Δελτίο της Ελληνικής Γεωλογικής Εταιρίας τομ. XXXII/3, 281-288, 1998
Πρακτικά 8ου Διεθνούς Συνεδρίου, Πάτρα Μάιος 1998

Bulletin of the Geological Society of Greece vol. XXXII/3, 281-288, 1998
Proceedings of the 8th International Congress, Patras, May 1998

SWELLING, RHEOLOGICAL AND CATION EXCHANGE PROPERTIES OF SOME BENTONITE DEPOSITS OF KIMOLOS ISLAND

G. E. CHRISTIDIS[1]

ABSTRACT

Bentonite deposits of Kimolos Island, Aegean, are investigated in order to determine important physical and chemical properties, including the CEC, swelling capacity, pH and rheological properties. Swelling is mainly influenced by the bentonite grade, while the rheological properties by the bentonite grade and the degree of disaggregation of the smectite quasicrystals, which is affected by the Na/Ca ratio of smectite, the presence of mordenite and undevitrified glass shards, the degree of iron oxidation and smectite-opal-CT interaction. The presence of small amounts of opal-CT may not affect rheological properties. High grade bentonites might be suitable for several industrial applicaStions if they are activated successfully.

KEY WORDS: Bentonite, smectite, cation exchange capacity, swelling index, rheological properties, viscosity, thixotropy.

1. INTRODUCTION

Bentonites are valued for their physical properties such as crystal shape and size, cation exchange capacity, hydration and swelling, thixotropy, bonding capacity, impermeability, plasticity and tendency to react with organic compounds (Highley, 1972, Patterson and Murray, 1983, Odom, 1984). After acid activation they aquire decolourizing properties and can be used in the clarificarion of edible and mineral oils (eg. Kheok & Lim, 1982, Srasra et al., 1989, Christidis et al., 1997). As a result they have many industrial applications including oil drilling, as a foundry sand bonding material, in iron ore and animal and poultry feed pelletization, in civil engineering, and in paints, cosmetics and pharmaceuticals etc (Harben, 1995).

Generalized laboratory experiments are often used for evaluation of the quality and grade of bentonites (Inglethorpe et al., 1993) and the physicochemical parameters which control their behaviour, especially the water-clay interaction (Callaghan and Ottewill, 1974, Low, 1980, van Olphen, 1977). The evaluation of the quality of bentonites for use in the various industries require more specific tests which control their suitability in each application using controlled laboratory experiments, which follow certain specifications and which simulate the use of the bentonite (eg. OCMA 1973, Odom, 1984).

The Aegean Islands of Milos and Kimolos are the bentonite extractive centres in Greece. In a recent contribution Christidis and Scott (1996) examined the physical and chemical properties of the Miloan bentonites and the influence of hydrothermal alteration on these properties. The purpose of this work is to examine some physical and chemical properties of the most important bentonite deposits from Kimolos island, assess the possibility for correlation between them and determine factors which control them.

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[1] Technical University of Crete, Department of Mineral Resources Engineering, 73133 Chania, GREECE.

2. GEOLOGY OF THE DEPOSITS MATERIALS AND METHODS

The bentonites studied are the Prassa and Loutra deposits located in the NE area of the island, and the Fanara deposit located in the southern part of the island (Fig 1). The deposits were formed in a shallow water environment. The Prassa deposit formed at the expense of an unwelded ignimbrite. It consists of pockets of high quality material restricted around fault systems, with N-S and NE-SW direction. The larger outcrop, presented in this contribution, is a 30mx35mx10m body which continues in depth; it has been divided into six distinct zones (Christidis, 1992, Christidis and Scott, 1997): a) fresh glass zone, b) zone of incipient alteration (smectite + glass), c) smectite + opal-CT zone d) smectite zone (i.e actual bentonite) e) smectite + mordenite zone (white bentonite) and f) smectite + opal-CT + mordenite zone.

