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DISSOLUTION OF THE FINE FRACTION OF JELŠOVÝ POTOK BENTONITE IN HYDROCHLORIC AND SULPHURIC ACIDS

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Dissolution of < 20 μm fraction of bentonite from Jelšový Potok, Czechoslovakia, in 6 mol . dm^{-3} HCl and 2 mol . dm^{-3} H_2SO_4 is compared. The sequence of the smectite structure decomposition, the shapes of the dissolution curves, and the changes in XRD patterns and IR spectra in the course of acid dissolution are similar. Differences in the structural formulas calculated from the dissolution data are attributed to the uncertainity introduced by a slow dissolution of volcanic glass in H_2SO_4. Structural formula calculated from the dissolution in HCl expresses more correctly the montmorillonite composition as the formula calculated from the bulk chemical analysis or from the dissolution than H_2SO_4. About one third of the mass of the sample was found to be extraneous to the montmorillonite and is supposed to be bound in feldspar and mainly in a volcanic glass.

INTRODUCTION

Decomposition of montmorillonites by acids is a complex of simultaneous processes. They can be described in terms of the montmorillonitic structure as an exchange reaction between interlayer cations and the surrounding acid solution, succesive dissolution of octahedral sheets, and succesive dissolution of tetrahedral aluminium ions. The mechanism and kinetics of smectite dissolution in HCl have been described by various authors, e.g. [1—10]. Literature dealing with smectite dissolution in H_2SO_4 is less frequent than the former, e.g. [11—14]. The data given are consistent with those of HCl as regards the mechanism of the processes. According to our knowledge, no data about dissolution of one and the same smectite in both HCl and H_2SO_4 have yet been published. Both these acids are used in bleaching earths production.

Decomposition of a smectite structure by an acid can be divided into the following steps: contact (wetting of the surface by the acid, filling of the interlayer space), chemical reaction, transport of the reaction products from the reaction zone and transport of fresh components to it. In the course of contact, the acid covers the dry surface of the smectite and fills the inerlayer space of the mineral. Simultaneously, an ion exchange reaction proceeds. This reaction is very fast. At least 70 % of the exchangeable cations are exchanged within the first five seconds at 25 °C [15].

H-smectites are known as unstable materials, undergoing autotransformation to (H, Al)-smectites. This process starts immediatly. According to the data by Barshad and Foscolos [16], the half-time of smectite autotransformation varies between 1.10^3 and 8.10^5 seconds for different smectites.

The dissolution of octahedral cations is much faster compared to tetrahedral aluminium [3—5, 17]. Since the dissolution of smectites in acids is a reaction

of a polydisperse system of solid particles with a liquid, its rate is also influenced by particle size distribution and defects in the structure [17].

The purpose of the present study was to investigate the differences between the HCl and H_2SO_4 treatments (1) with respect to the dissolution process of the fine fraction separated from Jelšový Potok bentonite and (2) with that to the structural formulas of motmorillonite calculated from the bulk chemical analysis and from the dissolution data.

EXPERIMENTAL

Material

Under 20 μm fraction of bentonite Jelšový Potok, Czechoslovakia, was used. Montmorillonite, feldspar and mica were identified by X-ray diffraction. The chemical analysis is given in Table I, and the formal structural formula calculated here from in Table II. The calculation was performed in the way usual for the monomineral montmorillonite. The high Si coefficient suggests some extraneous Si in the sample. Magnesium is present in both octahedral and exchangeable posi-

Table I

Chemical analysis (CA) of the sample and the distribution of SiO_2, Al_2O_3, Fe_2O_3, MgO and CaO calculated from the dissolution data in 2 mol . dm^{-3} H_2SO_4 and 6 mol . dm^{-3} HCl (exch. = = exchangeable, oct. = octahedral, tetr. = tetrahedral, extr. = extraneous)

