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THERMAL STUDY OF AN AGED DREDGED SLUDGE

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Abstract

A dredged sludge was studied to investigate the influence of ageing and of pretreatment on its drying rate, water sorption/retention, thermal mass loss, XRD and microstructure (SEM).

Ageing caused change in particle thickness and specific surface, a gradual aggregation to form units of the size 10–50 μm, formation of macropores of similar size, unhomogeneity and fissures between aggregates and "super-aggregates". Macropores were detectable by the initial drying rate especially at 45°C. They indicated a tendency of collapsing at a lower drying rate at 30°C. This is consistent with SEM observations. With ageing the aggregates were more compact and less sensitive to drying.

The aggregated system indicated a higher initial drying rate (higher permeability), whereas stirring induced a lower drying rate, favouring the formation of compact laminar structure.

XRD peak intensity was lowered with ageing due to decrease in crystallinity (stacking faults and/or decrease in crystallite size). The content of amorphous material was lowered as well, reducing water sorption/desorption, which indicated that the specific surface is lower.

From the suitable microstructure induced by ageing some new phases may form (feldspar, zeolites), preferably in the coarser fraction of the sludge. This is disturbed by stirring which operation expels also carbonates from the particle edges and this may reduce the structural strength of the sludge. In aged bentonite suspension a similar tendency was observed of formation of specific microstructures capable of phase transformation, e.g. to feldspar.

Keywords: ageing, aggregation, dredged sludge, microstructure, zeolite formation.

Introduction

It was shown previously that ageing of a dredged sludge resulted in a change of the clay particle thickness and in gradual aggregation of these particles [1, 2]. Also the microstructure as measured by scanning electron microscope (SEM) was found to be dependent on the drying method, on the sample age and on stirring [3]. In this paper the effects of sample age on the followings are presented: (a) drying rate of the sludge, (b) water sorption or retention by the dried or original sample at various relative humidity conditions, (c) thermal mass loss. To interpret properly these effects (d) XRD was studied and (e) an example is given of the microstructural study by SEM. Here the test results will be presented and discussed in relation to the

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SEM study as described elsewhere [3]. This interpretation will concern the clay microstructure and its change with ageing i.e.: (a) particle thickness and particle arrangement, (b) aggregation causing an increase in long range attraction, (c) macropore water content.

Main conclusions of geotechnical interest were presented at the CATS Congress III [4].

Experimental

Materials

Dredged sludge H-0 was taken from a canal in Holland (Oude Maas-Botlek); it was described in detail elsewhere [1–3]. It contained illite, partly in mixed layers with smectite, kaolinite, quartz, calcite, feldspar and amorphous silica as determined by XRD, SEM, and EDAX. NaCl, numerous diatomea and one grain of anatase (titanium oxide) were identified. Initial water content was about $W_0=250\%$, liquid limit $W_l=120\%$, plastic limit $W_p=41\%$, clay fraction content was 15%.

After about four year storage in a closed container these values changed to $W_0=228\%$, $W_l=129\%$, $W_p=63\%$ and the content of clay fraction was 25%.

Samples were studied as supplied (series 0), after three months of storage at a temperature below 10°C (series I), after storing for additional one month and at room temperature (series II) and after four years at ambient temperature in a closed container at the initial water content (series IV). A part of this sample was transferred into two small containers: (1) after mild mixing (IV-USt) and (2) after vigorous stirring (IV-St).

Methods

Drying rate

Samples of the dredged sludge in triplicate were placed in cylindrical glass beakers with a base area of 20 cm^2 and a height of 5 cm. They were air-dried at atmospheric pressure at constant temperature (30 or 45°C) and the mass change with time was measured.

Water sorption and thermal mass loss

Water sorption (*WS*) of undried samples (as supplied) and of samples dried at 30, 45 and 110°C (28 days, 13 days and 1 day, respectively) was done at various relative water vapour pressures.

Water sorption (*WS*) of each sample was measured successively at $p/p_0=0.5$ and 0.95 for two weeks at atmospheric pressure and 30°C in desiccators over suitable solutions (saturated $Mg(NO_3)_2$ and 10% H_2SO_4, respectively) at 30°C. Water "retention" (*WR*) was measured in an inverse order, namely, first at $p/p_0=0.95$ followed by 0.5. The different water sorption and retention values will be assigned as *WS*(0.5), *WS*(0.95), *WR*(0.95) and *WR*(0.5) respectively. After the termination of sorption/retention study the samples were heated for one day at 110°C, for 8 h at 220°C, for 4 h at 400°C and for 1 h at 800°C. The values of water content and mass loss ($-\Delta G$) were calculated in relation to the mass of the sample after drying at 110°C (in percent).

The results of *WS*, *WR* and mass loss measurements are presented in Figs 3–5.

Study of microstructure by SEM

Microstructural study was done at TFDL Wageningen (by Mr K. Holsteijn) using SEM PHilips 535 at various magnifications. Results are described in detail elsewhere [3]. Here only one magnification (1000×) will be discussed.

Study of XRD

XRD study was performed in a Siemens Kristalloflex D 501 instrument equipped with a graphite monochromator and a computer SICOMP PC 16–20 with files of basal spacings of various standard minerals (JCPDS – Joint Committee for Powder Diffraction Standards).

Initially the XRD study was done in the year 1990 (''parent material'' H-0 I) and it was repeated in the year 1993 parallel with the SEM study (H-0 IV, USt and St): The results for H-0 I will be presented here for comparison and characterization of the material, whereas the study of aged samples will be discussed in detail.

All specimens: H-0 I and H-0 IV, IV USt and IV St, were investigated by XRD (a) in wet state, (b) in air dry state; after proper sedimentation they were homoionized to (c) Mg, (d) Mg and glycerol treated, (e) K and heated at 110°C.

