Å which tails off with a shoulder at the low angle side (Fig. 1e–f) and layer charge greater than −0.470 phfu. They contain a

small fraction of low charge fully swelling (17 Å) layers and large fractions of partially- and non-swelling (13.5 Å and 10 Å respectively) layers. Finally smectites with layer charge between −0.425 and −0.470 phfu (group 1b smectites) have first order reflection between 16.6 Å and 16.0 Å, and irrational higher order basal reflections (Fig. 1c, d). They are characterized by a more even distribution of the three types of layers (Table 1), although a bimodal distribution (usually of fully and non-swelling layers) also is possible. It should be noted that so far high
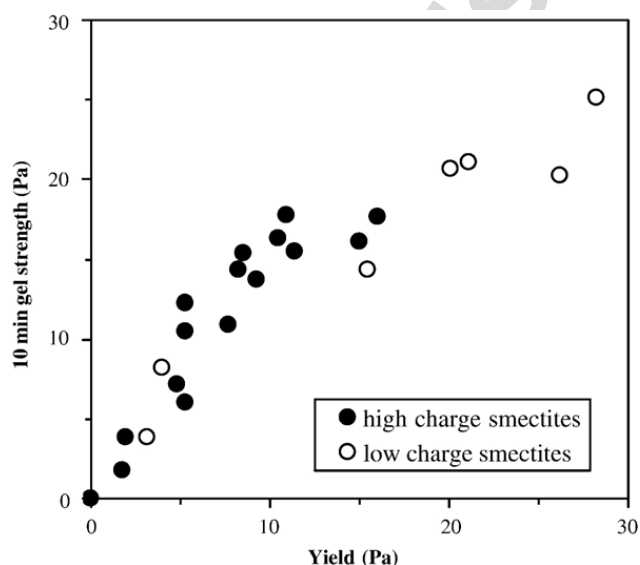

Fig. 3. Variation of the 10-min gel strength relative to yield in the bentonites studied.
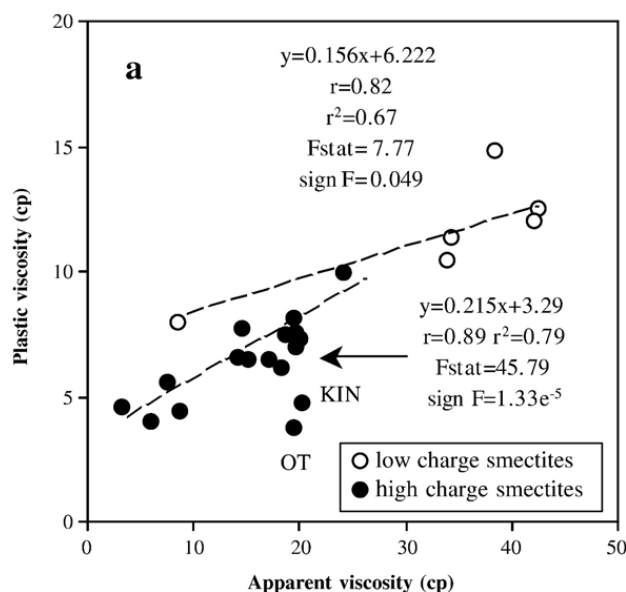

Fig. 4. Variation of the rheological properties of the bentonites studied. KIN = Kinney bentonite, OT = Otay bentonite. ANOVA was performed using a 5% level of significance ($\alpha = 0.05$).
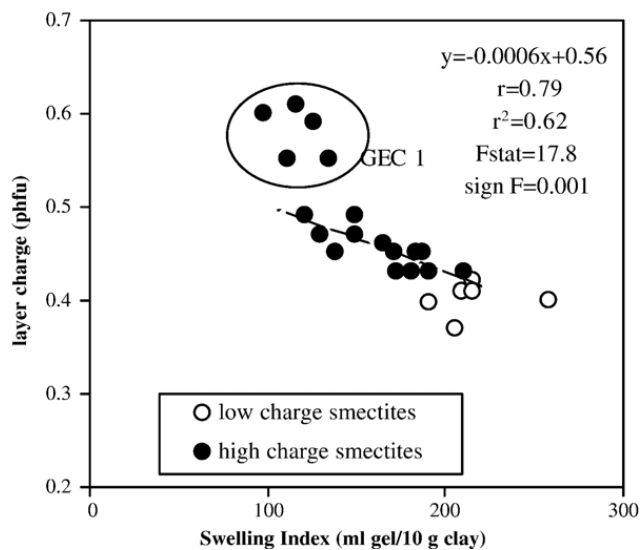
Fig. 5. Variation of the free swelling index of bentonites with layer charge of smectites. The encircled points belong to high charge smectites, with layer charge > -0.50 phfu which do not follow the overall trend of the high charge smectites. ANOVA was performed using a 5% level of significance ($\alpha = 0.05$).

charge smectites are considered those with layer charge greater than -0.425 phfu (Newman and Brown, 1987) and this characterization was followed in this study as well. However the XRD data (Fig. 1) and the results from the rheological and swelling properties (see below) will show that this classification scheme is not adequate.

