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VARIABILITY IN WATER SORPTION AND IN THERMOGRAVIMETRY OF BENTONITE

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SUMMARY

Macroscopic and microscopic /SEM/ arrangement of bentonite grains, the average particle thickness, δ and thermogravimetry, TG were found to be dependent on sample preparation and storing conditions, i.e. drying from suspension, water sorption, WS or water retention, WR. Decreased δ, increased TG-weight loss and compact microaggregates were observed after WR test. Increased δ, decreased TG and loose macroaggregates were the results of WR test.

INTRODUCTION

Mechanical processing of montmorillonite and other clay minerals may cause the variability in temperature of dehydration and dehydroxylation and in water sorption, which is inversely proportional to the particle thickness, δ. This was detected by water sorption test, WS test, water retention test, WR test, and weight loss in static heating, TG /refs. 1-2/. Dried bentonite suspensions indicated also a variability in water sorption properties and in TG. These values were dependent on initial concentration, on stirring energy, stirring time and storing time of the suspension before the drying procedure. These factors influenced the average thickness of clay particles and their arrangement, i.e. the microstructure, which appeared in SEM as parallel or cluster or floc structure /ref. 3/.

Increase in water sorption due to decrease in δ, i.e. delamination, was higher in parallel structure than in cluster structure, whereas floc structure was formed from thin flexible particles, delaminated already during the stirring procedure at high stirring energy. Microstructure influences also the possibility of formation of new mineral phases in drying and heating of the sample /refs. 3-4/. This may result in change of TG as compared to homogeneous random powder sample. There are data indicating

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that parallel structure may transform into paragonite, cluster structure into feldspar and floc structure into zeolite /ref. 4/.

Some results of the study performed at King's College London on bentonite suspensions used in Civil Engineering, as well as of the study of the parent bentonite, are presented below.

MATERIALS AND METHODS

Water sorption, WS water retention, WR and thermogravimetry by static heating, TG were measured on the following samples:

W/B - calcium bentonite from the Quarry at Woburn,
B/B-P - Berkbent bentonite as processed powdered clay,
B/B-A - its 6 % suspension stirred at 5000 RPM for 15 min and dried at 105°C.

Following methods were used:

WS test: ca. 0.5 g samples were dried at 105°C and stored for 10 to 20 days at room temperature, ca. 18°C, successively at p/p_o = 0.5; 0.95 and 1.0, followed by heating at 105°C 220°C and 400°C. All samples were photographed and powder samples were studied in SEM, see Fig. 1. Water sorption measurement at p/p_o = 0.5 was repeated and samples were reheated at 105°C, 220°C, 400°C and 800°C /Table 1, Fig. 2/.

WR test: ca. 0.5 g samples were stored successively at p/p_o = 1.0; 0.95 and 0.5 at room temperature ca. 18°C. Further treatment was identical as that of WS test /Table 1, Fig. 2/.

TG: ca. 0.5 g samples were heated successively at 105°C, 220°C, 400°C, 800°C and 1200°C. Weight loss ΔG in Fig. 2 is related to dry mass at 105°C.

WS and WR values are related to dry mass at 220°C because of specific surface calculations.

External specific surface, S, is calculated from water content at p/p_o = 0.5, using the coefficient 585 m^2 per g H_2O, or from water conent at p/p_o = 0.95, using the coefficient 390 m^2 per g H_2O, assuming dry mass at 220°C.

Particle thickness, δ is calculated in number of unit layers per particle from $\delta = 790/S$, both in m^2 per g clay.

DISCUSSION

Macroscopic and microscopic arrangement of grains, formed by separate particles of Berkbent bentonite powder, B/B-P was dependent on the relative water vapour pressure during the sample storage, see Fig. 1.

Grains were forming macroscopic aggregates after WS test, whereas at magnification 500 x the unhomogeneity within an aggregate was not observed.

After WR test samples appeared macroscopically homogeneous and more compact than those after WS test, whereas at magnification 500 x compact aggregates of grains were visible.

In spite of heating at 400°C all the grains remained swollen as compared to those of the initial powder; their volume was almost double after WS test:at p/p_o = 1.0 the WS was 78 %. It was somewhat less after WR test: at p/p_o = 0.5 the WR was 21 % and it was similar to the initial water content of the powder B/B-P, i.e. W_o= 20 %. Clay particles forming a grain were almost parallel in WS test samples, whereas after WR test they formed arrangements similar to flocs, observed in certain suspensions. Macroscopic differences in samples under study remained visible after heating at 800°C, see Fig. 1.