Results and discussion

Drying rate

Drying rate was calculated, as $-\Delta G/\Delta t$; the mean values of triplicates are presented in Figs 1 and 2.

Drying rate was found to depend on:

(1) temperature and relative humidity of the environment: the rate of evaporation must be higher than the rate of condensation. Quicker drying was observed at 45 than at 30°C (Figs 1 and 2),

(2) permeability of the sludge, which is lowered in case of dense arrangement of structural elements,

(3) long-range forces between structural elements, i.e., repulsion which prevents drying and attraction which expels water and favours drying and which increases with size of interacting bodies [5, 6].

The least strongly bound water in the clay-water system is the interaggregate water (macropore water in the interconnected or closed pores of the size similar to

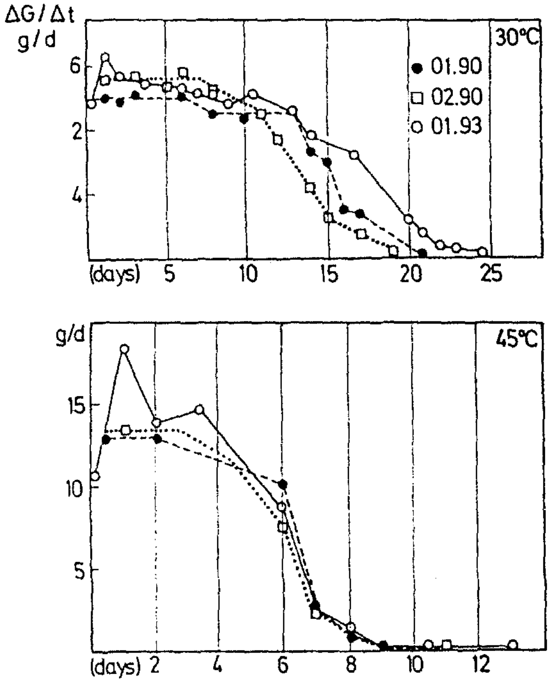

Fig. 1 Drying rate as a function of drying time of the dredged sludge stored for different times, series I, II and IV

aggregates themselves, by definition larger than about 500 Å [6]); it escapes in the first phase of drying.

At 45°C the biggest difference between samples stored for different periods of time is observed in this initial (and next "plateau") stage. Values for aged sample are the highest, which indicates aggregation with time and possible transformation of the intra-aggregate water into macropore water, which amount thus increases, whereas the density of aggregates must become higher. This effect is less pronounced in slower drying at 30°C but the escape of macropore water manifests in stepwise decreasing "plateaus" on the drying curve, the first one representing the escape of the macropore water. The following "plateau" represents the more strongly bound water.

This more strongly bound water occurs in mesopores (theoretically plane-parallel fissures between aggregates, clusters and between particles, defined as varying between about 20 and about 500 Å) [6]. A part of it escapes at a more or less constant drying rate forming the next "plateau stage", better discernible on drying at 30°C; it is possibly interaggregate water which escapes at this stage. On drying at this temperature a dense structure was formed. Such a structure indicated a lower permeability and a prolonged drying time, especially in aged samples (Fig. 1, drying at 30°C), which was not the case on drying at 45°C. Some influence may have also amorphous silica and/or alumina, "dissolved" or disrupted from the edges of

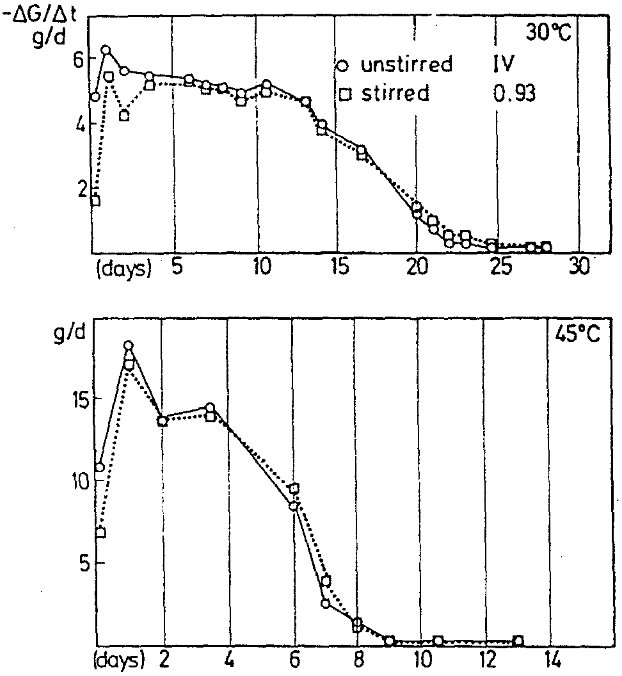

Fig.2 Drying rate as a function of drying time for the unstirred and stirred aged dredged sludge, series IV

clay particles and eventually forming colloids of a high specific surface. In this case the colloidal particles adsorb the cations in the diffuse layer on their surface causing the mutual repulsion. Also the particle size may decrease with storing time (see below, WST, SEM).

On further drying the drying rate decreases and it drops almost linearly with drying time which indicates that the water molecules are bound in the system with increasing strength. This stage may represent water loss from the spaces between clusters and between parallel particles.

Finally the micropore (interlamellar, intraparticle) water escapes forming a "tail" on the drying rate curve; by definition micropores are smaller than about 20 Å. This "tail" was especially long for the aged sample dried at 45°C (Fig. 1). It may be also due to the presence of small colloidal amorphous particles, formed during the long storage of the sludge (see below, XRD).

The drying is not completed and even at 110°C after long drying periods some water remains in the interlayer space. It is interesting to note, that at the end of drying the sample mass oscillates about the final mass by a fraction of mass percent.