3.2. Free swelling

The free swelling indices of the bentonites are shown in Table 2. The values in brackets indicate the amount (wt.%) of Na_2CO_3 added to obtain maximum swelling volumes. This amount of Na_2CO_3 depends on the abundance of smectite in the bentonite and the layer charge of smectite. Most smectite-rich SB samples, the Kimolian bentonites (K–G, K–W, K–Y) and the Turkish bentonite developed maximum free swelling after addition of 4–5% Na_2CO_3, suggesting that the smectites present are Ca-rich. The same is observed with the SAz-1, Otay and Kinney bentonites, which contain high charge smectites. By contrast SWy-1, Belle Fourche and SHCa-1 bentonites, which have smectite contents comparable to the previous materials, developed maximum free swelling volume after addition of 1–2% Na_2CO_3,
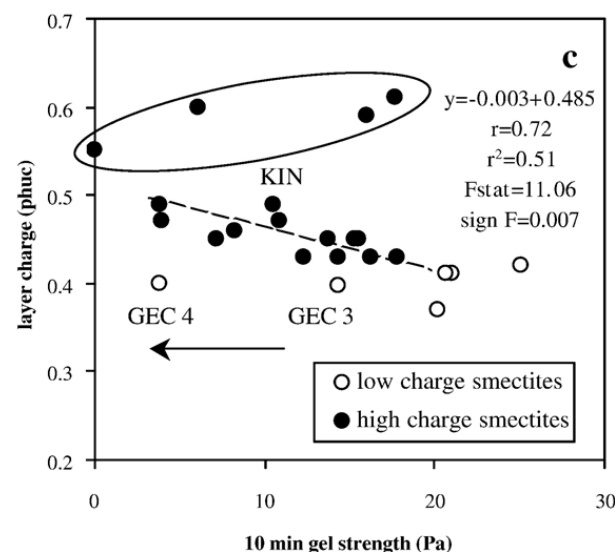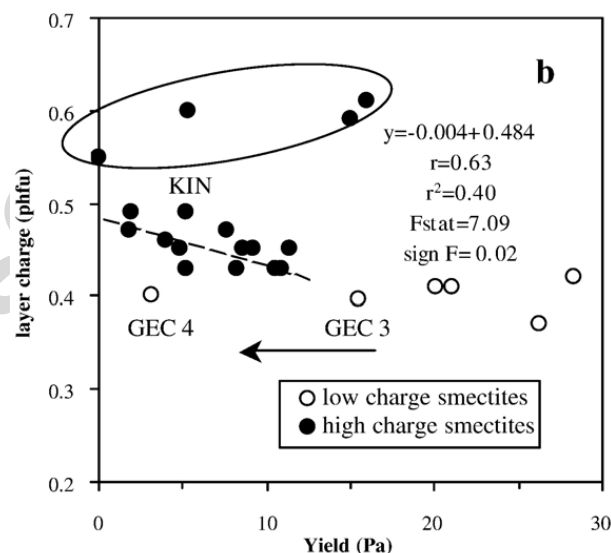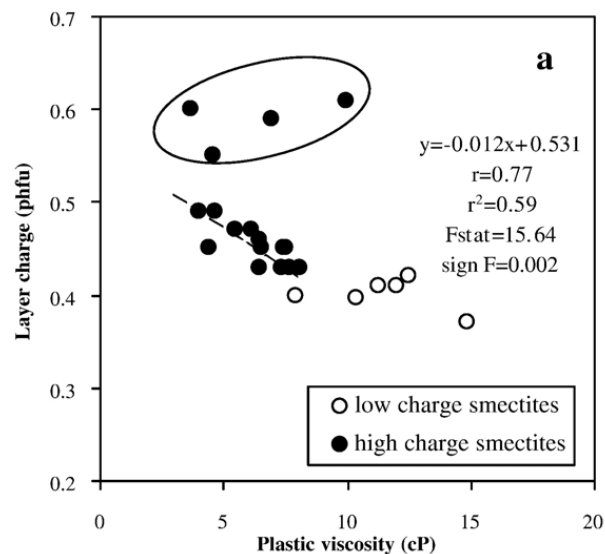

Fig. 6. Variation of the rheological properties of bentonites with layer charge of smectites. High charge smectites with layer charge > -0.50 phfu, which do not follow the overall trend of the high charge smectites are encircled. KIN = Kinney smectite. ANOVA was performed using a 5% level of significance ($\alpha = 0.05$).

suggesting that these smectites are Na-rich and have lower layer charge. In general, the low charge smectites develop greater free swelling volumes than high charge

smectites and require less Na_2CO_3 to develop maximum free swelling volume than high charge smectites. The influence of the magnitude of layer charge on the amount of Na_2CO_3 added could be observed by comparison of samples SB17 and SB18, which have similar smectite contents. Thus SB18 (low charge) required 4% Na_2CO_3, whereas SB17 (high charge) required 5% Na_2CO_3.

