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DISSOLUTION OF SMECTITES IN HYDROCHLORIC ACID: II. DISSOLUTION RATE AS A FUNCTION OF CRYSTALLOCHEMICAL COMPOSITION

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Abstract—A correlation was made of crystallochemical data from 15 smectites with the half time of dissolution (t_{05}) in 6 N hydrochloric acid at 96°C. From this the relation

$$\ln t_{05} = 3.95 - 1.96\ Fe^{VI} - 2.30\ Mg^{VI}$$

was developed. It shows a remarkable dependence of the apparent dissolution rate of the octahedral layer of the smectites on the substitution of Fe^{3+} and Mg^{2+} for Al^{+3} in the octahedral position.

Key Words—Crystallochemical, Dissolution, Hydrochloric, Nontronite, Smectite.

INTRODUCTION

The kinetics and mechanism of dissolution of smectites in HCl have been described by various authors such as Brindley and Youell (1951), Karšulin and Stubičan (1954), Osthaus (1954, 1956), Packter (1955), Granquist and Gardner-Sumner (1959), Fahn (1963), Turner (1964), Čičel et al. (1965), and many others.

Although there is sufficient data on the dissolution of smectites in HCl, no attempts have been made to find the relation between the crystallochemical characteristics of these minerals and the reaction rate of this process. Attention, therefore, is drawn to the role of substitutions in the structure of smectites as a possible reason for changes of the apparent dissolution rate, measured under constant temperature and concentration of the acid.

MATERIALS AND METHODS

Characteristics of the samples

Mineralogical and chemical analyses of purified and Ca-saturated samples are given in Table 1.

Acid dissolution

A 500-mg sample was extracted in 100 ml of 6 N HCl at 96°C for different time intervals. After leaching in HCl the samples were filtered and washed with distilled water. Leaching in HCl was performed for ¼, ½, ¾, 1, 1½, 2, 3, 5, 8, 12, 24, 48, and 72 hr. In each filtrate the content of Al_2O_3, Fe_2O_3, MgO, and CaO was determined. The leaching of octahedral ions was checked by IR spectrometry using the gradual disappearance of the absorption band at 490 cm^{-1} characteristic for Al_{oct}–O bond.

Expression of dissolution rate

To avoid the difficulties in expression of the true mechanism and kinetics and, finally, to compare the apparent dissolution rates of smectites, a new measure, the halftime of dissolution (t_{05}), has been introduced (Čičel and Novák, 1976). It is the time in which just 50% of the central atoms from the octahedra are leached out. Its value can be determined graphically from the plot of α or $(1 - \alpha)$ against time, where α is a portion of material reacted.

To find the halftime of dissolution for nontronites at 96°C it was necessary to adopt an indirect way because of the extremely high dissolution rate. We determined the t_{05} values at 35, 40, 50, and 70°C and extrapolated these values for 96°C.

Starting with the Arrhenius equation in the form

$$k = Ae^{-\frac{E}{RT}} \quad (1)$$

where k is the specific rate constant [hr^{-1}], A is a constant, E is the activation energy in [cal $mole^{-1}$], R is the gas constant [cal deg^{-1} $mole^{-1}$], T is the absolute temperature, and when we take the analytical form of the function

$$t_{05} = f(k) \quad (2)$$

then we may express the Arrhenius equation in a form, which would express the relation between the activation energy of the reaction and the halftime of dissolution of the sample as follows:

$$t_{05} = A'e^{-\frac{E}{RT}} \quad (3)$$

where A′ is a constant different from that in Equation 1. This is a linear dependence until E remains constant and thus the value t_{05} may be read for the temperature of 96°C, as it is shown in Figure 1 for the sample Nova Ves.

For the samples Otay, Belle Fourche, Polkville, Garfield, and Clay Spur we have calculated the t_{05} values

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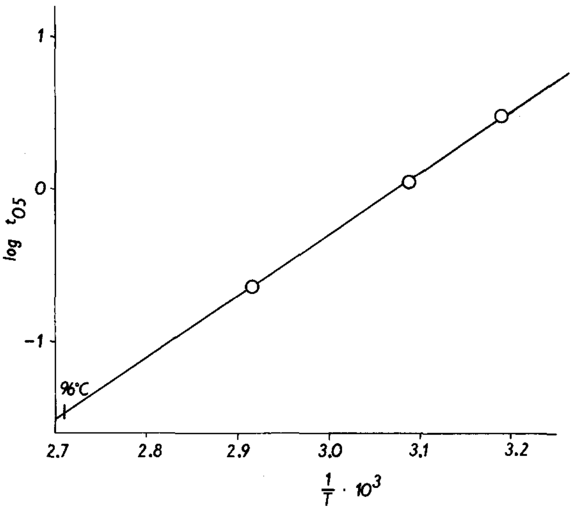

Fig. 1. Values of the natural logarithm of the t_{05} plotted against the 1/T values.

Table 2. Crystallochemical formulae of smectites and half-time of dissolution of the octahedral layer.