The shape of drying curves of the unstirred and stirred samples of the aged sludge is similar, but the drying rate of the stirred samples is lower, especially on drying at 30°C (Fig. 2). This indicates that stirring did not disturb aggregation of the system, thus it did not reverse the ageing effect (which was expected). The lowering of the initial drying rate on stirring may be due to the formation of the laminar structure of lower permeability, which was observed in SEM (more laminar structure on drying at 30°C).

As it was mentioned above the drying rate depends on permeability (which was measured in oedometer for geotechnical purposes) and they may be compared in the following way:

$$ki = [1/A]\,[-\Delta G/\Delta t] \qquad (1)$$

where k is the coefficient of permeability in cm s^{-1} (Darcy's law), i is the hydraulic gradient (dimensionless), A is the drying surface area, here assumed as 20 cm^2, and the second term in parentheses is the drying rate. It is tacitly assumed that the drying rate is higher than permeability, thus this factor is decisive in drying.

The amount of evaporating water is equal to that flowing to the sample surface due to hydraulic gradient caused by suction of the dry air.

Table 1 Estimation of the value of *ki* from the drying rate, Eq. (1)

Sample/ series	Drying time	*ki* in 10^{-6} cm s^{-1}	
		30°C	45°C
H-0/I	2–4 h	2.8	6.2
	1–2 d	2.9	7.5
		OED (0-2 h), $k=1$–4	
H-0/II	2–4 h	2.8	6.9
	1–2 d	3.2	7.7
H-0/IV USt	0–2 h	2.8	6.1
	0–1 d	3.6	10.6
	2–5 d	3.1	8.4
H-0/IV St	0–2 h	1.0	3.3
	0–1 d	3.2	9.9
	2–5 d	3.0	8.0
H-I	0–1 h	2.7	5.9
	0–1 d	4.6	11.1
	4–7 d	3.4	7.8
		OED (0–4') $k=4$–6	
		(0–2 h) $k=3$	

OED – oedometer test

The calculated values of *ki* are presented in Table 1 and compared with *k* values measured in oedometer test (OED, [1, 2]). This is done also for another sludge H-I. The *k*-values are of the same order of magnitude as the *ki* values calculated from the drying rate. They are almost equal to those calculated from the drying rate at 30°C (water vapour pressure 32 mm Hg), whereas they are about half of the values of those calculated from the drying rate at 45°C (water vapour pressure 72 mm Hg); *k* was measured at room temperature.

Water sorption and thermal mass loss

The results of *WS*, *WR* and mass loss measurements are presented in Figs 3–5 and Table 2a–b. The meaning of these values is the following:

WS(0.5) is proportional to the specific surface (the ratio of external to internal specific surface proved to be constant) and inversely proportional to particle thickness. *WS*(0.95) is also proportional to the specific surface and to the amount of water accomodated by the given system (strongly bound water, sorbed water), most probably three-molecular layer on the external surface and in the interlayer space. *WR*(0.95) starting from a high water content may include as well some water retained in the diffuse layers. Also in this case more than three molecular layers may be present in the interlayer space. Both these cause the hysteresis, i.e. higher water retention than water sorption.

Table 2a Water desorption at p/p_0=0.5 and 0.95 and mass loss on heating betweeen 110°C and the temperature indicated, of the samples as supplied

Sample series	W_0/ %	*W*/% (0.95)	*W*/% (0.5)	110–220	110–400	110–800	400–800
				°C			
"0"	234	189	6.27	5.03	10.0	18.2	8.2
IV USt	220	155	7.04	4.16	9.6	17.7	8.1
IV St	230	172	7.29	4.64	9.2 [7.1]*	17.8	8.6

*This value was different than the remaining two in triplicate.

Table 2b Discrepency of test results in water sorption at p/p_0=0.95

Sample/ series	Dried at			
	30 and 110°C *WS*	45 and 110°C *WS*	30°C *WR*	45°C *WR*
I	34±7	36±13	38±14	38±14
IV USt	23±3	27±6	24±6	29±4
IV St	33 and 18*	26±10	27±3	25±8

*This value was different than the remaining two in triplicate.

Mass decrease on heating between 110 and 400°C is by definition "zeolitic" water (if organic matter is absent), including some interlamellar water in smectite. Mass loss between 400 and 800°C corresponds to dehydroxylation of clay minerals (4.5% for illite and smectite, 14% for kaolinite and 9% for chlorite, related to the sample mass at 400°C) and it may include decomposition of carbonates.

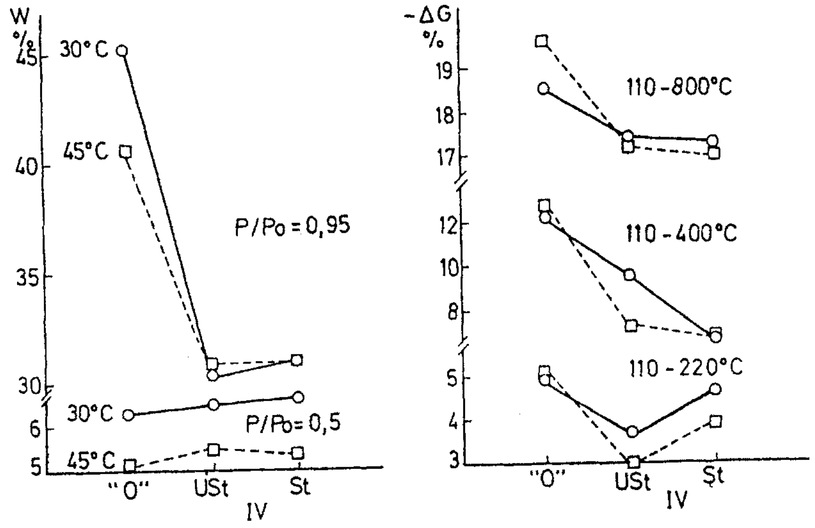

Fig. 3 Plot of the influence of ageing (series "0" compared to series IV) and stirring (IV USt compared to IV St) on water sorption (a) and on the thermal mass loss (b) of samples as supplied (circles) and dried at 110°C (squares). The initial water content was the following: sample "0" 252–264% (234% in *WR*), sample USt 222%, sample St 230–235%

Analysis of water sorption *WS*(0.5) indicates that some particle delamination with time occured during storage of the dredged sludge, i.e. the particle thickness decreased and the specific surface increased.