	CA	2 mol . dm^{-3} H_2SO_4				6 mol . dm^{-3} HCl			
		exch.	oct.	tetr.	extr.	exch.	oct.	tetr.	extr.
	mass %								
SiO_2	62.59	—	—	39.78	22.81	—	—	37.47	25.12
Al_2O_3	19.65	—	14.34	2.12	3.19	—	11.99	1.24	6.42
Fe_2O_3	2.61	—	1.28	—	1.33	—	1.30	—	1.31
MgO	4.29	0.60	2.19	—	1.50	0.60	2.92	—	0.77
CaO	1.94	1.40	—	—	0.54	1.42	—	—	0.52
K_2O	0.34				0.34				0.34
Na_2O	0.28				0.28				0.28

Table II

Structural formulas of Jelšový Potok motmontmorillonite calculated for $O_{20}(OH)_4$ from the bulk chemical analysis (CA)[1] and from the dissolution data in 2 mol . dm^{-3} H_2SO_4 and 6 mol. dm^{-3} HCl

	Si	Al	Al	Fe	Mg	Ca	Mg	K	Na
CA	8.01	—	2.97	0.25	0.78	0.27	0.04	0.06	0.07
H_2SO_4	7.56	0.44	3.25	0.18	0.57	0.28	0.12		
HCl	7.74	0.26	2.95	0.20	0.85	0.31	0.23		

[1] This formula shows the statistical distribution of atoms only since it was calculated as for monomineral montmorillonite.

tions. Its distribution was calculated using the condition of electroneutrality (the negative charge of the layers compensates for the positive charge of the exchangeable cations).

Methods

Acid dissolution. 500 ml of acid in a 1000 ml glass reaction vessel with a reflux was placed in a constant temperature water bath and heated to 369 K. Five grams of the sample were added. The reaction mixture was occasionaly stirred and allowed to react for the desired time. After that it was filtered, the filter cake was washed twice with 200 ml water, dried at 333 K, ground to pass through 200 μm sieve. The filtered liquid combined with the washing solutions was analysed for Al, Fe, Mg and Ca using standard methods UV—VIS spectroscopy and AAS. The data reported in Fig. 1 and 2 are the mean values of duplicates. α is the relative amount of the cation dissolved at time t ($\alpha = w_t/w_0$, w_t is the amount of the cation dissolved at time t and w_0 is its amount in the untreated sample).

A modified method of Osthaus [3, 4, 17] was used for the calculations of fast soluble, octahedral, tetrahedral, and extraneous aluminium, ferric iron, magnesium and calcium from dissolution curves. Unsoluble (under the conditions of treatments) portions of Al^{3+}, Fe^{3+}, Mg^{2+} and Ca^{2+} were considered to be extraneous to the montmorillonite structure.

X-ray diffraction. A Philips X-ray set, model PW 1050, Cu—Kα, 40 kV, 18 mA, and randomly oriented samples were used.

IR spectroscopy. A Perkin-Elmer 983 G spectrometer, and KBr pressed disk technique (0.3 mg sample + 200 mg KBr) were used.

RESULTS AND DISCUSSION

The dissolution curves of the 20 μm fraction of Jelšový Potok bentonite in 6 mol . dm^{-3} HCl and 2 mol . dm^{-3} H_2SO_4 at 369 K are given in Figs. 1 and 2, respectively. The curves in both figures are extrapolated to $t = 0$ to obtain the distribution of cations in the untreated sample. The distribution of Si, Al, Fe, Mg, and Ca, as calculated from both dissolution data, is given in Table I. The shapes of the respective curves are similar with both acids, showing the similar

