INFLUENCE OF FREEZING - UNFREEZING CYCLES ON THE THERMAL
BEHAVIOUR OF A MARINE CLAY

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ABSTRACT

After ten freezing - unfreezing cycles a marine cley indica-
ted an important change of water sorption /particle thickness/
and of weight loss in static heating up to 800 $^{\circ}$C. This is due
to changes in microstructure during freezing.

INTRODUCTION

Variability in water sorption, WS, is attributed here to
change in specific surface, S, and in particle thickness, $\tilde{\delta}$. It
was observed in several processes, e.g. mechanical treatment,
drying, storage at a high water content etc., see [7].
These processes may influence as well weight loss in static hea-
ting, Δ G. All these influences depend not only on pretreatment
but also on form and size of sample under study. In powdered
sample these effects may disappear, though some change in beha-
viour of Berkbent bentonite powder, depending on sample pretre-
atment, was observed. Also its microstructure was different
whether it was stored at decreasing or at increasing relative
humidity [8].
Here a study will be presented of the influence of cyclic
freezing on WS and on TG behaviour of a marine clay [6]. A si-
milar influence, i.e. a decrease in WS and increase in particle
thickness was observed in a silty leam by Skarżyńska [3]. SEM
study of this soil indicated some microstructural changes [10]
which may occur also in this marine clay. Some phase transfor-
mations are possible as well, during freezing and/or drying
and/or heating which are discussed in the adjoining paper [9].

MATERIALS AND METHODS

Three samples of a marine clay were taken from the Baltic sea bottom at depths of /1/ 3.6 m, /2/ 5.4 m, and /3/ 5.5 m.

Mineral composition of clays from this region was studied previously. They contain montmorillonite, partly interstratified with illite, and keolinite in variable proportions, as well as quartz and feldspar in coarser fractions. Clay fraction may give XRD patterns of an almost amorphous matter, showing better crystallinity after homoionization to Mg or K /Fig. 1/.
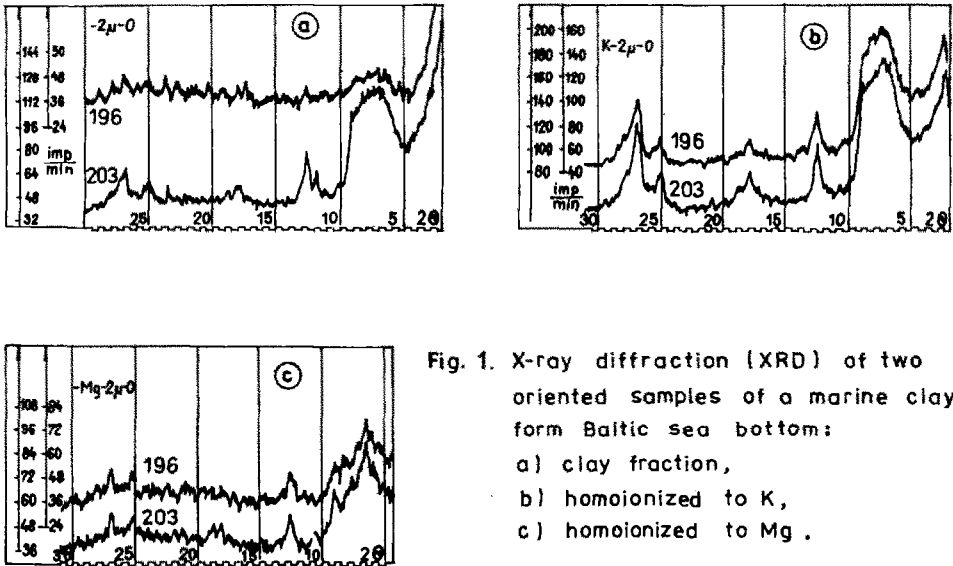
Fig. 1. X-ray diffraction (XRD) of two oriented samples of a marine clay form Baltic sea bottom:
a) clay fraction,
b) homoionized to K,
c) homoionized to Mg .

Geotechnical properties are indicated in Table 1. The natural water content was high, W_n = 42 - 66 %. Content of crystal phase water was estimated at W_h = 13 - 15 %, diffuse layer water at W_d = 16 - 19 % and macropore /interaggregate/ water W_{mac} = 13 - 32 %. Plastic limit was W_p = 21 - 28 % and liquid limit W_l = 51 - 69 %. Undrained shear strength was low, $S_u/U/$ = 5 - 11 kPa and it decreased after remolding to $S_u/R/$ = 2 - 6 kPa. Thus sensitivity $S_u/U/:S_u/R/$ varied between 1.8 and 2.5.