This is indicated by a slight increase in *WS*(0.5) of aged samples as supplied (USt, Fig. 3), as compared to the unstored ones ("0", Fig. 3). "Dissolution" of oxides may also occur to form amorphous material (see disscussion of drying rate). Drying at 110°C resulted in a significantly lower value of *WS*(0.5), thus particle collapse occured on drying, which is frequently observed in clays. The higher was the drying temperature the higher was its influence (compare drying at 30 and 45°C).

Thus aged and air dried samples (USt, Fig. 4) indicated also a lowering of *WS*(0.5), i.e. the particle collapse as compared to unstored samples (I, Fig. 4). This is due ruther to air drying than to ageing (which influence is indicated in Fig. 3).

This collapse was more efficient in aged samples and more efficient in drying at 30°C in which case the lowering of *WS*(0.5) is more pronounced.

A partial reversal of particle collapse was observed after stirring: small increase in *WS*(0.5) was found if the sample was either not dried (Fig. 3) or dried at lower temperature (Fig. 4). These observations are significant as the standard deviation of *WS*(0.5) was less than 0.1%.

In Table 2a there is presented the water desorption and mass loss on heating of the samples as supplied. In this case ageing increased the rate of water desorption at $p/p_0=0.95$ in the sample USt which was caused by aggregation but this effect was lowered after stirring (St). At $p/p_0=0.5$ water retention was higher in aged samples

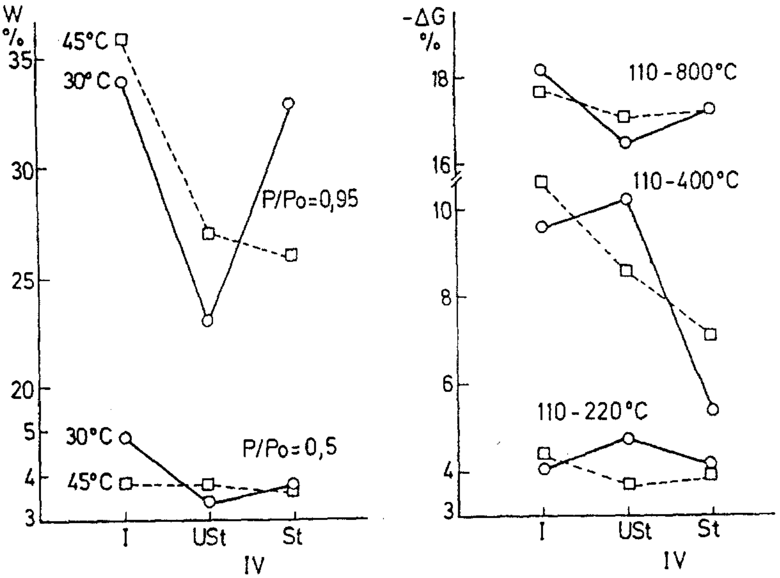

Fig. 4 Plot of the influence of ageing (series I compared to series IV) and stirring (IV USt compared to IV St) on water sorption (a) and on the thermal mass loss (b) of samples dried at 30°C (circles) and 45°C (squares). The air dry water content was the following: series I dried at 30 and 45°C, 3.96 and 2.74% respectively, series IV dried at 30 and 45°C, 2.8–2.9% and 2.2–2.4% respectively

(especially in the stirred one), which indicates particle delamination on ageing. Mass loss on heating was lowered with sample age, but this influence decreased with heating temperature and it concerned mainly the heating below 400°C (compare $-\Delta G$ 400 to 800°C).

All the sorption values of the air dried samples, as measured at $p/p_0=0.95$ indicate a high discrepancy, especially in unstored samples (Table 2b). This may be due to a high unhomogeneity of the sludge, which separated in storage into various microstructural phases and which was observed in freeze dried samples. In one case (IV-St-30°C) two values in triplicate were very similar but the third differed by 15% (Table 2b).

Whereas the *WS*(0.95) of unstored samples was lowered after drying at 110°C (Fig. 3, both in aged samples and in stirred samples these values are identical), it was higher in samples dried at 45°C than in those dried at 30°C (Fig. 4).

Lowering of *WS*(0.95) with sample age was more pronounced than that of *WS*(0.5), due either to the particle collapse with time, which in most cases was irreversible, or to the geometric hindrances for water sorption of the dense aggregated system. The stirring and drying at 30°C caused an almost complete reversion of this effect (Fig. 4). This value for samples stirred and dried at 45°C is lower for the average of three repetitions (Fig. 4) but the discrepency is high: two values were about 33% (i.e. close to the initial one) whereas the third was 18% (Table 2b).