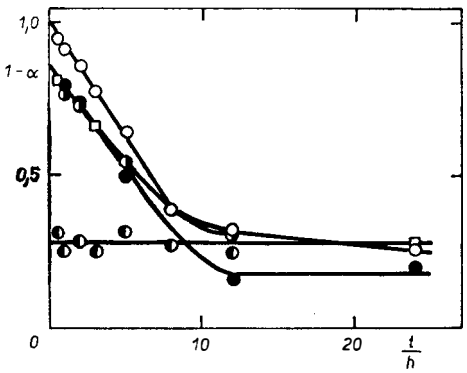

Fig. 1. Dissolution curves (extrapolated to $t = 0$) of Jelšový Potok bentonite in 6 mol . dm^{-3} HCl at 369 K. α — relative amount of the cation dissolved. ○ Al, ▫ Fe, ● Mg, ▪ Ca, ▫ double point.

course of the dissolution process. The fastest part of this process is the exchange of interlayer cations, mainly calcium and magnesium in this sample. Both HCl and H_2SO_4 treatments showed about 72 % of total calcium, and about 14 % of total magnesium to be soluble very rapidly. These Ca^{2+} and Mg^{2+} ions are considered to be bound in the montmorillonite interlayer.

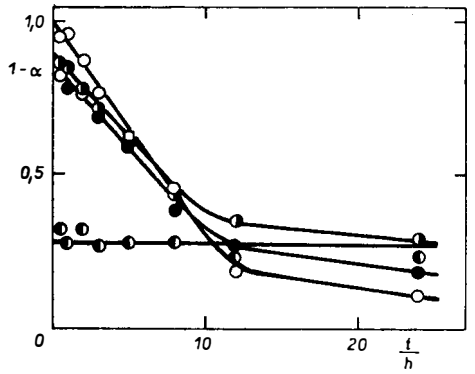

Fig. 2. Dissolution curves (extrapolated to $t = 0$) of Jelšový Potok bentonite in 2 mol . dm^{-3} H_2SO_4 at 369 K. α — relative amount of the cation dissolved. o Al, ▫ Fe, • Mg, ▪ Ca, □ double point.

The rest of Ca^{2+} (0.54 wt. % CaO) is insoluble in both acids under these conditions, and not a part of the montmorillonite structure. The amount of extraneous Mg depends on the acid used. The dissolution of Mg in HCl is concluded after about 12 hours, but the dissolution in H_2SO_4 proceeds at a slower rate even after this time (Figs. 1 and 2). Since no magnesium is supposed to be bound in the tetrahedra, the slow dissolution in 2 mol . dm^{-3} H_2SO_4 is that of some other, nonmontmorillonitic phase, probably feldspar and/or volcanic glass. This different solubility results in the different amounts of extraneous and octahedral magnesium calculated from dissolution curves. Extrapolation of the straight lines ($t > 12$ hours) of the curves to $t = 0$ gave the extraneous magnesium, and the difference between the total, exchangeable and extraneous Mg corresponds to octahedral magnesium (Figs. 1 and 2, Table I).

The differences in the share of fast soluble iron, 16 % of total Fe in HCl and 11 % in H_2SO_4 (Table I), are not significant according to the standard deviation of the method used (± 3 % of the total Fe content). Iron oxide phases were recently identified in various size fractionated smectites [18—20].

According to Mossbauer's investigation, no iron is bound in the tetrahedra. Neither the octahedral nor the extraneous iron, calculated from HCl and H_2SO_4 dissolutions, differ significantly (Table I).

Fast soluble aluminium was found neither in HCl, nor in H_2SO_4. Extrapolation of both dissolution curves to $t = 0$ led to $\alpha = 0$. The amounts of tetrahedral and extraneous aluminium differ according to the different solubilities in the acids used. The higher solubility in H_2SO_4 gave 27 % of total Al as tetrahedral plus extraneous aluminium, while the respective result in HCl was 39 %. Using a modified method by Osthaus [3], more tetrahedral and less extraneous Al was calculated from H_2SO_4 dissolution data than from the HCl data (Table I).

As expected from the CA structural formula (Table II), extraneous SiO_2 was

found using both H_2SO_4 and HCl data. The respective result from dissolution in HCl was 25.12 % (Table I).