3.3. Rheological properties

The flow diagrams of the bentonites are shown in Fig. 2. Three types of flow diagrams can be distinguished. Diagrams, which are typical for Newtonian flow (e.g. SAz-1), diagrams, which indicate ideal (Bingham) plastic flow (e.g. SB4, SB9, SB10, K–G, K–W, Turkey, Kinney, Otay) and flow diagrams, which indicate plastic flow described by the Herschel–Bulkley equation (Lucklam and Rosi, 1999) (e.g. Belle Fourche, SWy-1, SHCa-1, K–Y, SB2, SB14, SB17). Bentonites showing a Bingham behaviour have a yield stress < 5 Pa. The flow diagrams, indicative of plastic flow, have yield stress because of the formation of links between the aggregated smectite particles (elastic flocs), which thus form a network in the bentonite supension (Firth and Hunter, 1976a,b).

Several of the bentonites display flow diagrams with thixotropic loops (Fig. 2). Also the gel strength is clearly related to yield stress (Fig. 3) suggesting that the network of particles formed when the suspension is at rest is related to the network of particles when the suspension is under shearing strength. Although the thixotropic behaviour is attributed to the aggregation of smectite particles which form a network, and thus it might be expected to be related to the plastic flow behaviour, several bentonite suspensions displaying plastic flow with significant gel strength are not thixotropic. This behaviour tends to be characteristic mainly for bentonites containing high charge smectites (Otay, SAz-1, Kinney, several Miloan bentonites). However there are exceptions to this tendency. Thus, Belle Fourche bentonite containing low charge smectite is not thixotropic, whereas SB5 and SB17, containing high charge smectite are slightly thixotropic (Fig. 2). An attempt to correlate the area of the thixotropic loops, which is proportional to the extent of thixotropy, with yield stress or gel strength yielded weak positive relationships with considerable

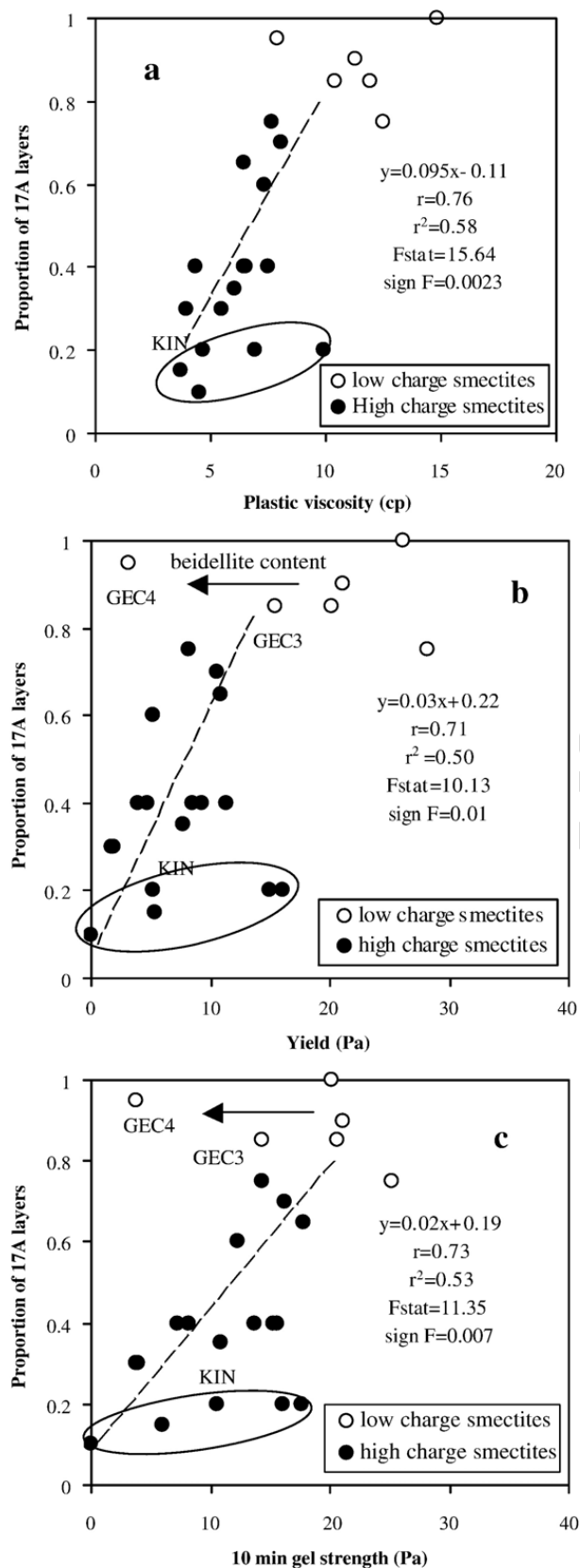Fig. 7. Variation of the rheological properties of bentonites with the proportion of the low charge layers of smectites. The arrows indicate the influence of the beidellitic layers. High charge smectites with layer charge > −0.50, phfu which do not follow the overall trend of the high charge smectites are encircled. KIN = Kinney smectite. ANOVA was performed using a 5% level of significance ($\alpha = 0.05$).

scattering (data not shown). This may be explained by considering that thixotropic behaviour is attributed to the aggregation of already flocculated smectite particles in the secondary energy minimum (Barnes, 1997), whereas yield strength may be related to the aggregation of particles and the formation of an open network in the primary energy minimum.