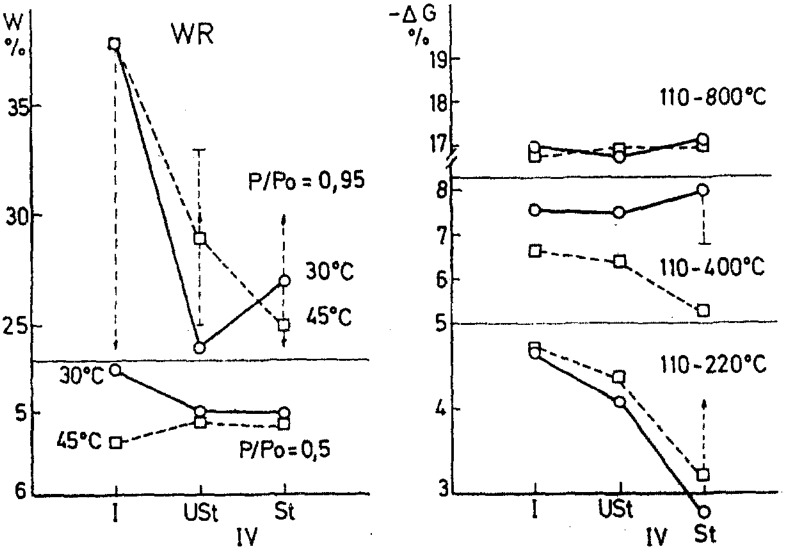

Fig. 5 Plot of the influence of ageing (series I compared to series IV) and stirring (IV USt compared to IV St) on water "retention" (a) and on the thermal mass loss (b) of samples dried at 30°C (circles) and 45°C (squares). The air dry water content was the following: series I dried at 30 and 45°C, 3.9 and 2.5% respectively, series IV dried at 30 and 45°C, 2.7–2.8% and 2.1–2.2% respectively

Similar results were obtained in water "retention" measurements (at decreasing relative water vapour presssure) of samples dried at 30 and 45°C (Fig. 5). The values of *WR*(0.5) are higher after drying at 30°C of the unstored sample, but they are similar after ageing and after stirring.

Most of the values of *WR*(0.95), Fig. 5, are a little higher than the respective values of *WS*(0.95), Fig. 4 (by 1–4%, hysteresis), except the stirred samples where the amount of sorbed water was lowered by 2–6%, most probably due to formation in stirring of the laminar structure, which is sensitive to particle collapse.

The interlamellar and "zeolitic" water content (mass loss both between 110 and 220°C and between 110 and 400°C, respectively) decreased pronouncedly with sample age in both the sludge as supplied and that predried at 110°C (Fig. 3). Water was somehow trapped in the sample structure. Stirring reversed this effect concerning the interlamellar water, but the decrease in zeolitic water content remained after stirring. It amounted to 2.6–3.5% in aged unstirred sample and to 5.5–5.9% in the aged stirred sample. A part of this is due to trapping of water molecules inside the structural elements and its escape at a more elevated temperature. There must be though some other effect, as the total mass loss between 110 and 800°C decreased as well by 1.2–2.7%, from 18.5 to 17.3% and from 19.7 to 17.0% (sample as supplied and sample air dried respectively) . This may be due to some phase transformation.

The difference is less apparent in Fig. 4, but a similar tendency is observed, with one exception of the aged stirred sample (IV USt) dried at 30°C. Possibly also here the interparticle and interlamellar water escaped at more elevated temperatures or there occured a formation of some new phase (zeolite-like phase?, see XRD, Figs 7–8). The total mass loss decreased only by 1.0–1.7% in sample dried at 30°C and by 0.5–0.6% in that dried at 45°C being in the first case 18.2–16.5% and in the second case 17.7–17.1%.

Different results were obtained in *WR* test (Fig. 5): the escape of interlamellar water was removed to more elevated temperatures, exceeding 220°C. This was completely (sample dried at 30°C) or partly (sample dried at 45°C) recovered on heating at 400°C and the differences in mass loss are much lower. Finally the total mass loss between 110 and 800°C was almost the same in all the three samples, i.e. 16.8–17.1%.

The results described above indicate that they are sensitive to sample microstructure which depends on sample preparation as well as on measurement conditions (sequence of relative humidity). The measured value always concerns the sample prepared in the given way and studied by the given method. The extrapolation to the undisturbed state must be done with caution.

Microstructural study by SEM

SEM study must be performed on the dried system, but properties and microstructure of clays both depend on the drying conditions [7, 8]. Here the simplest method was chosen of air drying at two constant temperatures, i.e. 30 and 45°C. In freeze drying, which is frequently used in sample preparation for SEM [9–14] specific artifacts are formed. Also the critical point drying does not preserve the microstructure of the clay-water system [12, 15, 16].

The unstored sludge indicated a more or less homogeneous microstructure but with time the unhomogeneity and aggregation increased [1]. This unhomogeneity was the reason of the high dispersion of test restults obtained in sorption test.

Figure 6 shows that ageing caused an increase in size, thickness and compactness of some structural elements, which resulted in an increase in attraction between them (aggregation) and thus caused a higher initial drying rate and a lower water sorption after drying (particle collapse). Some differences are visible in the Fig. 6 between the samples dried at different drying temperatures and between the unstirred and stirred samples.

In sample dried at 30°C the aggregates of the size about 10–50 μm have an ellipsoidal shape and are more compacted and more uniformly distributed; a similar size and shape have the macropores. After drying at 45°C both the aggregates and the macropores of a similar size are more isodimensional.

Stirred sample dried at 30°C shows lamina of dense parallel clay particles which lamina are in more or less random orientation and have the thickness of about 3–10 μm. The permeability in the direction perpendicular to the lamina is small. Also one can expect that diffuse layer repulsion is prevailing inside them, delaying drying and thus extending the "plateau" stage on the drying curve and also the final drying stage (Figs 1 and 2). In the sample dried at 45°C lamina are less compact,