Calculation of the montmorillonite content in the sample from the montmorillonitic and extraneous parts of the oxides yielded 68 % of montmorillonite in the sample using the H_2SO_4 dissolution data, and 63 % from the HCl data.

The structural formulas of the montmorillonite were calculated using the data of Si, Al, Fe, Mg, and Ca distribution from the dissolution in 2 mol . dm^{-3} H_2SO_4 and in 6 mol . dm^{-3} HCl (Table I). K_2O and Na_2O are considered to be components of feldspar and mica, and therefore are not included in the calculation of the structural formulas. The results are given in Table II.

Both formulas calculated from acid dissolution differ from that calculated from bulk chemical analysis mainly in the tetrahedral population. This difference is mostly due to the rather high extraneous SiO_2 content in the sample. The tetrahedral substitution also influences the negative charge on the montmorillonite layer, associated with the calculation of the interlayer cationic population. This is indicated by the low coefficient of exchangeable magnesium in the structural formulas (Table II).

No substantial differences were found in the coefficients of exchangeable cations and octahedral iron in H_2SO_4 and HCl structural formulas (Table II). Solubility of these parts of smectite, and the distribution of Fe and Ca is about the same in both acids used (Table I). The slow dissolution in 2 mol . dm^{-3} H_2SO_4 of extrane-

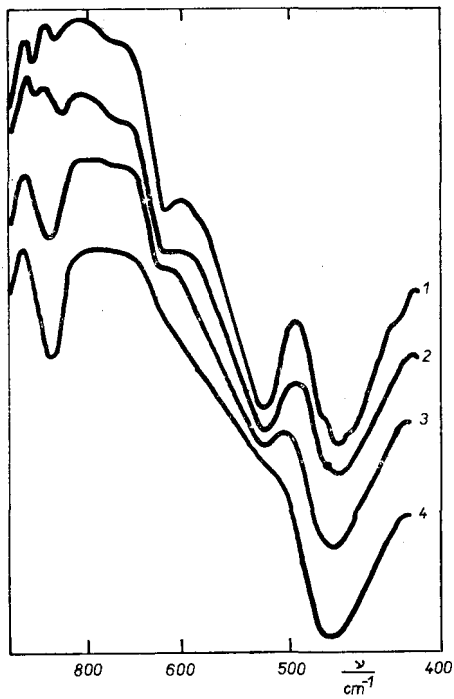

Fig. 3. IR spectra of Jelšový Potok bentonite. Untreated — 1, treated with 2 mol . dm^{-3} H_2SO_4 at 369 K for 4 hours — 2, 8 hours — 3, 12 hours — 4.

ous components, which are insoluble in 6 mol . dm^{-3} HCl, is reflected in the different coefficients of octahedral Al and Mg, and tetrahedral cations. In view of these facts, the structural formula calculated from the dissolution data in 6 mol . dm^{-3} HCl is considered to express most correctly the real composition of this montmorillonite.

The IR spectra and XRD patterns of the untreated and H_2SO_4 treated samples are given in Figs. 3 and 4, respectively. The changes in the course of HCl treatment were very similar. The R_2OH (R = Al, Fe, Mg) absorption band intensities in 800—950 cm^{-1} region decrease with the prolongation of the acid treatment. A new absorption band of free SiO_2 appears at 805 cm^{-1}.

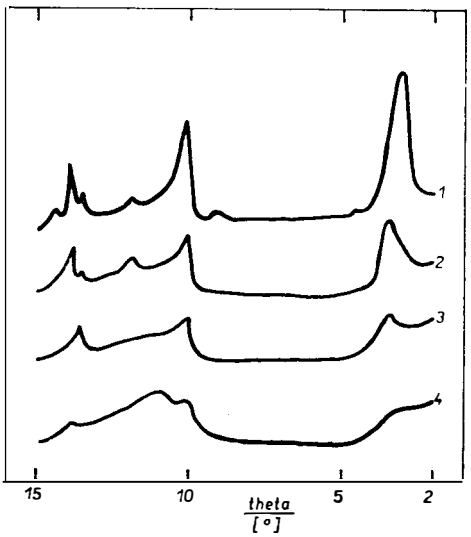

Fig. 4. X-ray patterns of Jelšový Potok bentonite. Untreated — 1, treated with 2 mol . dm^{-3} H_2SO_4 at 369 K for 4 hours — 2, 8 hours — 3, 12 hours — 4.