The rheological properties are interrelated. This is evident for plastic and apparent viscosity (Fig. 4), viscosity and gel strength and viscosity and yield strength (data not shown). This is expected because the network of smectite particles formed in thick suspensions modifies the flow properties of water due to particle-interactions and increases viscosity. However, in most cases a dual rather than a single trend is observed, because the high charge smectites and the low charge smectites follow different trends. In Fig. 4 the points deviating from the observed trend for the high charge smectites belong to the Otay and Kinney bentonites. Both smectites have almost entirely octahedral charge. Suspensions of low charge smectites develop in general greater viscosity and gel strength than suspensions of high charge smectites (Fig. 4).

3.4. Correlation between layer charge and swelling and rheological properties

The correlation between the layer charge of smectites and free swelling index and the rheological properties (plastic viscosity, yield strength and gel strength) is shown in Figs. 5 and 6. Swelling index displays a clear negative relationship with layer charge ($r = -0.79$) in smectites with layer charge between -0.425 and -0.490 (Fig. 5). A breaking point is observed at a layer charge -0.500 phfu because smectites with greater layer charge, although in general follow the same relationship, deviate from the overall trend. The rheological properties show less well-defined patterns (Fig. 6). They are inversely correlated with layer charge only for smectites having layer charge between -0.425 and -0.470 phfu (mainly group 1b smectites and lower limit of group 2 smectites according to Christidis and Eberl, 2003). Such a trend is not observed either in low charge smectites or the high charge smectites with layer charge greater than -0.500 phfu, which display extensive variation in rheological properties over a rather limited variation of layer charge. In the low charge smectites the existence of abundant beidellitic layers in samples GEC3 and GEC4 (Christidis and Dunham, 1997) shifts rheological properties to lower values (arrows in Fig. 6).

A similar correlation is observed between the proportion of low charge layers of smectites (fully expandable 17 Å layers) and the rheological properties of bentonites (Fig. 7). Thus plastic viscosity, gel strength and yield stress of the bentonites increase with the proportion of the low charge layers. However, the observed correlation holds for the smectites having layer charge between -0.425 and -0.470 phfu, whereas the low charge smectites and high charge smectites with layer charge greater than -0.470 phfu (encircled points in Fig. 7) deviate from the overall trends. Similar to the total layer charge (Fig. 6) the rheological properties of the low charge layers deteriorate with an increase in the beidellitic component (arrows in Fig. 7). A similar relationship is observed between the free swelling index and the proportion of low charge layers in smectites (Fig. 8a). The difference between the index and the rheological properties is that both the low charge and the
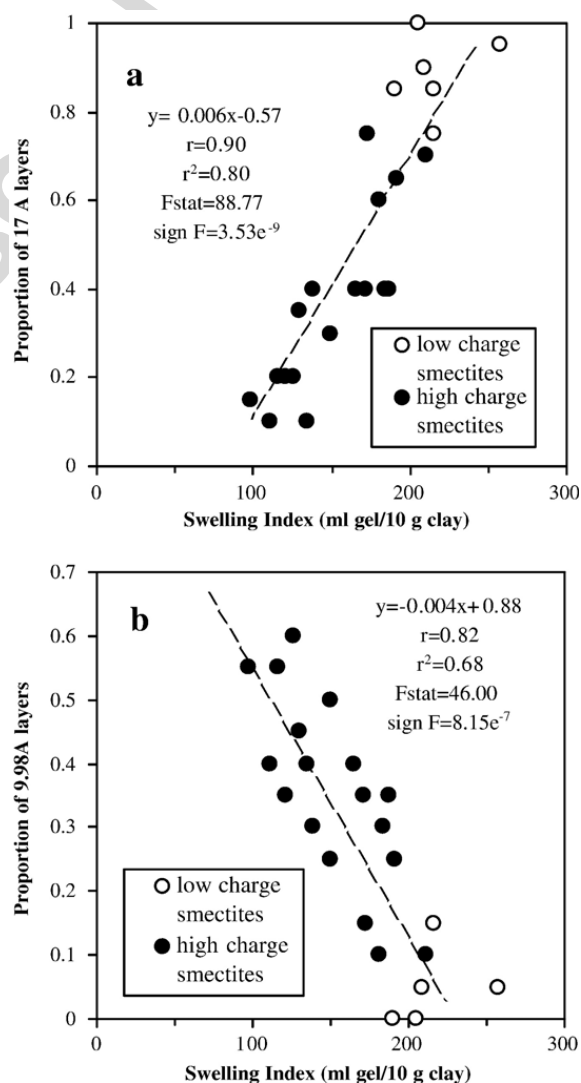