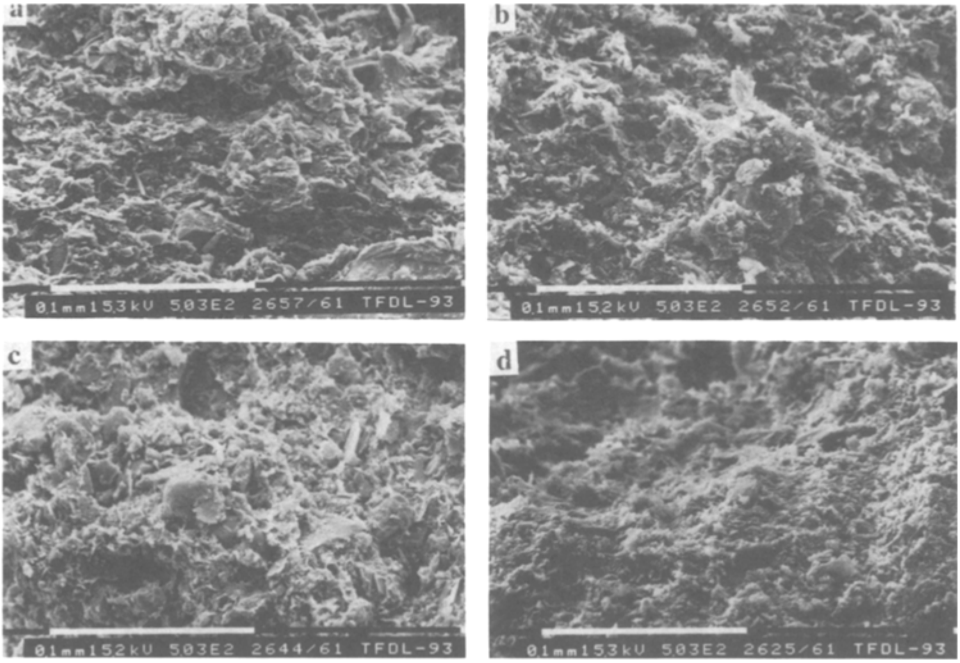

Fig. 6 Microstructure revealed by SEM at primary magnification 503×. Samples dried at 30°C a) USt, 2657, b) St, 2652. Samples dried at 45°C c) USt, 2644, d) St, 2625

less distinct and have a more wavy shape. The sample surface is uneven and it contains big macropores in top left corner (Fig. 6d).

The difference in thickness of the lamina indicates that the particles were properly oriented in stirring, the lamina formed on drying and their density was higher after slower drying at lower temperature.

All these results indicate, that drying at 45°C influences the least the microstructure of the system under study, which was observed also in other systems.

Study by XRD

In the Fig. 7 there are compared the XRD traces of wet and dry dredged sludge, both unstored (I) and stored for four years (IV) in the original container, or transferred half the year earlier to a smaller container, unstirred (IV USt) or after vigorous stirring (IV St). In Fig. 8 the XRD traces are compared of the clay fraction of the samples mentioned above, homoionized to K, Mg and Mg-glycerol treated.

To obtain the mineral composition of the dredged sludge, the XRD trace of IV (dry) was compared with the ASTM d-spacings of standard clay minerals (JCPDS file). The peaks were interpreted as belonging to: (1) low quartz, (2) calcite (3.02 Å etc), (3) kaolinite (eventual chlorite, 14, 7, 3.5 Å etc), (4) illite (trioctahedral, 10, 5, 3.34 Å etc), (5) microcline with possible albite, thus K- and Na-feldspars (3.24 Å).

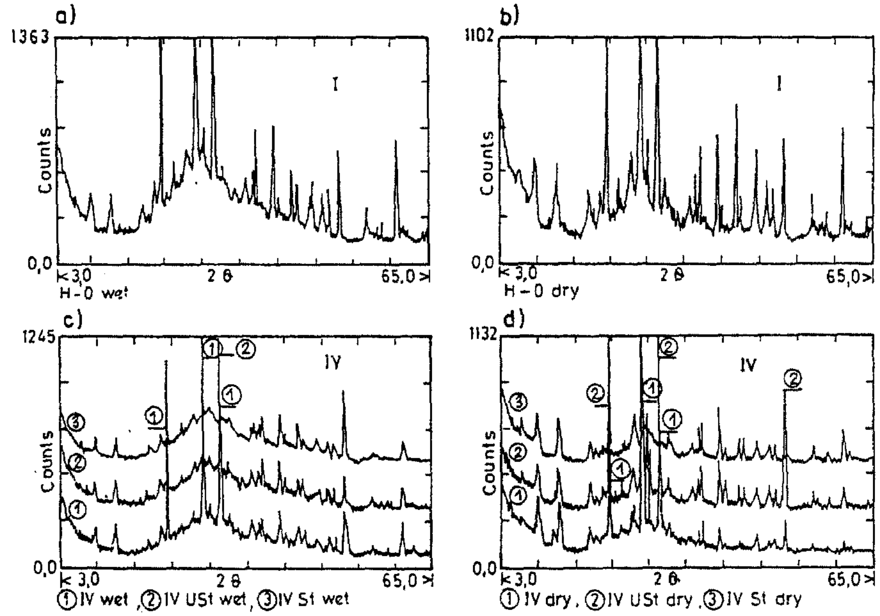

Fig. 7 XRD traces of the dredged sludge unstored, H-0 (a–b) and that aged, series IV (c–d) in wet state (a and c) and in air dry state (b and d)

Table 3 Basal spacings (XRD) of the dredged sludge H-0 I dry and their relative intensities (compare Fig. 7b)

No.	*d*/Å	*I*/%	No.	*d*/Å	*I*/%	No.	*d*/Å	*I*/%
1	14.2	7	9	3.340	100	17	2.125	12
2	9.95	8	10	3.192	10	18	1.995	6
3	7.09	8	11	3.030	32	19	1.978	9
4	4.98	6	12	2.884	7	20	1.909	7
5	4.46	6	13	2.556	5	21	1.871	6
6	4.24	32	14	2.489	7	22	1.816	10
7	3.846	7	15	2.453	9	23	1.540	11
8	3.526	9	16	2.278	10	24	1.451	4

Some new peaks were observed and/or the peak intensity increased in certain aged samples as compared to the original one. This is interpreted here as topotaxial phase transformation of a suitable microstructure, formed on storing and/or drying, which was also observed in aged bentonite suspensions [17]. On the other hand the accessoric minerals could have been unevenly distributed in the sludge and could have appeared in certain diffractograms only.

