SWELLING OF ACID TREATED BENTONITES

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Five smectites and one illite-smectite mixed-layer clay were treated in 1.5 mol.dm^{-3} HCl. High swelling materials were prepared from SWy-1, Jelšový Potok and Komloska montmorillonites. The swelling (or sedimentation) volumes (SV) achieved after 10 minutes activation were not affected by temperature in the range 22 to 96 °C. The duration of the acid treatment at 22 °C in the range 5 to 30 minutes increased the SV of Komloska, but had negligible effect on SWy-1 and JP-3. The order of the SV SWy-1 > JP-3 > Komloska was achieved under any investigated preparation conditions.

Smectites are the main minerals in bentonites. Their physicochemical properties determine the chemical and industrial utilization of bentonites. The most common and important smectite is montmorillonite. It consists of negatively charged sheets, each composed of one octahedral and two tetrahedral layers. The exchangeable cations in the interlayer space compensate for the negative charge of the sheets, arising from the heterovalent substitution of the central atoms in both octahedra and tetrahedra. The expanding layer lattice and the presence of exchangeable cations are the most unique properties of smectites. Where Na^{+} is the predominant exchangeable cation, smectites may have a high swelling capacity. Sodium tends to promote the development of many oriented water layers on interlamellar surfaces. The hydration associated with Na may produce swlling to the extent of complete dissociation of the individual smectite crystals [1].

Both the smectite layers and the exchangeable cations influence the structure and properties of interlayer water [2]. Swelling does not depend directly on the cation exchange capacity or on the surface charge of the sheets and it decreases with increasing substitution of Fe and Mg for Al [3, 4]. Stucki et al. [5] reported a reversible relationship between the oxidation state of octahedral Fe and the swellability of smectites. Increasing the amount of Fe(II) in the octahedral sheet decreased the water content of smectites at any given swelling pressure [6]. Wu et al. [7] found the reduction of Fe affects the short-range interlayer forces, but not the long-range ones.

H-forms of smectites are known as unstable materials, undergoing autotransformation to (H,Al) – or (H,Al,Mg)-forms [8]. Except Na-smectites, also their Li- and H-forms are good swelling ones [9, 10]. The formation of high sedimentation volume is due not only to the ion-exchanging complex in the interlayer, but also to an inhomogeneous distribution of charge (adsorbed ions) on the surface of the particles. This volume was found to be affected by the clay and by the kind and concentration of the acid used, by the temperature and the duration of the reaction, and by the ageing of the activated samplex [11, 12].

The aim of this study was to investigate the effect of time and temperature of treatment in 1.5 mol.dm^{-3} HCl on preparation of high swelling materials from the fine fractions of six bentonites.

MATERIALS AND METHODS

Materials

The less than 2-μm fractions of bentonites from Crook County, (Wyoming, USA, Source Clays Repository of the Clay Minerals Society, SWy-1) Jelšový Potok, (Slovakia, JP-3), Los Trancos (Almeria, Spain, LTA), Ond (Hungary), Komloska (Hungary, KOM), and Friedland (Germany) were used. The clays were Ca^{2+} saturated, dialyzed, air-dried at 60 °C and ground to pass through a 0.2 mm sieve.

Montmorillonite was the main mineral in all samples except Friedland. No other minerals were identified by X-ray diffraction in Jelšový Potok, quartz was found in SWy-1, Ond and Los Trancos Almeria, quartz and feldspar (sanidine) in Komloska. The structural formulas calculated from the chemical analyses using the method of Kelley [13] are given in Table I. The mineralogical composition of the clay from Friedland is 44 wt% swelling silicates, 24 wt% quartz, 12 wt% muscovite, 11 wt% kaolinite, 5 wt% feldspar, traces of carbonate and pyrite [14]. The mixed-layer illite-smectite contains 60–70% swelling layers [15].

Methods

Acid treatment

One gram of the sample was added to 100 ml of 1.5 mol.dm^{-3} HCl preheated to the required temperature. The mixture was kept at this temperature for ten minutes and stirred every three minutes. After that it was let to sediment for five minutes in a graduated cylinder. The liquid was discarded and about

Table I

Structural formulas of <2-μm fractions of Ca-saturated montmorillonites calculated from the chemical analyses

	tetrahedral		octahedral			interlayer
	Si	Al	Al	Fe	Mg	Ca
SWy-1	7.95	0.05	3.07	0.40	0.49	0.33
JP-3	7.92	0.08	2.94	0.32	0.73	0.40
LTA	7.53	0.47	3.18	0.17	0.75	0.61
Ond	7.54	0.46	3.08	0.22	0.70	0.58
KOM	7.90	0.10	2.66	0.62	0.82	0.46

	Temperature [°C]				
	22	40	60	80	96
Sample	SV [cm^3g^{-1}]				
SWy-1	49	50	49	60	55
JP-3	41	36	35	38	38
KOM	20	24	21	21	17
Ond	6	6	5	5	6
LTA	7	6	7	6	6
Friedland	5	4	5	4	4

10 ml H_2O was added to the sediment. The suspension was put on filter and washed with 250 ml H_2O, dried at 60 °C and ground to pass through a 0.2 mm sieve.

Swelling volume

Swelling volume (SV) was determined by pouring successively 400 mg of the sample into 25 ml of H_2O in a graduated cylinder. Next batch of the sample was added always after the previous amount sank to the bottom. The volume of the gel (SV) was measured two hours after the first part of the sample was poured in. The SV was determined about four hours after the acid treatment has been finished. Two parallel measurements were made, they did not differ more than ±10% from their average value.