TABLE 1

Water sorption and water retention at various relative water vapour pressure conditions, related to dry mass at 220°C

Sample	W_o		W % at p/p_o =			WS /0.5/ %
	%		0.5	0.95	1.0	after 400°C
W/B	20.6	WS	21.4	40.5	51	
	19.3	WR	25.8	45.4	49	
B/B-P	20.5	WS	13.3	42.7	78	7.7
	19.1	WR	23.3	52.6	59	6.2
B/B-A	7.7	WS	14.2	39.3	53 - 71	9.0
	7.2	WR	21.0	45.8	47 - 51	8.9

WS test and WR test results, see Table 1, will be discussed here in terms of the calculated particle thickness, expressed as number of unit layers per particle /u.l./, see Table 2.

In powder sample, B/B-P, the particle thickness varied from δ = 6 - 10 u.l. at low relative water vapour pressure to δ = 3.8 - 4.7 u.l. at p/p_o = 0.95, see Table 1 and 2. Somewhat higher values of δ were measured in samples dried from suspension, B/B-A

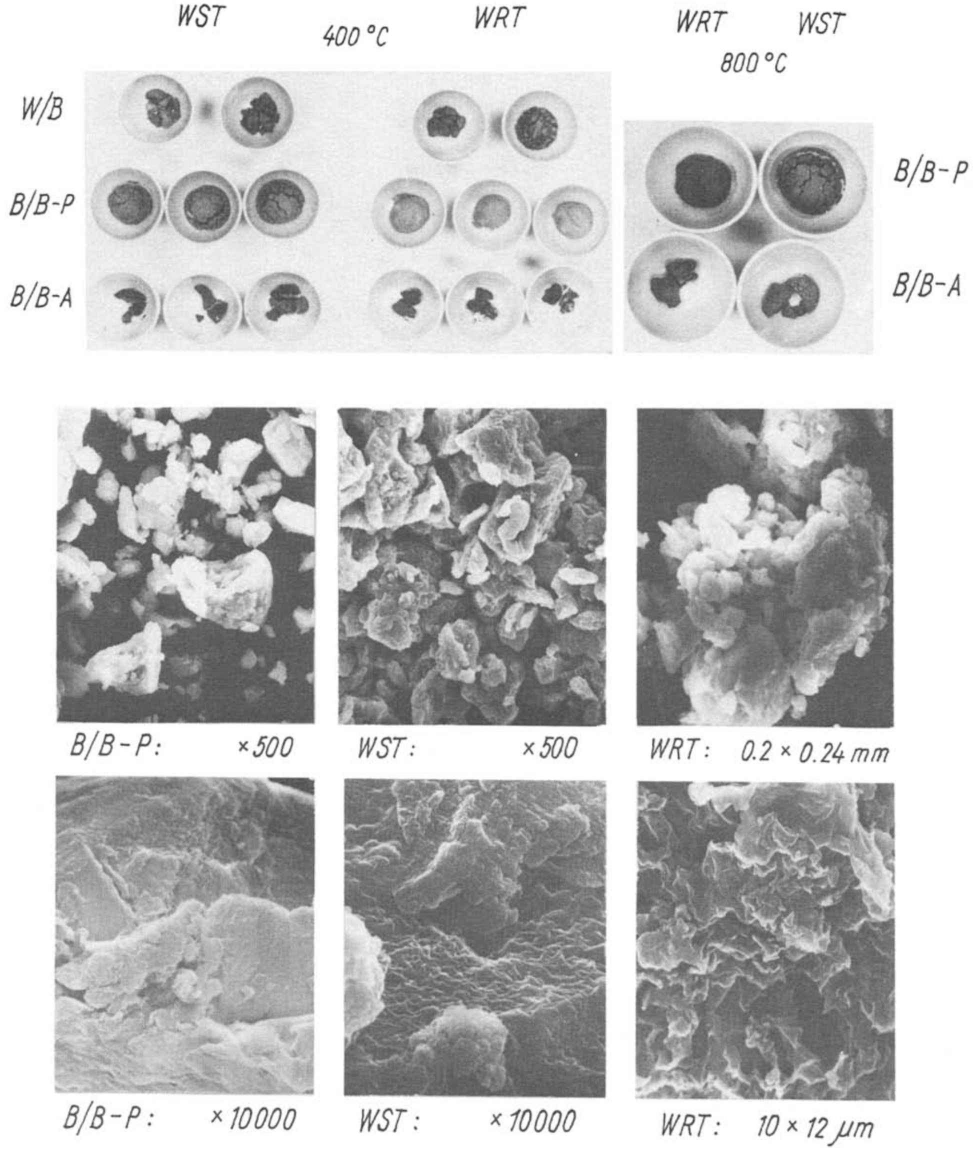
WST
400 °C
WRT
WRT
WST
800 °C
W/B
B/B-P
B/B-A
B/B-P
B/B-A
B/B-P: ×500
WST: ×500
WRT: 0.2 × 0.24 mm
B/B-P: ×10000
WST: ×10000
WRT: 10 × 12 µm