Figures 7 and 8 indicate that all the peaks are better formed and are of higher intensity (show better crystallinity or bigger crystallites) in the parent material H-0 I (called below shortly I) than in the aged samples IV. On the other hand the water sorption increased after ageing only if measured at $p/p_0=0.5$ (Fig. 3), whereas at $p/p_0=0.95$ its decrease was found. This apparent inconsistency may be explained by the formation of stacking faults [20] on storing and/or stirring as the cause of decrease in XRD peak intensity (and not particle delamination).

Delamination of crystallites and their disintegration into smaller units was observed in some other clays on storage for 1 month, whereas after more prolonged storage water sorption decreased thus either the particle thickness was higher or geometrical hindrances impeded water sorption.

The background between $d=4.2$ and 2.5 Å is higher in unstored sample (I) and in the wet state, which is logical (more amorphous material before drying). There

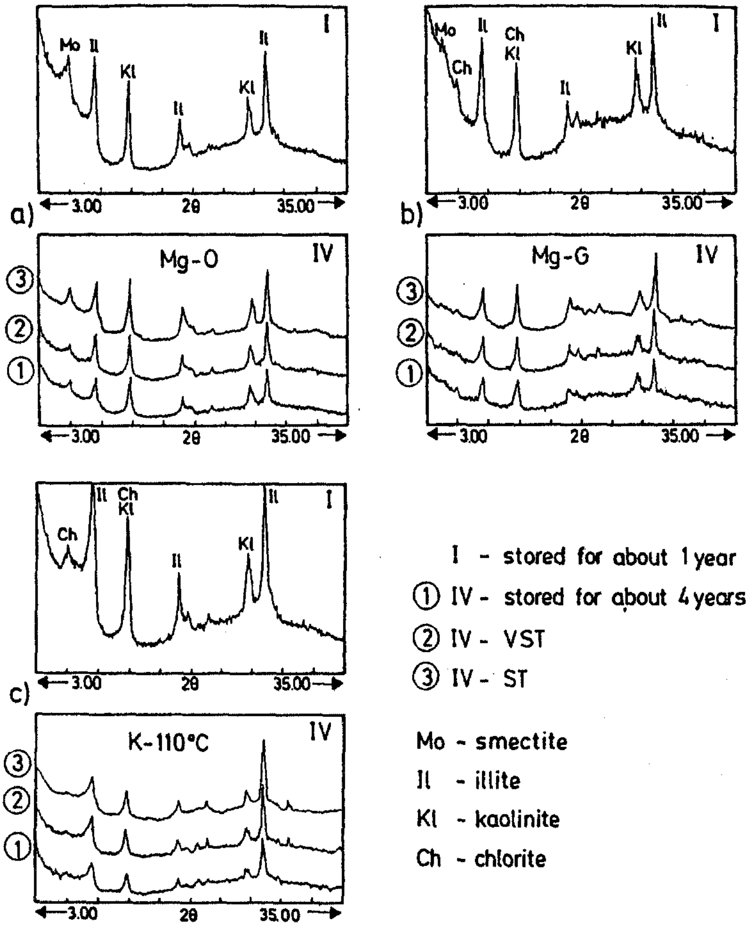

Fig. 8 XRD traces of the dredged sludge unstored (H-0) and that aged, series IV, fraction <2 μm homoionized to Mg (a) and glycerol treated (b), homoionized to K and heated at 110°C (c)

are more peaks in sample I than in samples IV, either due to dissolution and recrystallization of some amorphous compound or to phase transformation on drying.

All the three aged samples (IV) indicate in wet state a similar peak intensity (Table 2, Fig. 7). Only the peak at 1.81 Å (quartz) of the stirred sample (St), is the highest, and that of unstirred sample (USt) is the lowest. The broad band about 3.18–3.20 Å increases somewhat in intensity in the sequence IV < USt < St.

The sample IV (dry), Fig. 7, is the only one which indicates a strong peak at 3.24 Å, which may belong to microcline and which may have formed during drying of the sample from the suitable microstructure formed in ageing (topotaxial phase transformation [17]). Also this sample indicates more peaks at lower spacings than any other one, which supports the assumed possibility of formation of new phase on drying. The suitable microstructure was disturbed on sampling (USt sample) and on stirring (St sample), thus the new phase could not form.

The intensity of some peaks at high 2Θ angles is in samples USt and St higher than in the sample IV. Also the quartz and calcite peaks at 4.24 and 3.02 Å, respectively increase in the sequence IV < USt < St. Stirring might have caused

(1) "uncovering" of feldspar grains from the interiour of aggregates and
(2) dissolution of some calcite and its recrystallization in a better form including

the amorphous carbonate and/or calcium compounds attached to particle edges and forming contact bonds, which was observed in other similar systems [19]. The feldspar peak at 3.24 Å, which is so strong in sample IV (dry), is visible also in sample USt (dry), whereas in sample St (dry) it is barely detectable at 3.19–3.24 Å, which indicates the possibility of its formation from the suitable microstructure, disturbed by sampling and stirring.

Most of the homoionized samples, Fig. 8, were well oriented and did not show the 4.45 Å *hkl* peak, except IV-Mg and all the K-samples (4.49 Å). This is in agreement with the tendency to form the laminar structure (SEM).

In the clay fraction the crystallinity decreased also with ageing (similarly as in Fig. 7): the peaks are better formed and indicate higher intensity in the parent material (I) than in the aged one (IV).

The clay fraction of the unstored sludge (I) contains appreciable amount of smectite and mixed layers: the high background at low 2Θ angles and the 14 Å peak of smectite, moving partly to 19 Å after glycerol treatment, both decrease in intensity in the aged samples (Fig. 8 a–b). This explains the lowering of water sorption with ageing.