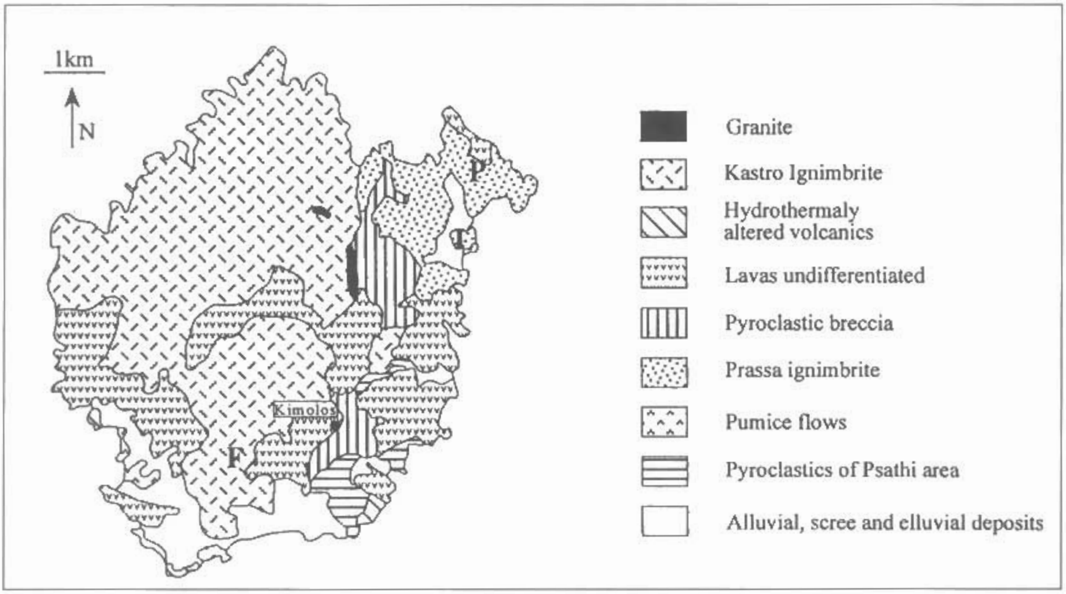

Fig. 1: Geological map of Kimolos Island (modified after Fyticas and Vougoukalakis, 1993). P= Prassa, L=Loutra and F= Fanara deposit.

The Loutra bentonite is a stratiform, well bedded, light-grey material, derived from fine grained volcanic ash. Devitrification increases with depth. Deposition of Fe-oxides along fault zones is common. The Fanara bentonite formed at the expense of a volcanic conglomerate indicating epiclastic reworking. Pebble size grades to volcanic sand towards the lower topographic levels of the quarry, suggesting increase of the depositional depth. The higher stratigraphic horizons have been silicified. At the lower topographic levels of the quarry, a high quality white bentonite derived from an unwelded ignimbrite occurs. Mineralogy is summarized in Table 1.

Sixty samples were collected from the bentonite deposits, along horizontal and vertical profiles. Subsequently they were homogenized according to their geological and mineralogical features. These samples were used to determine the cation exchange capacity (CEC), the swelling index and the rheological properties of the bentonites. Samples were dried at 60°C for 12 hours, crushed with pestle and mortar down to 125μm. CEC, was determined with a Kjeldahl microsteam apparatus after saturation with 1N ammonium acetate. Swelling index was determined using the method of Inglethorpe et al., (1993) modified (cf. Christidis, 1992). Swelling volume provides an indirect indication of the bentonite grade (Christidis and Scott, 1993, Inglethorpe et al., 1993).

In order to determine their rheological properties, materials were dried for 12 hours at 60°C, gound in a Tema mill for 45sec, passed through a 250μm sieve, treated with the optimum concentration of Na_2CO_3

and allowed to age overnight. Apparent and plastic viscosity and yield were determined with a 35S Fann V-G viscometer according to OCMA specifications (OCMA, 1973). In samples with apparent viscosity greater than 10cP, filtrate loss was determined with a Baroid ½-area cell. Complete rheograms, thixotropic loops and gel strength measurements were obtained in certain samples from the Prassa deposit. pH measurements were performed with a WPA CD30 digital pH-meter using a Russell pH-electrode.

Table 1: Mineralogical composition of the Kimolian bentonites. M= major, Min=minor and T= accessory phase. TA= Tatatilla-type montmorillonite, CH= Chambers-type montmorillonite, 1= igneous K-feldspar, 2= authigenic K-feldspar (Christidis, 1992).