Figure 1

Raw material in calcium form, W/B, indicated WS /0.5/ = 21 % and

TABLE 2

Particle thickness, δ /p/p$_o$ as calculated from WR and WS, Table 1

Sample		δ /0.5/ u.l.	δ /0.95/ u.l.	after 400°C δ /0.5/ u.l.
W/B	WS:	6.3	5.0	
	WR:	5.2	4.46	
B/B-P	WS:	10.2	4.74	17.4
	WR:	5.8	3.85	21.8
B/B-A	WS:	9.5	5.15	15.0
	WR:	6.4	4.12	15.2

$$\delta\ /0.5/ = \frac{790}{WS\ /0.5/ \times 5.85} \qquad \delta\ /0.95/ = \frac{790}{WS\ /0.95/ \times 3.9}$$

therefrom δ = 6.3 u.l., whereas the delamination of its particles in water vapour occured in a smaller degree than in processed - Berkbent bentonite in Na - form and it was similar to the value measured in calcium Zrecze Male bentonite: δ /0.95/ = 4.5 to 5 u.l.

Berkbent bentonite dried from suspension at 105°C, which may have caused phase transformation /refs. 3 and 4/, indicated during heating within the whole temperature range a decreased weight loss as compared to the initial powder, see Fig. 2.
The parent material, W/B showed at 400°C an intermediate value, whereas at 800°C and 1200°C the smallest weight loss was observed. This was probably due to the addition of sodium carbonate to the commercial Berkbent bentonite.

Samples heated after sorption measurement had a somewhat lower weight loss than the untreated ones, whereas generally the highest weight loss was measured in powder samples after WR test, Fig. 2, e.g. ΔG at 400°C was in B/B-P respectively: WS - 2.4 %, TG - 4.4 %, WR - 4.0 %. This may be connected with respective rearrangement of sorbed water molecules, causing increase in temperature of dehydration after water retention test, and/or with rearrangement of particles to the given microstructure, and/or with phase transformation, see Introduction. **Dried suspensions indicated a similar weight loss after all the three types of treatment: ΔG at 400°C was in B/B-A respectively: WS - 2.0 %, TG - 2.1 %, WR - 2.3 %.** Apparently all the possible particle rearrangement and

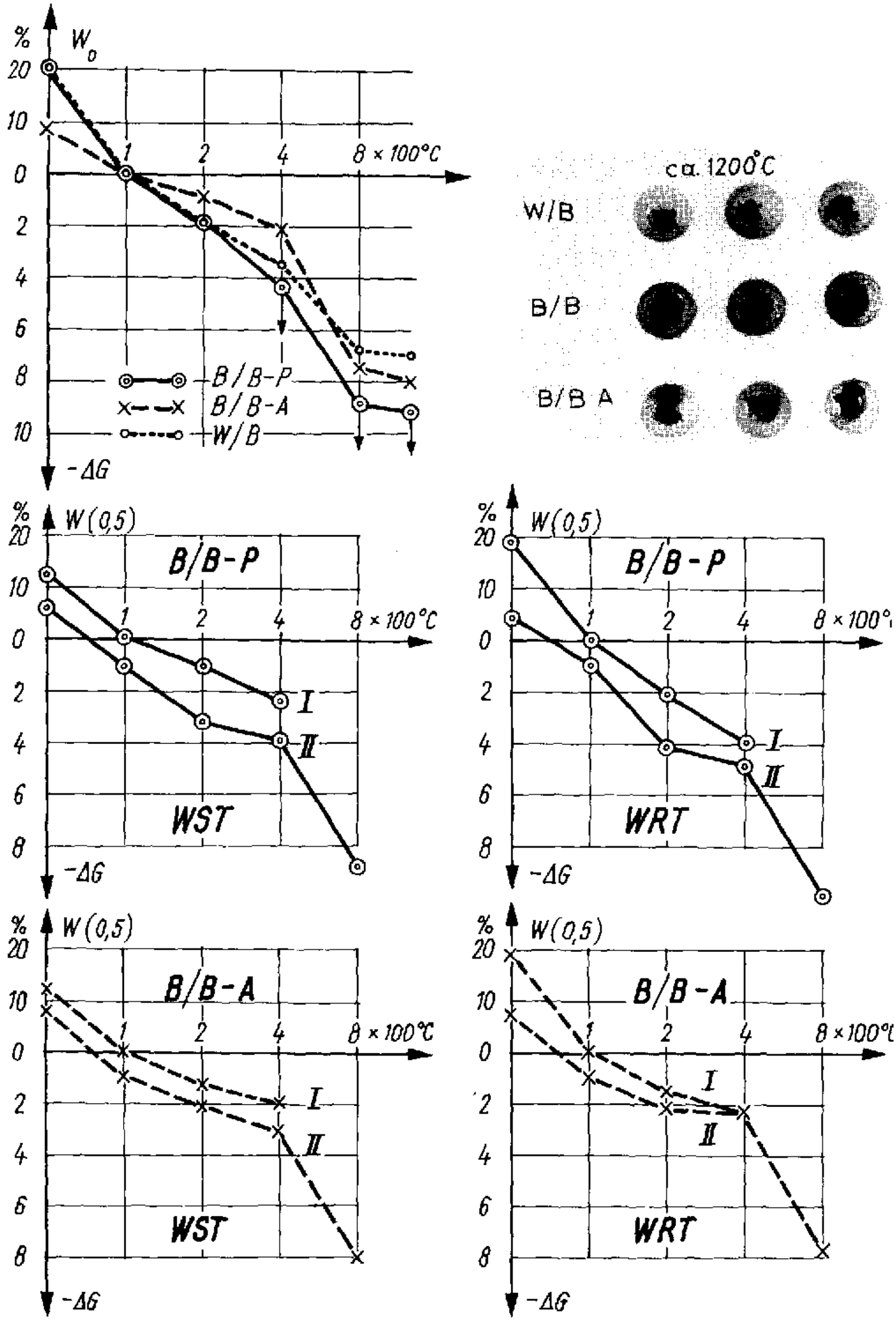
%
W_0
20
10
0
2
4
6
8
10
1
2
4
8 × 100°C
$-\Delta G$
B/B-P
B/B-A
W/B
ca. 1200°C
W/B
B/B
B/B A
%
W(0,5)
B/B-P
WST
I
II
B/B-P
WRT
I
II
8 × 100°
B/B-A
WST
I
II
B/B-A
WRT
I
II
8 × 100°C