RESULTS AND DISCUSSION

The swelling volumes of 1.5 mol.dm^{-3} HCl treated clays are given in Tables II and III. Three of the clays used – SWy-1, JP-3 and Komloska – produced good swelling materials. Swelling of the other three ones – Ond, Almeria and Friedland – was not affected by the acid treatment and remained low (Table II). The low swellability of the mixed-layer clay from Friedland was expected according to its mineralogical composition. Poor swelling of the acid treated smectites Ond and Almeria is unknown. It could be caused by their specific surface areas and cation exchange capacities, which affect the interaction between the layer surfaces and water. This interaction was found to be the most important in the swelling of montmorillonite [16].

The temperature of the treatment affected the SV of the clays insignificantly. The same order of SV was achieved after the treatments at any temperature: SWy-1 > JP 3 > Komloska (Table II). Wyoming montmorillonite is known as a very good swelling one. Both samples from Upton, Wyoming, ranked in swelling first to third among 35 Na-smectites investigated by Low [16] at various swelling pressures.

The influence of the treatment time at 22 °C on the SV was investigated with the three good swelling clays from Table II. The results are presented in Table III. The duration of the reaction had negligible effect on swelling of SWy-1 and JP-3. The SV values of Komloska were increasing with the treatment time.

The exchange of interlayer cations in smectites is very rapid. Over 75% of cations were exchanged at 25 °C within first three seconds of the reaction [17]. Consequently, the transformation of the original Ca-forms of the clays to their H-forms was finished within the first five minutes of the reaction, which was the

Table III

Swelling volumes of clays treated by 1.5 mol.dm^{-3} HCl at 22 °C for various duration of the reaction

	Time [min]			
	5	10	20	30
Sample	SV [$cm^3.g^{-1}$]			
SWy-1	53	49	50	59
JP-3	40	41	41	43
KOM	13	20	22	29

shortest duration time used (Table III). High SV values were reported also for samples treated only three minutes in HCl [12].

No substantial differences in the exchangeable cations of the materials prepared were expected (Table II and III). The degree of decomposition of the octahedral layer is low. The half-time of dissolution of the octahedral layer decreases with increasing substitution of iron and magnesium for aluminium [18]. It is about 13 hours for Jelšový Potok montmorillonite at 96 °C in 1.5 mol.dm^{-3} HCl. Significant decomposition of the clays could occur neither in ten minutes at 22 to 96 °C, nor in 30 minutes at 22 °C. That means the composition of the layers of each clay after the mild acid treatment was close to the composition of the untreated clay. Slight differences in the population of interlayer cations could be expected, however, after ageing of materials prepared by different HCl treatments. Ageing causes autotransformation of H-smectites to their (H,Al,Mg)-forms, and H^+ concentration in the interlayers affects this process. The swelling of acid treated clays was observed to decrease on ageing because of autotransformation and equalization of the originally inhomogeneous surface charge distribution [11].

Hydrated protons in the interlayer space are important for formation of a voluminous sediment. The SV are affected by both exchangeable cations and sorbed anions present in the system [12] . The cations compensate for the negative charge of the 2:1 sheets, the anions saturate the broken bonds on the edges. In other words, the cation compensation prevails on the faces and the anion compensation on the edges of the particles. Stabilization of the anionic sorption complex on the edges of the crystallities is supposed to be influenced by the treatment conditions and the clay used. Favourable conditions for the origin of voluminous gels were not affected by the treatment time with SWy-1 and JP-3, but longer treatment at 22 °C increased the SV values of Komloska (Table III).

CONCLUSIONS

High swelling materials could be prepared from the fine fractions of bentonite SWy-1, Jelšový Potok and Komloska by activation in 1.5 mol.dm^{-3} HCl. The SV achieved after a 10 minutes activation were not affected by temperature in the range 22 to 96 °C. The duration of the acid treatment at 22 °C in the range 5 to 30 minutes increased the SV of Komloska, but had negligible effect on SWy-1 and JP-3. The order of the SV SWy-1 > JP-3 > Komloska was achieved under any investigated preparation conditions.

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NAPUČIAVANIE BENTONITOV UPRAVOVANÝCH KYSELINOU

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Jemné frakcie bentonitov SWy-1 (Wyoming, USA), JP-3 (Jelšový Potok, Slovensko), Los Trancos (Almeria, Španielsko), Ond a Komloska (oba Maďarsko) a zmiešanovrstevnatého ílu Friedland (Nemecko) sa aktivovali 10 minútovým pôsobením 1.5 mol.dm^{-3} HCl pri teplotách 22 až 96 °C. Po premytí sa vzorky usušili pri 60 °C, rozdrvili a stanovili sa ich sedimentačné objemy (SV). Z bentonitov SWy-1, JP-3 a Komloska sa získali materiály s vysokými SV, kým u ostatných ílov boli tieto objemy nízke. To sa očakávalo u zmiešanovrstevnatého ílu Friedland, zatiaľ čo príčina nízkych SV vzoriek Los Trancos a Ond zatiaľ nie je známa. Teplota reakcie mala v skúmanom intervale zanedbateľný vplyv na hodnoty SV (Tab. II). S rastúcim časom pôsobenia kyseliny (5 až 30 minút) rástli SV vzorky Komloska, kým SV SWy-1 a JP-3 sa podstatne nemenili (Tab. III). Pri všetkých použitých reakčných podmienkach prípravy vzoriek bolo poradie nameraných sedimentačných objemov rovnaké: SWy-1 > JP-3 > Komloska.