Mineral	Prassa	Loutra	Fanara
Smectite	M	M/Min	M
Type	Mont/nite Cheto (TA/CH)	Mont/nite Cheto (TA/CH)	Mont/nite
Fresh glass	- -	- -	Min
Kaolinite	- -	- -	Min/T(±)
Mica	T(±)	T(±)	- -
Opal CT	M/Min	M/Min	- -
Quartz	- -	Min	M/Min(±)
Mordenite	M/Min (±)	- -	- -
Clinop/lite	- -	Min(±)	- -
K-feldspar^1	T(±)	- -	- -
Plagioclase	T/Min	M/Min)	?
K-feldspar^2	- -	T(±)	Min
Calcite	- -	- -	M/Min(±)
Gypsum	T(±)	- -	- -
Halite	T(±)	- -	- -

3. RESULTS

The results from the CEC measurements and the swelling volumes are given in Table 2. The values obtained reflect differences in mineralogy of the various bentonites. The smectite zone in the Prassa deposit displays maximum swelling, while the mordenite bearing zone has maximum CEC (Fig. 2a). Both properties yield minimum values in the smectite+opal-CT zone. Sample SM281 from this zone is an exception to this trend due to its high smectite content. In the Loutra deposit both the CEC and swelling increase with depth. Although the material contains clinoptilolite it has a low CEC, due to the limited devitrification and the presence of opal-CT. These factors also dictate the inferior swelling capacity of the

Table 2: Cation exchange capacity (CEC) and swelling volumes of bentonite samples from the Prassa, the Loutra and the Fanara deposits. In the Prassa deposit SM261 and SM277 come from the mordenite bearing zone, SM278, SM279 and SM280 from the smectite zone, and SM281 and SM265 from the smectite + opal-CT zone. In the Fanara deposit SM307 comes from the white bentonite body, while SM306 from the volcanic conglomerate (Christidis, 1992). The values in brackets are the amount of Na_2CO_3 (%) added to obtain maximum swelling.

Prassa deposit			Loutra deposit		
Sample	CEC (meq/100g)	Swelling Index (ml gel/10g clay)	Sample	CEC (meq/100g)	Swelling Index (ml gel/10g clay)
SM261	*124.8*	*131 (4)*	SM295	40.75	33 (3)
SM277	126.35	110 (4)	SM296	46	40 (3)
SM278	94.9	189 (4)	SM297	56.55	59 (4)
SM279	99.8	235 (4)	SM298	59.25	80 (3)
SM280	99.55	206 (4)			
SM281	94.3	205 (5)		Fanara deposit	
SM265	63.95	121 (3)	SM306	35.25	38 (3)
			SM307	90.25	230 (5)

material relative to the smectite zone in the Prassa deposit. The volcanic conglomerate (SM306) in the Fanara deposit has also inferior CEC and swelling properties reflecting a moderate smectite content. On the contrary, the white bentonite (SM307) has high CEC and good swelling properties, i.e it is similar to SM281 from the Prassa deposit.

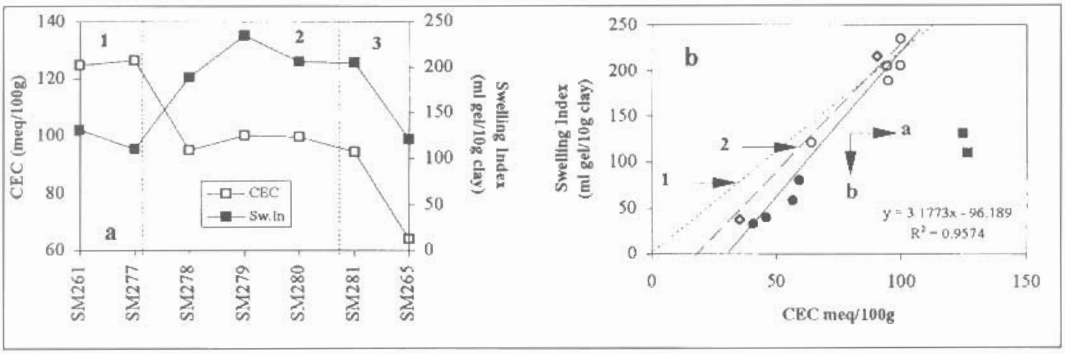

Fig. 2: (a) Variation of CEC and swelling index in the Prassa deposit. 1= mordenite bearing zone, 2= smectite zone, 3= smectite+opal-CT zone. The length of zone 2 is 8m.(b) CEC vs swelling index in the bentonites studied. Dashed line 1 was drawn considering that a smectite-free bentonite does not swell. Line 2 is the regression line for the Miloan bentonites (Christidis and Scott, 1993). Arrow (a) indicates deviation from line 1 caused zeolites and arrow (b) deviation caused by by glass and opal-CT. Circles= smectite zone Prassa, solid circles= Loutra, diamonds= Fanara, solid square= zeolite bearing zone, Prassa.