The absorption band at 623 cm^{-1} attributed to R—O—R vibrations, as well as the band at 520 cm^{-1}, attributed to Si—O—R, gradually disappeared as the decompostion of octahedral sheets proceeded. The gradual changes in absorption band intensities associated with the decomposition of octahedral sheets by HCl are given in [6, 17].

The dissolution of octahedral sheets can be considered complete if no more bands are detectable at 623 and 520 cm^{-1}. In our case this occurred after 12 hours of digestion in H_2SO_4 (Fig. 3) or HCl.

Intensities of both the 001 and hk diffractions are influenced by the leaching of octahedral layers, but the 001 are more sensitive (Fig. 4). The 001 diffraction disappears nearly completely in the course of 12 hours of treatment, and the 005 diffraction at 14.5 degrees theta is not distinguishable after four hours. The ordering in the direction Z (perpendicular to plane 001) is more dependent on the degree of the octahedral sheet decomposition. The diffuse diffraction band between 9 and 14 degrees theta, visible in XRD pattern N° 4, indicates the presence of an amorphous matter.

CONCLUSIONS

A high degree of similarity has been found in the dissolution of Jelšový Potok montmorillonite in 6 mol . dm^{-3} HCl and 2 mol . dm^{-3} H_2SO_4 at 369 K. Similar were sequences of the smectite structure decompostion, the shapes of the dissolution curves, and the changes in XRD patterns and IR spectra. Differences were found in the structural formulas calculated from the dissolution data in both acids. With respect to the slow dissolution of volcanic glass in sulphuric acid, the structural formula calculated from HCl dissolution is considered to express more correctly the real composition of this montmorillonite. The montmorillonite content in the sample amounts to about two thirds. Most of the extraneous mass is supposed to be bound in volcanic glass and feldspar.

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ROZPÚŠŤANIE JEMNEJ FRAKCIE BENTONITU JELŠOVÝ POTOK V KYSELINE CHLOROVODÍKOVEJ A SÍROVEJ

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Porovnáva sa rozklad v 6 mol . dm^{-3} HCl a v 2 mol . dm^{-3} H_2SO_4, frakcie pod 20 μm, separovanej z bentonitu Jelšový Potok. Pre obe kyseliny je podobný postup rozkladu štruktúry smektitu, tvar rozpúšťacích kriviek (obr. 1 a 2), a zmeny infračervených spektier a röntgenových difrakčných záznamov (obr. 3 a 4) v priebehu reakcie. Pomalý rozklad vulkanického skla v H_2SO_4 ovplyvňuje výpočet rozdelenia jednotlivých katiónov na časť viazanú v oktaédroch a tetraédroch smektitu a na časť viazanú mimo štruktúry smektitu (tab. I). Kryštalochemický vzorec vypočítaný z rozpúšťacích kriviek v HCl vyjadruje presnejšie reálne zloženie montmorillonitu ako vzorce vypočítané z chemickej analýzy alebo z rozpúšťania v H_2SO_4 (tab. II). Približne tretina hmotnosti frakcie pod 20 μm nie je viazaná v montmorillonite. Jej časť je viazaná v živci a predpokladá sa, že väčšina tohto materiálu je súčastou vulkanického skla.