Fig. 8. Variation of the free swelling index of the bentonites with the proportion (a) of the low charge layers of smectites and (b) of the high charge layers of smectites. ANOVA was performed using a 5% level of significance ($\alpha = 0.05$).
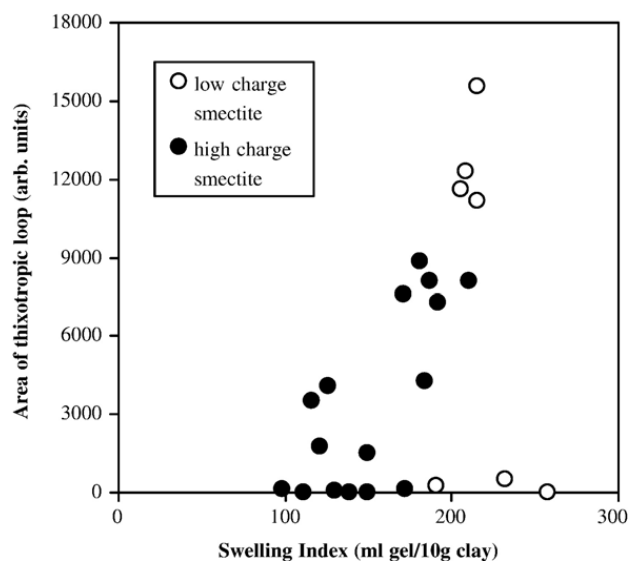
Fig. 9. Variation of the free swelling index with the thixotropic properties of the bentonites studied.

high charge smectites follow the overall trend for the index. Moreover the free swelling index is inversely correlated ($r=-0.82$) with the proportion of the totally collapsed high charge layers (10 Å layers; Fig. 8b). In both cases the regressions include both low and high charge smectites. A similar relation, although with considerable scatter, also holds between the free swelling index and the proportion of the partially swelling 13.5 Å layers (data not shown). Therefore the layer charge and charge distribution of smectites, expressed by the proportion of the low charge layers, and the presence of beidellitic layers seem to affect significantly the rheological properties of the bentonites.

The swelling index also is correlated with the tendency of the bentonites to form thixotropic suspensions (Fig. 9). Thus bentonites, which develop significant free swelling volumes, form in general thixotropic suspensions. However, there are exceptions to this trend. The thixotropic behaviour of the bentonites is inversely related ($r=-0.80$) to the layer charge of the smectites present (Fig. 10a). This trend includes smectites with layer charges from -0.425 to -0.490 phfu, i.e., it includes group 1b smectites and those group 2 smectites with lower layer charge (c.f. Christidis and Eberl, 2003). Moreover some group 1a (i.e. low charge) smectites also plot in the same trend. Note that those smectites with layer charge greater than -0.500 phfu (encircled points in Fig. 10a) as well as some low charge smectites, which are not thixotropic, deviate from the overall trend. SB9 with layer charge -0.430 phfu also deviates from the overall trend. The area of the thixotropic loop is clearly affected by charge heterogeneity being positively related

($r=0.72$) to the proportion of the low charge layers for smectites with layer charge from -0.425 to -0.480, except for SB9 (Fig. 10b). In contrast to Fig. 10a low charge smectites do not follow the same trend. Smectites with layer charge greater than -0.500 phfu (encircled points in Fig. 10b) deviate from the overall trend, since they do not develop suspensions with significant thixotropy. The same is valid for Kinney smectite with layer charge -0.490. The thixotropic behaviour is inversely related to the proportion of the high charge
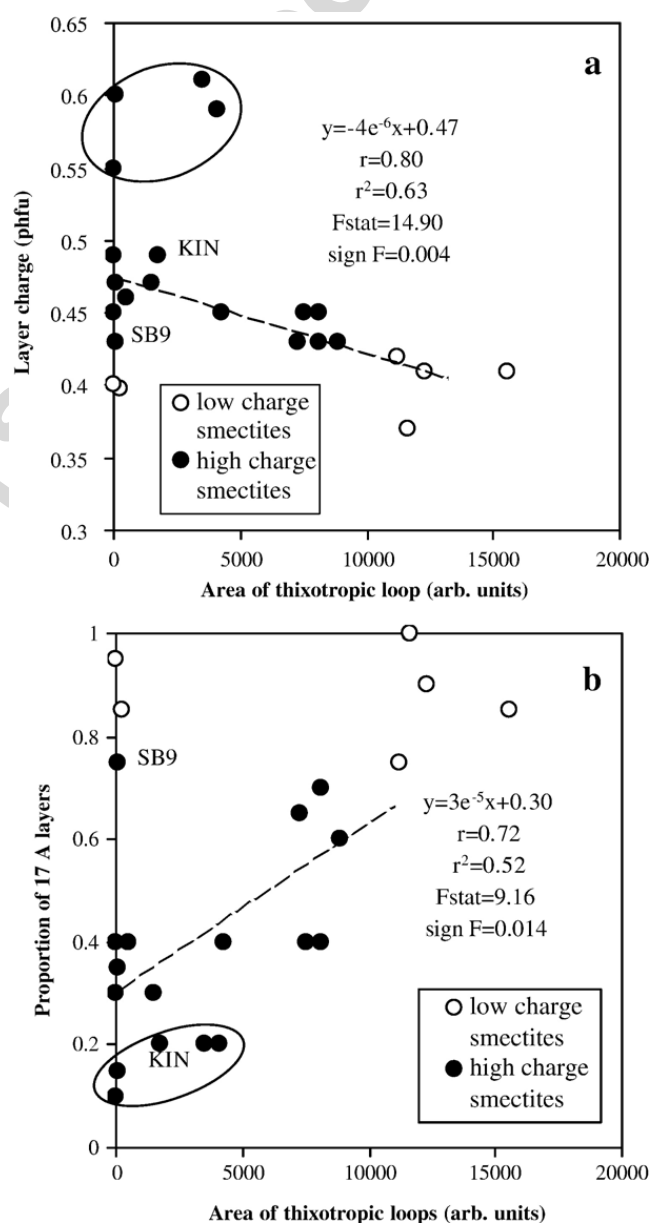

Fig. 10. Variation of the thixotropic properties of the bentonites (a) with the layer charge of smectites and (b) with the proportion of the low charge layers of the smectites. High charge smectites with layer charge > -0.50 are encircled. ANOVA was performed using a 5% level of significance ($\alpha=0.05$).

layers (data not shown). However the relation is characterized by considerable scatter.