Swelling volume and CEC display a well expressed linear relationship (Fig. 2b). Samples from the mordenite bearing zone, Prassa deposit, deviate from the overall trend. Similar but less well determined linear correlation (line 2) has been observed in the Miloan bentonites (Christidis & Scott, 1993). Smectite rich samples from the smectite zone, Prassa deposit, plot on line 1.

Except for SM265 which has a low CEC, the Prassa bentonites were activated with 4 and 5% sodium carbonate, while the Loutra bentonites with 3% carbonate. SM307 was activated with 5% and SM306 with 3% carbonate. The amount of sodium carbonate added to obtain maximum swelling (see Table 2), depends on the abundance of exchangable Na and the smectite content in the bentonite. The lower amount of Na_2CO_3 added in the Loutra deposit and samples SM265 and SM306, reflect their low grade. In the high grade materials the higher amount of Na_2CO_3 added is due to the predominance of exchangeable Ca and Mg (Christidis, 1992).

Results of rheological properties are given in Table 3. Loutra bentonite and sample SM306 (Fanara deposit) have very poor rheological properties. Samples from the Prassa deposit develop higher viscosity; however except for SM278, samples from the smectite zone do not meet OCMA specifications. On the contrary SM281 (smectite + opal-CT zone) and samples from the mordenite-bearing zone meet OCMA specifications. Moreover SM307 (Fanara deposit) with small amounts of opal-CT yields exceptionally high viscosity (Table 3). Finally, except for SM307 and SM277 the Kimolian bentonites have low plastic viscosity, compared to Wyoming bentonites (Elzea and Murray, 1990).

The smectite zone at the Prassa deposit yielded alkaline pH values. The pH of the Loutra bentonites decreases with depth (Table 3). SM306 yielded the lowest pH (Table 3), reflecting the presence kaolinite due to hydrothermal alteration. Finally filtrate loss varies between broad limits(Table 3). The Prassa bentonite, the lower sectors of the Loutra deposit and the white bentonite body in the Fanara deposit (SM307) yielded low filtrate loss indicating good filter cake characteristics. The higher sectors of the

Table 3: Rheological Properties of the Kimolian bentonites.

Deposit	Apparent Viscosity (cP)	Plastic Viscosity (cP)	Yield (kg/m^2)	Filtrate loss (cm^3)	pH
Prassa					
SM261	15.5	7	0.83	10.0	7.7
SM277	36	14.5	1.05	7.2	7.5
SM278	25	7.5	1.71	7.6	8.3
SM279	9.8	7	0.27	7.0	8.0
SM280	11.3	6.5	0.46	6.8	8.5
SM281	25	11	1.32	8.1	7.7
Loutra					
SM295	1.5	1.5	0	- -	8.2
SM296	1.3	1.5	0.07	55	8.3
SM297	2.5	2	0.1	18.5	7.6
SM298	3.7	2.5	0.12	10.0	7.4
Fanara					
SM306	2.5	2	0.05	18	6.8
SM307	114	68	4.49	4.0	7.2

Loutra deposit and SM306 yielded a high filtrate loss.

The complete rheograms of SM278 and SM280 from the smectite zone, Prassa deposit, are shown in Fig. 3. It is evident that SM278 is more thixotropic and develops higher plastic viscosity than SM280, corroborating the plastic viscosity measurements (Table 3). Due to the similar treatment of the materials, the "shear history factor" (Mewis, 1979) probably has not affected the thixotropic loops. Both materials are thixotropic under high and antithixotropic under low rates of shear. This is a common behaviour at such pH values (Brandenburg and Lagaly, 1988).