Obr. 1. Rozpúšťacie krivky (extrapolované k t = 0) bentonitu Jelšový Potok v 6 mol . dm^{-3} HCl pri 369 K. α — rozpustené relatívne množstvo daného katiónu

Obr. 2. Rozpúšťacie krivky (extrapolované k t = 0) bentonitu Jelšový Potok v 2 mol . dm^{-3} H_2SO_4 pri 369 K. α — rozpustené relatívne množstvo daného katiónu

Obr. 3. Infračervené spektrá bentonitu Jelšový Potok. Pôvodný — 1, po rozklade v 2 mol . dm^{-3} H_2SO_4 pri 369 K 4 h — 2, 8 h. — 3 a 12 h — 4

Obr. 4. Röntgenové difrakčné záznamy bentonitu Jelšový Potok. Pôvodný — 1, po rozklade v 2 mol . d.$^{-3}$ H_2SO_4 pri 369 K 4 h — 2, 8 h — 3 a 12 h — 4

РАСТВОРЕНИЕ ТОНКОЙ ФРАКЦИИ БЕНТОНИТА ЕЛШОВЫ ПОТОК В ХЛОРОВОДОРОДНОЙ И СЕРНОЙ КИСЛОТАХ

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В предлагаемой работе сравнивается выщелачивание фракции ниже 20 μм, выделенной из бентонита Елшовы Поток, в 6 мол дм$^{-3}$ HCl и в 2 мол. дм$^{-3}$ H_2SO_4. Для обеих кислот подобна последовательность разложения структуры смектита, форма кривых растворения (рис. 1 и 2) и изменения инфракрасных спектров и рентгеновских дифракционных записей (рис. 3 и 4) во время хода реакций. Свидетельством медленного разложения вулканического стекла в H_2SO_4 является расчет разделения отдельных катионов на часть, связанную в октаэдрах и тетраэдрах смектита и на часть, связанную вне структуры смектита (табл. 5). Кристаллохимическая формула, рассчитанная на основании кривых растворения в HCl более точно отражает реальный состав монтмо риллонита, чем формулы, расчитанные ра основании химического анализа или на основании растворения в H_2SO_4 (табл. II). Приблизительно одна треть веса фракции ниже 20 μм не связана в монмориллоните. Ее часть связана в полевом шпате и предполагается, что большинство данного вещества является составной частью вулканического стекла.

Рис. 1. Кривые растворения (экстраполированные к t = 0) бентонита Елшовы Поток в 6 мол. дм$^{-3}$ HCl при 369 K; α — относительно растворенное количество данного катиона.

Рис. 2. Кривые растворения (экстраполированные к t = 0) бентонита Елшовы Поток в 2 мол. дм$^{-3}$ H_2SO_4 при 368 K; α — относительно растворенное количество данного катиона.

Рис. 3. Инфракрасные спектры бентонита Елшовы Поток. Исходный — 1, после разложения в 2 мол. дм$^{-3}$ H_2SO_4 при 369 K после 4 часов — 2, после 8 часов — 3 и после 12 часов — 4.

Рис. 4. Рентгеновкие дифракционные записи бентонита Елшовы Поток. Исходный — 1, после разложения в 2 мол. дм$^{-3}$ H_2SO_4 при 369 K после 4 часов — 2, после 8 часов — 3 и после 12 часов — 4.

NOVÉ DRUHY KERAMICKÝCH MATERIÁLŮ byly vyvinuty pracovníky University of California v Los Angeles. Jde o tzv. amorfní kovalentní keramiku — nekrystalickou verzi známých druhů keramiky na bázi nitridu Si nebo karbidu W. Výhodami této keramiky je snížení teploty vypalování z 1650 °C na 425 – 760 °C, zkrácení doby vypalování z několika hodin na 20 minut a velmi snadná tvarovatelnost. Amorfní keramika není tak tvrdá a žáruvzdorná jako její krystalické protějšky, ale je možné ji tvarovat vstřikováním i nanášet stříkáním na různé povrchy před vypalováním.

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Frynłová