Figure 2

phase transformations, connected with the microstructure of the sample, occured already during drying at 105°C. SE micrographs of oven dried suspension, B/B-A are not available.

Storage at $p/p_0 = 0.5$ after heating at 400°C caused only a partial rehydration, which indicates the increase in the average particle thickness. Rehydration was higher in sample B/B-A: $\delta = 15$ u.l., WS /0.5/ = 9.0 %, as compared to $\delta = 18$ to 22 u.l. and WS /0.5/ = 7.7 % in sample B/B-P. After this rehydration weight loss in heating was higher in all the samples, most probably due to a change in dehydration and dehydroxylation temperature by up to ca. 50°C, see Fig. 2. Air dry suspensions of Berkbent bentonite indicated in DTG a variation in temperature of dehydration by ca. 20°C and in that of dehydroxylation also by ca. 20°C, depending on their initial concentration /ref. 3/.

Increase in temperature of dehydration observed after water retention measurement might have caused also differences in the measured values of water content Wo and differences in values of water resorption of powder samples after WS test and WR test: resorption related to dry mass at 105°C was at $p/p_0 = 0.5$ respectively 6.2 and 4.9 %, whereas weight loss at 220°C was 3.1 and 4.1 % and at 400°C it was 3.9 and 4.8 %. Thus a part of sorbed water escapes after WR test at more elevated temperatures, exceeding 105°C, than after WS test, due to differences in arrangement of clay particles, Fig. 1. Also it may be expected, that the temperature of dehydroxylation may be lower in case of thin flexible particles of floc structure in WR test, Fig. 1, than in case of almost parallel particles after WS test, suitable for phase transformation.

These differences in temperature of dehydration and dehydroxylation might be used to study the microstructure of the clay - water system, but further research is to be done.

CONCLUSIONS

1/ Humidity conditions of storage of the bentonite powder influence the arrangement of its grains observed both microscopically and macroscopically. They influence also the arrangement of particles. These effects remain after oven drying and heating of the sample.

2/ Conditions of preparation, storage and drying influence the weight loss in heating as the temperature of dehydration and dehydroxylation may be changed and phase transformation dependent on microstructure may occur.

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REFERENCES

1 E.T.Stępkowska, Sorption properties of consolidated and compressed clays, Developments in Sedimentology 27, Elsevier, Amsterdam, 1979, pp. 457-464

2 E.T.Stępkowska, Influence of mechanical processing on thermogravimetric behaviour of natural clays, Thermal Analysis, ICTA 80, Birkhauser Verlag, Basel 1980, V. 2, pp. 333-338

3 E.T.Stępkowska and S.A.Jefferis, The influence of microstructure on thermal behaviour of bentonite, 7th ICTA 1982, Kingston Ontario, Canada; Przegląd Geologiczny 3 /1983/, pp. 156-161

4 E.T.Stępkowska and S.A.Jefferis, Possibility of zeolite formation in bentonite slurries during storage and drying, "Zeolite 85", Budapest, 1985, Volume of Abstracts, pp. 22-23, article submitted for publication