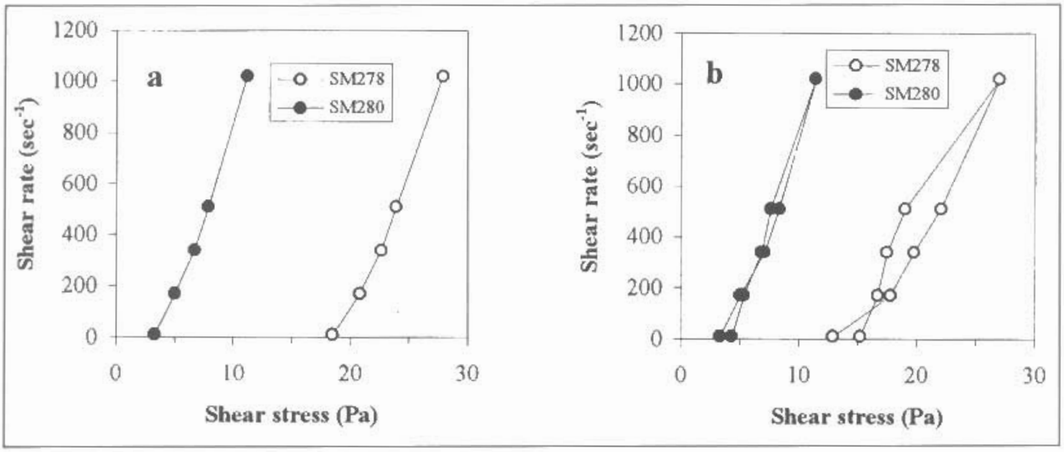

Fig. 3: (a) Complete rheograms and (b) thixotropic loops of bentonite samples from the smectite zone, Prassa bentonite.

4. DISCUSSION

The positive correlation between CEC and swelling index (Fig. 2b) underlines the importance of the *grade component* (Christidis and Scott, 1996) for swelling of bentonites. The regression line does not pass from the origin as expected. Except for the Loutra bentonites, all other samples plot on regression line 2, obtained for the Miloan bentonites, while the smectite rich samples from Prassa deposit plot also on theoretical line 1. Note that regression line 2 also deviates from the theoretical line 1, although to a lesser degree. Deviation from line 1 is maximized for low grade bentonites, which in the case of Milos contain abundant silica polymorphs, especially opal-CT.

Smectite chemistry does not vary in the Kimolian bentonites (Table 1). Hence variation of CEC due to differences in smectite layer charge (Schultz, 1969, Newman and Brown, 1987), i.e the *pure swelling factor* (Christidis and Scott, 1996) is minimized. Then deviation from the regression line 1 gives valuable information about the mineralogical influence on both properties. In Fig. 2b it is evident that the presence of opal-CT and fresh glass cause migration of plotting points from theoretical line 1 parallel to the swelling index axis (arrow b). The influence of glass is more significant. The type of association of fine grained opal-CT with smectite might be important, since intimate intergrowths of these minerals are expected to retard separation of smectite flakes thus reducing the swelling (Christidis and Scott, 1996). The influence of other coarse grained minerals without swelling or cation exchange properties (e.g. feldspars, carbonates etc) is not known, although it is expected to be less important. This is because, zeolites which possess CEC substantially higher than smectites, cause migration of the plotting points from line 1 parallel to the CEC axis (arrow a), without affecting swelling.

The strength of a bentonite gel has been attributed to the repulsive forces of the interactive double layers (secondary electroviscous effect) or/and to the formation of three-dimensional band-like structures and the formation of the effective double layers is a result of swelling (Callaghan and Ottewill, 1974, Rand et al., 1980, Permien and Lagaly, 1994). Therefore a relationship between plastic viscosity and swelling is expected, which is observed (Fig. 4b). Unlike the Kimolian bentonites, Christidis and Scott, (1996) observed a dual trend in the Miloan bentonites, suggesting that high viscosity develops only after smectite flakes have swollen beyond a certain limit. This difference can be explained from the uncertainty in the exact location of the breaking point of the curves in the Miloan bentonites, the variable degree of disaggregation of smectite and the heterogeneity of smectites in the Miloan deposits (Christidis and Scott, 1996).