The regression analyses carried out show that although in some cases the correlation coefficients are rather low (e.g. Fig. 6b), the linear relationships obtained between layer charge and charge distribution and the various rheological properties and swelling are meaningful. Indeed all F tests show that the null hypotheses, which claim that the linear models used to describe the observed relationships between the various variables have a random correlation with the experimental values (i.e. the linear regression models do not describe the observed variations, Figs. 4–10), can be rejected.

4. Discussion

4.1. Definition of high charge and low charge smectites

Although the terms high charge and low charge smectites are used extensively in the literature, there is no actual definition concerning the exact meaning of these terms. In general, low charge smectites are synonymous with Wyoming-type montmorillonites. However, there are beidellites with comparable layer charge but different XRD characteristics, such as the Glen Silver Pit beidellite. Newman and Brown (1987), following Schultz (1969), divided smectites in 4 groups according to the layer charge and charge distribution, i.e., essentially based on crystal-chemical criteria. In this classification scheme only Wyoming montmorillonites are low charge smectites with layer charge less than −0.425 phfu, whereas beidellites have layer charge greater than −0.425 phfu. However, our recent studies have shown that this classification scheme is not adequate for all dioctahedral smectites. For instance, certainly there are beidellites with layer charge lower than −0.425 phfu (Table 1, also Christidis and Dunham, 1997; Christidis and Eberl, 2003), and Fe-poor montmorillonites with layer charge lower than −0.425 phfu and octahedral charge lower than 15% of the total charge (Christidis, 2006), which cannot be included in this classification scheme. The same holds for the high charge smectites according to the classification scheme of Newman and Brown (1987), which essentially fill a large gap in layer charge between low charge smectites (−0.425 phfu) and vermiculites (−0.6 phfu).

Recent systematic work, including this study, has shown that low charge smectites with layer charge less than −0.425 phfu yield distinct XRD traces as do smectites with layer charge greater than −0.470 phfu (Christidis and Eberl, 2003). Interesting enough, these layer charge boundary values separate another type of smectite with distinct XRD characteristics, in which important rheological properties are related to the variation of layer charge (Figs. 6, 7). Thus, between the typical low charge smectites and those smectites with layer charge greater than −0.490 phfu, there is a group of smectites in which rheological properties vary proportionally to the layer charge. These smectites have been classified as group 1b smectites by Christidis and Eberl (2003) and may include beidellites as well, such as the Glen Silver Pit beidellite. In this study we propose a new classification scheme with more functional definitions for the high and low charge dioctahedral smectites, which are based on the magnitude of layer charge and the XRD characteristics of K-saturated, ethylene glycol solvated oriented clay fractions. This scheme is in accordance with the rheological properties of these smectites.

According to the proposed classification scheme, the low charge smectites must have, in general, layer charges lower than −0.425 phfu for montmorillonite (−0.365 for beidellite and nontronite because tetrahedrally charged smectites yield XRD traces like montmorillonites with fewer low charge layers), and XRD traces with first order reflections (for K-saturated, glycolated samples) that range from 16.6 to 17.1 Å, and well defined rational higher order basal reflections. Such smectites consist predominately of low charge (17 Å), fully swelling layers, develop suspensions with high viscosity and have high swelling volumes. Typical examples of low charge smectites examined in this study are SWy-1, Belle Fourche, GEC-3, GEC-4 and K−Y. Trioctahedral hectorite also has similar layer charge and XRD characteristics and develops suspensions with high viscosity. High charge dioctahedral smectites must have layer charges of at least −0.470 phfu and XRD traces characterized by a first order maximum at 14 Å and a 003 diffraction maximum at 4.6–4.7 Å. Such smectites contain a significant proportion of high charge (9.98 Å), non-swelling layers, develop suspensions with low viscosity and have low swelling volumes. Typical examples of high charge smectites in this study are SAz-1, Otay, SB5, SB17, and GEC-1. The rheological properties of the low and the high charge dioctahedral smectites do not seem to be affected by the layer charge. Finally those smectites with layer charge between −0.425 and −0.470 phfu (−0.365 and −0.415 for beidellite and nontronite), which have XRD traces characterized by first order reflections from 16.6 to 16.0 Å and irrational higher order basal reflections, will be defined as *smectites with intermediate layer charge*. The rheological properties of these smectites vary according to the layer charge and the proportion of the low charge layers. Note that the layer charge −0.415 phfu

is comparable to the suggested lower boundary for beidellites (-0.425 phfu) according to Schultz (1969) and Newman and Brown (1987), who consider them high charge smectites.