The intensities of the 14 Å (Mg) peak and 19 Å (Mg-glycerol, Fig. 8 a–b) are roughly equal that of illite at 10 Å, which in turn has a higher intensity than the 7 Å peak of joint chlorite and kaolinite. After prolonged storage (IV) the background at low 2Θ angles decreased, the lowered intensity of the 14 Å peak and of other peaks changed in the sequence IV < USt < St and the intensity of the 10 Å peak became similar to that at 7 Å.

In K-110°C samples the intensity of the 10 Å peak became higher exceeding that of 7 Å peak, whereas the peak intensity at 3.34 Å was considerably enhanced in the sequence IV < USt < St. This proves the tranformation of smectite into illite on K-treatment. All the peaks indicate though a much lower intensity in the aged samples.

The incomplete collapse of the 14 Å spacing in K-treated sample may be due to (1) the presence of chlorite, (2) the unhomogeneous surface charge of the parent smectite and (3) the presence in the interlamellar space either of polymerized aluminum or iron ions (oxyhydroxides) or of organic matter.

Calcite (peak at 3.02 Å) was not observed in the fine fraction of homoionized samples (only in IV St-Mg sample the 3.04 Å peak was detectable). Probably the carbonate particles sedimented in the coarser fraction, where they were eventually present as cementing material.

It is interesting to note that both the wet and dry samples indicated systematically a slightly lower spacing of illite (9.84–9.95 Å) and kaolinite (7.05–7.09 Å), than the homoionized fine fraction (10.0–10.05 Å and 7.15–7.17 Å respectively). It is suggested here that this might be due to a mineral of coinciding peaks which was present in the untreated sample and sedimented with the coarser fraction before homoionization. As such a mineral, one of the zeolites is possible, e.g. chabasites indicate peaks at 9.26–9.44 Å, 4.29–4.33 Å, 3.84–3.89 Å, 3.55–3.66 Å, 2.911–2.998 Å, etc. Natural mordenite has the peaks at 9.06 Å, 4.00 Å, 3.476 Å, 3.394 Å, 3.221 Å, 3.201 Å etc. [18].

Also the double peaks at 3.57–3.59 Å and 3.53–3.54 Å may be due to (1) the third order reflexion of chlorite, (2) the second order reflexion of kaolinite or (3) zeolite, e.g. chabasite 3.55–3.66 Å.

Conclusions

Drying rate

Comparative measurements of the drying rate on the clay-water system of a high water content may give some valuable information on the microstructural changes occurring with time and/or stirring.

The initial increased drying rate indicates (1) the free macropore water; its content is higher in the aged samples, which is better manifested on drying at 45°C than at 30°C, (2) stepwise aggregation proceeding with time which causes an increase in attraction between structural elements, and expulsion of water from the pores and fissures between them.

Stirring of the aged sludge did not change the shape of the drying curve, but caused its lowering: the aggregates were little disturbed but there was induced the formation of laminar structure, which lowered the drying rate due to lowered permeability (SEM). This caused also a longer drying time of aged samples dried at 30°C. From the drying rate the coefficient of permeability may be estimated, comparable to that measured in oedometer.

Water sorption and thermal mass loss

Water sorption/desorption at $p/p_0=0.95$ decreases with ageing, indicating an increase in aggregation and possibly in particle thickness: the rate of water desorption is higher after storage of the sludge and the final value is lower. This is partly reversible after stirring and air drying (Fig. 4). Some particle delamination is shown by *WR*(0.5).

Zeolitic water content is smaller after storage and after stirring, but the change of mass loss 400–800°C is reversed. Thus the escape of zeolitic water may be moved to higher temperature, possibly due to formation of laminar structure.

The mass loss 400–800°C of unstored samples after sorption measurement (6.3–8.6%) was generally lower than that of aged ones (6.3–9.9%) and it was even higher after stirring (10.1–11.8%, related to oven dry mass at 110°C); it is 4.5% in smectite and illite and 14% in kaolinite (as related to the mass at 400°C). This value was higher in *WR* samples (8.2–10.2%) and it changed only slightly both after ageing and stirring (8.1–11.7%).

Some phase transformation is possible in the aged samples as the mass loss 110–800°C decreased after sorption measurements in most of the aged samples by 0.5–2.7%. Thus

(1) water sorption depends on sample age, sample preparation and sequence of p/p_0 conditions, due to variation in size of structural elements,
(2) mass loss on heating depends strongly on sample pretreatment (age, storage conditions, etc.) causing variations in microstructure, geometrical hindrances of water escape and possibly topotaxial phase transformation.

Microstructure studied by SEM

Ageing causes the formation of aggregates and macropores between them which increases the drying rate and is better discernible after drying at 45°C. Stirring induces the partial formation of laminar structure which prevents drying, thus decreasing drying rate and is better discernible after drying at 30°C due to suction on drying [21].

Study by XRD

Definite conclusions are difficult to draw, but it is suggested here that ageing and/or eventual stirring of the sludge causes some minute changes in XRD patterns, indicating the decrease in crystallinity (peak intensity) with ageing and decrease in content of amorphous material. The content of smectite and mixed layers is also lowered. This is in agreement with the changes of water sorption after prolonged storage.

There is a possibility of the formation of some new phases on drying of the stored sludge due to the presence of a suitable microstructure, e.g. K- and Na-feldspar (microcline) could have formed during drying of the stored sludge H-0 IV. This microstructure is disturbed by stirring which prevents new phase formation on drying of the sludge H-0 IV St.

Stirring resulted in a better crystallinity of calcite peak at 3.02 Å. This compound could have been adsorbed on the particle edges, whereas it can be removed and recrystallized after stirring.

Some evidence was found of the presence of zeolite, especially in the coarser fractions of the dredged sludge.

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