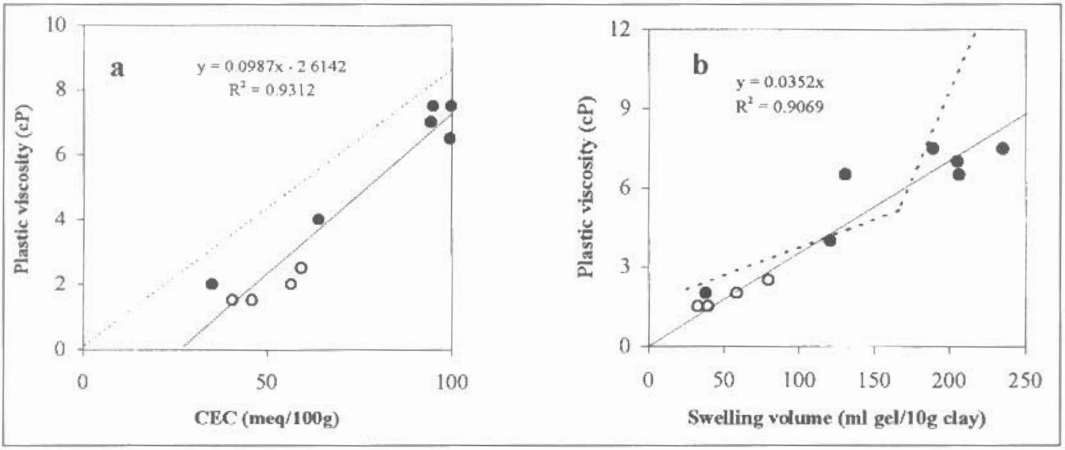

Fig. 4: Correlation (a) between plastic viscosity and CEC and (b) between plastic viscosity and swelling. The dashed lines corrrespond to the regression lines obtained for the Miloan bentonites (Christidis and Scott, 1996). Solid circles Prassa deposit, Open circles= Loutra deposit.

Similar to the Miloan bentonites a well expressed (R^2= 0.93) positive linear trend holds between CEC and plastic viscosity (Fig. 4a), suggesting that in bentonites with similar smectite chemistry, materials with higher grade yield more viscous suspensions. However the regression line does not pass through the origin as in Miloan bentonites (dashed line in Fig. 4a). The observed deviation is caused principally by the Loutra bentonites which contain glass shards; if samples from Loutra bentonite are excluded the regression line passes close to the origin (see Fig. 4a).

Treatment with Na_2CO_3 is expected to homogenize interlayer cation differences, unless activation was incomplete due to incomplete disaggregation of smectite quasicrystals. The shape and size of the smectite particles should also be considered since the original Ca-rich particles are expected to form long stacks consisting of several layers (Brandenburg and Lagaly, 1988, Kleijn and Oster, 1982). Organic matter, which might affect the rheological properties of the clay suspension by adsorption on the clay surface (van Olphen, 1977), is absent.

Important factors which might affect rheological properties are the type of association of opal-CT with smectite, the Na/Ca+Mg ratio in the untreated materials and oxidation state of iron (Alther, 1986). Intimate association of opal-CT affects rheological properties in the same manner as swelling (Christidis and Scott, 1996). Thus only materials with minor amounts of opal-CT (SM281, SM307) yield high viscosity. Ferrous iron leads to the formation of thicker smectite stacks than those containing ferric iron (Stucki and Tessier, 1991), especially in the presence of Ca ions. Although oxidation of Fe due to exposure of the material in the atmosphere is expected, colour measurements indicate that ferrous iron is probably present (Christidis and Scott, 1997). The swelling tests indicate a low Na/Ca+Mg ratio in the exchangeable cations. Therefore thick quasicrystals are expected to form in bentonite suspensions (Schramm and Kwak, 1982) retarding Na-activation. Na-bentonites have good rheological properties in contrast to their Ca-counterparts, because the latter form thick crystallites (Brandenburg and Lagaly, 1988, Kleijn and Oster, 1982, van Olphen, 1977).

The high apparent viscosity observed in mordenite-bearing zone, Prassa deposit is attributed to the presence of mordenite. The treatment of bentonites with Na_2CO_3 during preparation of viscous suspensions results in Na for Ca+Mg exchange in smectites. Mordenites are predominately Na-Ca rich zeolites (Gottardi and Galli, 1985) although some mordenites from Prassa contain also exchangable K (Christidis, 1992). Therefore during Na-activation most Na_2CO_3 is expected to be consumed by smectite. The silt size mordenite crystals settle yielding a more dilute suspension, facilitating ion exchange and subsequently disaggregation of the smectite quasicrystals. Since the smectites from the different zones of the Prassa deposit have similar chemical characteristics, samples SM279 and SM280 should yield viscous suspensions, if the are activated succesfully, i.e. if Na for Ca+Mg exchange is complete.

5. CONCLUSIONS

The variability of most physical and chemical properties of the Kimolian bentonites is related to differences in the non clay mineralogy, (glass, opal-CT and zeolites), because smectite chemistry is controlled.

The swelling capacity of the Kimolian bentonites is closely related to their CEC. Undevitrified glass and opal-CT reduce swelling. Viscosity depends on swelling and the amount of smectites present. Under certain conditions impurities might not affect rheological properties. Several high grade bentonites do not yield viscous suspensions due to existence of smectite quasicrystals. Disaggregation of smectite quasicrystals depends on the presence of opal-CT associated with smectite crystals, the oxidation state of iron and the original Ca/Na ratio of smectites.

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