4.2. Influence of layer charge of smectites on the rheological properties of bentonites

Layer charge is probably the most important property of smectites that has economic and geologic importance, because it strongly affects key smectite properties such as swelling (e.g., MacEwan and Wilson, 1984; Güven, 1988; Laird, 1999), cation exchange capacity, and ion exchange selectivity (e.g., Maes and Cremers, 1977). This study has shown that it affects also the rheological properties (viscosity, gel strength, yield stress and thixotropy) at least to a degree, since smectites with different layer charges yield suspensions with different rheological properties. The bentonites tested consist of smectites with layer charges varying between broad limits and can be classified into all three groups of smectites proposed by Christidis and Eberl (2003). In general, they are montmorillonites with the exception of samples GEC3 and GEC4 which contain abundant beidellitic layers as well (Christidis and Dunham, 1997). Note that we prepared suspensions containing 6.42% solids, i.e. the concentration used in industrial testing and application. Inasmuch as several of the SB samples with great variability in layer charge and charge distribution (Table 1) come from a single bentonite deposit (S&B Industrial Minerals personal communication), it follows that the rheological properties of a bentonite deposit may vary considerably. Thus the variability of layer charge and charge distribution in a bentonite deposit may explain, at least to some extent, the great variability in the rheological properties often encountered in bentonite deposits.

The magnitude of layer charge controls the electrostatic component of interaction of the smectite particles, which can be important especially in high charge Ca-smectites, like most materials used in this study (Kleijn and Oster, 1982). Such smectites tend to form quasicrystals even at very low electrolyte concentrations, the thickness of which varies according to the layer charge (Kleijn and Oster, 1982). Although all bentonites were rendered homoionic after activation with Na_2CO_3 following the industrial practice, Na for Ca exchange is not expected to be complete, especially in high charge smectites, due to their higher selectivity for Ca, which is often associated with steric effects linked with swelling (Laird et al., 1995). Even if the Na for Ca exchange is complete, the high charge smectites will tend to form

large quasicrystals, which will develop considerably smaller diffuse double layers and thus will bind less water molecules compared to peptized smectite suspensions. Therefore, the electroviscous effect will not be important in these smectites. In the alkaline pH of the present study, in which the quasicrystals tend to form band-like (ribbon) structures (Brandenburg and Lagaly, 1988; Tombacz and Szekeres, 2004), the links between them will be weak due to the large floc size and break upon shearing even at low shear rates. Thus, these smectites are expected to develop inferior rheological properties approaching the behaviour of vermiculites. It is interesting that high charge smectites with layer charge -0.480 to -0.490 phfu (e.g. Kinney smectite) follow the trend of the intermediate type smectites. This is because they have a significant proportion of low charge layers and intermediate charge layers (Table 1), which form thinner quasicrystals and thus can form more viscous suspensions. In contrast, the low charge smectites can be activated more effectively because they can form thin quasicrystals and thus the steric effects during swelling are less important. The influence of layer charge on the thixotropic behaviour of bentonite suspensions can be explained in a similar manner. The thixotropic behaviour is associated with the kinetic properties of dispersed particles and their ability to re-establish lateral interactions, which have been disrupted by shear forces. It is dependent on the size and the volume fraction of the particles present in the dispersion. The latter is affected by the size of quasicrystals, which in turn is influenced by the layer charge.

The great variability observed in the rheological properties of these smectites (Fig. 6) suggests that factors other than the magnitude of layer charge are also important. Four additional possible factors are considered here, namely the concentration of the Na_2CO_3, which affects the ionic strength of the suspensions, the pH of the suspensions, the magnitude of the tetrahedral charge (proportion of beidellitic layers) and the presence of other fine-grained minerals such as opal-CT. The influence of smectite particle size and shape, which is affected by the size distribution of quasicrystals and thus, at least partly, by layer charge, may also be important but it was not tested in this study. The different ionic strengths of the bentonite suspensions can affect the thickness of the diffuse double layer of smectites and hence their rheological properties. However except for Swy-1, hectorite and Belle Fourche, in which the concentration of Na_2CO_3 was 0.006 M (6 mmol dm^{-3}), in the remaining samples the concentration of Na_2CO_3 varied between 0.018 M and 0.03 M (18–30 mmol dm^{-3}, Table 2). The resistance of sols to electrolyte

increases with the increasing pH of the aqueous medium and their stability is high in the pH range used in this study. Moreover, the electrolyte concentration is too low to destabilize the bentonite suspensions at such pH values (Tombacz and Szekeres, 2004). Also, the ionic strength of the suspension will be considerably lower because after ion exchange the released Ca ions will form less soluble $CaCO_3$, which will precipitate. Formation of by product $CaCO_3$ is a well-known process during Na-activation of Ca-bentonites. Therefore although the flocculation power of Ca is greater than Na, the concentration of Ca, which will remain in the suspension, is expected to be low. With the existing data it is not possible to estimate the amount of Ca in the suspension, because the precipitation rate of $CaCO_3$ is not known. In any case the variation of ionic strength of the bentonite suspensions is not expected to have affected significantly rheological properties.