Remolded clays /R/ were placed in Wasiliew apparatus, were wrapped in plastic foil and freezed ten times for 6-7 h at - 20 °C leaving for ca. 18 h to unfreeze to room temperature. Changes in sample height were recorded: after shrinking in the first to third freezing cycle, some swelling was observed which was dependent on sampling depth, i.e. decreased from

TABLE 1

Geotechnical properties of the marine clay

Nr	Depth m	W_n %	W_p %	W_l %	S_U kPa	R	Sensi-tivity	W_h %	W_d %	W_{sec} %	Mo %
1	3.6	66	28	69	5	2	2.5	15	19	32	43
2	5.4	50	22	51	9	3	3.0	13	16	21	36
3	5.5	42	21	52	11	6	1.8	13	16	13	37

/1/ 21 % to /2/ 13 % and /3/ 6 %. Montmorillonite content /Mo/ decreased in a similar sequence from 43 % to 37 %.

Grain size distribution was measured before and after cyclic freezing and mainly some increase in content of coarser fractions was observed /Table 2/, especially in sample /3/ taken from the highest depth. This indicates aggregation processes.

TABLE 2

Final increase in volume $\Delta h/h_0$ and change in grain size distribution after freezing

Nr	Depth m	$\Delta h/h_0$ %	Content of fraction %		
			sand 0,05-2 mm	silt 0,002-0,05 mm	clay < 2 μm
1	3,6÷3,7 after freezing	21	6 1	36 41	58 58
2	5,4÷5,5 after freezing	13	19 20	31 26	50 54
3	5,5÷5,6 after freezing	6	12 26	34 24	54 50

To measure WS three unground specimen of ca. 300 mg of each sample were placed in aluminium containers, were dried at 110^0C and were stored for 10 days in a desiccator over the saturated $Mg/NO_3/_2$ solution /p/p_0= 0.5/, after which they were transferred to p/p_0 = 0.95 /over the 10 % H_2SO_4 solution/ for 16 days. They were dried again at 110 ^{0}C and heated successively at 220 ^{0}C, 400 ^{0}C and 800 ^{0}C. Weight changes were recorded and $\Delta G/G_0$ was calculated assuming as G_0 the initial weight of the oven dried specimen /Table 3/.

TABLE 3

Water sorption and weight loss in static heating in percent
/mean of three samples/

Nr	Sample Depth	State	W at p/p_0 = 0.5 %	W at p/p_0 = 0.95 %	ΔG /100- 800 °C %	W/0,95/ $-\Delta G$ %
1	3.6 - - 3.7 ▪	U R F	2.9 ± 0.2 2.5 0.2 1.6 0.3	15.2 ± 0.5 16.6 1.3 10.0 1.6	-10.8 ± 0.2 -11.6 0.7 -15.4 0.8	26 28 25
2	5.4 - - 5.5 ▪	U R F	1.7 ± 0.1 1.8 0.2 1.4 0.2	12.8 ± 0.8 11.8 1.0 10.5 0.3	-14.3 ± 0.4 -14.5 0.5 -15.1 1.5	27 26 26
3	5.5 - - 5.6 ▪	U R F	1.8 ± 0.2 2.0 0.3 1.9 0.2	13.0 ± 1.5 13.2 0.5 11.3 1.9	-15.0 ± 0.04 -15.0 0.3 -11.6 0.9	28 28 23

U - undisturbed, R - remolded, F - frozen cyclically

DISCUSSION

All the data /XRD, WS, TG/ indicate that marine clays from
the given region have a very unstable particle thickness, espe-
cially at lower sampling depth /sample 1/. WS at high p/p_0 = 0.95
is much bigger than that at p/p_0 = 0.5. Their ratio has an exce-
ptionally important value of 5.2 to 7.5, whereas in case of a
constant particle thickness it is ca. 1.5.

Prolonged storage in dry state caused a decrease in WS /thus
particle collapse/ by ca. 50 % [7] . Here freezing has a similar
effect, also dependent on sampling depth. Relative change in WS
varied from 36-40 % /1/ to 26-11 % /2/ and 4-14 % /3/ for p/p_0 =
= 0.5 and 0.95 respectively.