The pH of the bentonite suspensions varied between 7.6 and 8.9. In this pH range the viscosity of bentonite suspensions increases after a minimum observed at pH 6.5–7 (Brandenburg and Lagaly, 1988; Tombacz and Szekeres, 2004). Note that the low charge smectites, which display the lower viscosity values (GEC3 and GEC4), also have the lowest pH values (7.6 and 7.7 respectively), i.e., close to the minimum quoted in the literature (Brandenburg and Lagaly, 1988; Tombacz and Szekeres, 2004). In the remaining samples pH varies between 8.3 and 8.9 and thus is not expected to affect significantly the variability of rheological properties. The existence of beidellitic layers also is expected to affect the rheological properties, because they control the location of maxima and minima of the potential curves on the surface of smectite (Bleam, 1990). Finally clay-size opal-CT crystallites may disrupt the network of smectite particles in the suspensions, and weaken the links between the smectite flocs, thus deteriorating rheological properties (Christidis and Scott, 1996). Note that GEC3 and GEC4 bentonites contain beidellitic layers and abundant opal-CT, and all Miloan and Kimolian bentonites have beidellitic layers (Christidis and Dunham, 1993, 1997).

The aforementioned intrinsic properties are important factors affecting also the scattering observed in the regression lines between layer charge of smectites with intermediate charge and rheological properties (Figs. 6–8,10). However the goodness of fit (r^2), which expresses the fraction of the total variance of the two parameters that is explained by the linear relationship, with the exception of yield (Fig. 6b), is greater than 0.50 (0.40 in the case of yield). This confirms that the layer charge is an important parameter, which affects variability of the

rheological properties and in the case of swelling layer charge it is the controlling factor (Fig. 8a). Note that although the correlation coefficient is closely related with the goodness of fit, the former is an approximation of the covariance of the two variables within the population, whereas the latter is an estimation of the variability of variable y, which is explained by variable x. Furthermore the correlation coefficient is only a measure of the linear correlation or dependence of two variables. (Davis, 1986)

An important result of this study is the observation that the rheological properties of smectites are controlled by the proportion of the low charge, fully expanded layers and are negatively affected by the high charge layers (Figs. 7, 8, 10). This outcome, although expected, has not been reported previously. The smectites with intermediate layer charge display an intermediate behaviour, acting as a link between the low charge smectites with pronounced rheological and swelling properties and their high charge counterparts with poor rheological and swelling properties. The low charge smectites with layer charge lower than −0.425 phfu display little variation of layer charge, because they consist almost entirely of low charge layers, and the magnitude of charge is low enough to allow formation of thin quasicrystals. Similarly the high charge smectites with layer charge greater than ~ −0.500 phfu contain a considerable proportion of high charge, non-swelling layers which favour the formation of thick quasicrystals. Although the charge of the non-swelling layers may vary considerably (Christidis and Eberl, 2003), they do not contribute to the rheological properties. The rheological behaviour of the intermediate type smectites is more complicated because their layer charge inhomogeneity results from the variable proportions of all three types of layers, which display a more even distribution. The gradual increase of layer charge in these smectites reflects the decrease of the low charge layers and the concomitant increase of the intermediate and high charge layers, thus adversely affecting the rheological properties.

The results of this study could be useful in industrial practice because they could be used to predict the flow behaviour of different bentonite suspensions. Hence it would be possible to replace a bentonite used as a drilling fluid with another consisting of smectites with comparable layer charge and charge distribution and thus has comparable flow behaviour. This is especially important for smectites with intermediate layer charge, in which the rheological properties vary linearly with layer charge and the proportion of low charge layers. Further refinement of this study would involve the use of the clay fraction of the bentonites, in order to control

the influence of particle size and mineralogical composition on the flow behaviour of smectite suspensions. In such a case empirical linear equations would be obtained which would correlate layer charge or/and charge distribution of smectites with rheological and swelling proprties and would allow safer prediction of those properties from layer charge. However even in this case the influence of mineralogy on the rheological properties cannot be eliminated totally, because the clay fraction of almost all bentonites usually contains other minerals except for smectite, such as kaolinite, opal-CT and/or clay size quartz and feldspars, which may affect flow behaviour.

5. Conclusions

We have shown that layer charge and charge distribution affect the rheological properties of bentonite suspensions. Low charge smectites with low abundance of beidellitic layers develop viscous suspensions because they consist predominately of low charge, fully swelling layers and thus form thinner quasicrystals and have a limited tendency for flocculation. By contrast the high charge smectites with layer charge greater than -0.500 phfu yield suspensions with low viscosity because they contain abundant non-swelling high charge layers, which favour the formation of thick quasicrystals. For these two types of smectites layer charge does not vary systematically with the rheological properties. In smectites with intermediate charge (-0.425 to -0.470 phfu) and in the lower limit of the high charge smectites (-0.480 to -0.490 phfu) the rheological properties vary proportionally to the layer charge because of the systematic variation of the various types of smectite layers. The observed deviations from the overall trends and the scattering in regression lines must be looked for in intrinsic properties, such as proportion of tetrahedral charge and smectite quasicrystal size and shape, rather than external experimental parameters such as exchangeable cation and suspension ionic strength and concentration, which were controlled throughout the experiments. Also with the exception of two low charge smectites, variation of pH is less important in the present study because the pH of the suspensions was alkaline and did not vary significantly.

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