It was found that around ice lenses there is formed a paral-
lel particle arrangement both in monomineral clays [2] and in
soils [10]. This increase in domain thickness is due to /1/ cryo-
suction [1] and /2/ pressure exerted by the ice crystal being
formed. Such a microstructure may have an influence on WS, on
temperature of dehydration and on that of dehydroxylation as
well as on phase transformation during heating, see [9]. If un-
restricted, the parallel structure may sorb water and swell fre-
ely, thus high particle delamination may occur [4]. If trapped
within the cluster structure /Fig. 2/ its water sorption and
swelling is restricted, water escape during heating and dehy-

droxylation is hindered and phase transformation is most probable. Indeed decreased water sorption and important differences in Δ G were observed during heating /Table 3/.

After WS measurement the weight of the oven dried specimen decreased by 0.1 to 0.4 % = ΔG/110 $^{\circ}$C/. After heating at 220 $^{\circ}$C it decreased only by 0.8 to 1 %, whereas sample pretreatment influenced Δ G/400 $^{\circ}$C/, which varied between 1.5 and 2.7 %; even more the Δ G/800 $^{\circ}$C/ was influenced /11 to 15 %/, which change was just opposite to that of W /0.95/. To show this tendency the sum of W/0.95/ and - Δ G/800 $^{\circ}$C/ is presented in the last column of Table 3. This total change in weight varies in undisturbed samples and in the remolded ones between 26 and 28 %, whereas in freezed samples this variability ranges between 23 and 25.6 %. Thus the smallest total change in weight was indicated by freezed samples, where much parallel particle arrangement is to be expected. In this case not only increase in temperature of dehydration may occur, but also phase transformation is possible. Berkbent bentonite of parallel structure did not dehydrate completely at 400 $^{\circ}$C /and possibly even at 800 $^{\circ}$C/, which was indicated by a broadened peak at 9.7 $\overset{\circ}{A}$. This was possible due to surface melting of the parallel structure at 800 $^{\circ}$C.

Heating of bentonite resulted in phase transformation, which was indicated by new XRD peaks, that were most abundant in parallel structure, with cristoballite prevailing, whereas in cluster structure feldspar could be found. Depending on these transformations weight loss in heating may be either increased or decreased.

It may be concluded that suitable study of water sorption and weight loss in static heating of the pretreated specimen may give some information on changes in microstructure during the given process. Grinding or pulverization of the specimen may annihilate the investigated effect.

SUMMARY

In marine clays water sorption and weight loss in static heating change after cyclic freezing. The most probable explanation is the development in freezing of parallel structure /face-to-face contacts/. At lower sampling depth this causes mostly a decrease in WS and increase in temperature of dehydration. At higher sampling depth the additional effect may be the phase

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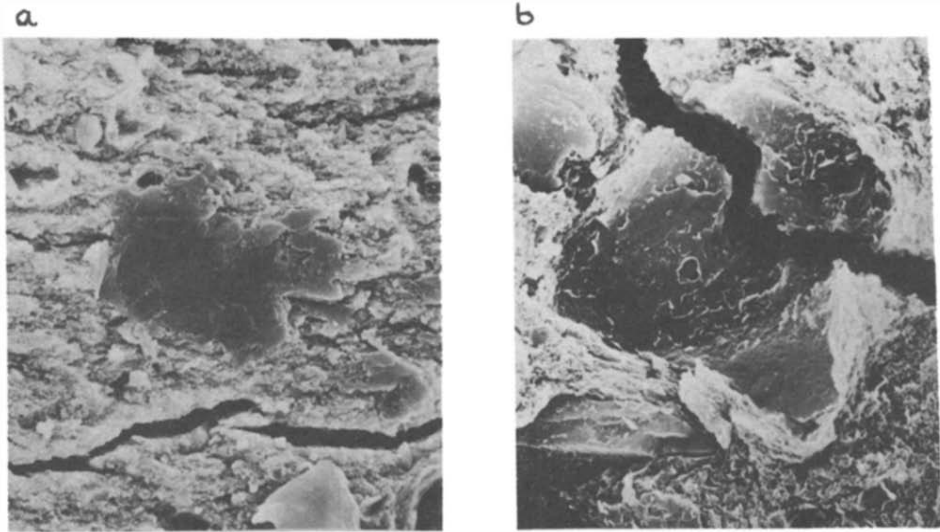
Fig. 2. Parallel structure formed within cluster matrix of
bentonite suspensions:/a/ Brabant, B/R-2, 500x, picture
breadth 200 µm, /b/ Barkbant, B/B-A, 2000x, picture
breadth 50 µm 9

transformation, which causes a decrease in Δ G /800 °C/.

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