No. Sample	Substitution Tetrehedral Si	Al	Fe	Octahedral Al	Fe	Mg	$t_{0.5}$ hours
1 Garfield[1]	7.05	0.18	0.77	0.97	2.98	0.05	0.158
2 Polkville[1]	8.00	0.00	0.00	2.93	0.12	0.98	3.65
3 Belle Fourche[1]	7.61	0.39	0.00	3.10	0.43	0.46	15.1
4 Clay Spur[2]	7.73	0.23	0.04	3.17	0.36	0.51	12.6
5 Ottay[1]	8.00	0.00	0.00	2.56	0.12	1.41	6.25
6 Kuzmice	7.86	0.14	0.00	3.11	0.23	0.62	3.24
7 Fintice	7.79	0.17	0.04	2.74	0.33	0.93	2.12
8 Askangel	7.92	0.08	0.00	2.78	0.36	0.80	1.87
9 Kriva Palanka	7.74	0.26	0.00	2.96	0.27	0.75	1.52
10 Badín	7.20	0.65	0.15	1.82	2.02	0.14	0.276
11 Sampor	7.30	0.57	0.13	0.00	3.84	0.02	0.029
12 Nová Ves	7.26	0.27	0.47	0.00	3.91	0.00	0.029
13 Skl. Teplice	7.43	0.57	0.00	2.21	1.30	0.43	5.03
14 St. Kremnicke	7.27	0.60	0.13	2.40	1.36	0.25	2.88
15 Braňany	7.10	0.90	0.00	2.50	1.25	0.32	2.15

[1] B. B. Osthaus (1956)
[2] R. Turner (1964)

using the analytical data of Osthaus (1954, 1956) and Turner (1964).

RESULTS

For the correlation of crystallochemical characteristics of smectites with the apparent dissolution rate of the octahedral layer in HCl we have used the data from 15 samples of montmorillonites and nontronites. This is given in Table 2. The t_{05} values are for the leaching of octahedral aluminum in montmorillonites and octahedral iron in nontronites.

The measured values of t_{05} have been used for calculating coefficients for the relation

$$t_{05} = f(Me^{IV}, Fe^{VI}, Mg^{VI}) \qquad (4)$$

where t_{05} is the halftime of dissolution [hr]; Me^{IV} is the sum of Al and Fe atoms present in tetrahedra; Fe^{VI} is the amount of Fe atoms present in octahedra; Mg^{VI} is the amount of Mg atoms present in octahedra.

The amount of Me^{IV}, Fe^{VI}, and Mg^{VI} is expressed in the form of coefficients from the crystallochemical formulae calculated per unit cell.

The general equation for the regression analysis is

$$\ln t_{05} = a + b_1Me^{IV} + b_2Fe^{VI} + b_3Mg^{VI} \qquad (5)$$

Table 1. Mineralogical and chemical analyses of the samples.

Chem. anal.	KUZMICE	FINTICE	ASKANGEL	KRIVA PALANKA	BADÍN	SAMPOR	NOVÁ VES	SKLENÉ TEPLICE	STARÁ KREMNIČKA	BRAŇANY
SiO_2	55.02	60.75	51.66	51.73	46.32	45.40	46.09	53.71	54.65	44.22
Al_2O_3	18.80	12.19	15.60	17.71	13.48	2.99	1.30	11.70	15.65	17.95
Fe_2O_3	2.46	2.93	3.10	2.81	18.56	32.85	33.56	12.90	10.64	10.32
TiO_2	—	0.88	0.24	nd.	—	nd.	—	nd.	—	4.10
MgO	2.81	2.80	3.43	2.80	0.60	0.10	—	2.42	0.88	1.34
CaO	2.84	2.48	3.14	2.71	2.94	3.36	2.73	1.18	0.93	2.83
Total H_2O	17.88	16.65	21.54	21.78	18.09	15.17	15.94	16.10	15.31	19.05
Total:	99.81	98.68	98.71	99.54	99.99	99.87	99.62	99.29*	99.47**	99.81
Free SiO_2	9.0°	25.6°	—	—	—	—	—	20.49°	34.08°	—
Free Al_2O_3	2.60	1.8	—	—	—	—	—	2.30	3.66	—
Free Fe_2O_3	0.66	0.7	—	0.81	—	—	—	5.50	2.14	—
Kaolinite	—	—	—	—	—	—	—	—	—	<5%
Illite	—	<5%	—	—	—	—	—	10%	15%	—
Anatase	—	—	—	—	—	—	—	—	—	4%

* K_2O = 1.20%, Na_2O = 0.08%
° calculated from formula derived by the method of B. B. Osthaus (1954)
** K_2O = 1.28%, Na_2O = 0.13%

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The following regression relations were evaluated:

A. $\ln t_{05} = f(Me^{IV})$
B. $\ln t_{05} = f(Fe^{VI})$
C. $\ln t_{05} = f(Mg^{VI})$
D. $\ln t_{05} = f(Me^{IV}, Fe^{VI})$
E. $\ln t_{05} = f(Me^{IV}, Mg^{VI})$
F. $\ln t_{05} = f(Fe^{VI}, Mg^{VI})$
G. $\ln t_{05} = f(Me^{IV}, Fe^{VI}, Mg^{VI})$.

The best correlation was found between the decomposition rate expressed as the halftime of dissolution and the octahedral substitution in smectites. The decomposition rate of smectites in 6 N HCl increases with increasing substitution of iron and magnesium in octahedra.

The numerical values of Equation 5 were calculated by the method described by Ezekiel and Fox (1959) from the data given in Table 2. The best fitting eventuality (F) has the following form:

$$\ln t_{05} = 3.95 - 1.96Fe^{VI} - 2.30Mg^{VI} \pm 0.52 \quad (6)$$

The correlation coefficient, r, is equal to −0.97 for this given empirical relation.

DISCUSSION

Starting from a model of acid attack similar to that given by Granquist and Gardner-Sumner (1959), the system is expected to have the following properties: 1) it consists of disk-shaped particles; 2) the rate of progress of the interfacial boundary between the solid particle and surrounding liquid is constant in the course of the whole process of dissolution; 3) the dissolution begins only on edges and proceeds toward the center of the particle.

As potential reasons for the experimentally found phenomena we consider the size of the particles, the defect sites in the structure and the leaching rate of the octahedral layer. If the particle size is actually the decisive factor we have to suppose that the dissolution rate is approximately equal for all smectites. In such a case the mean particle size of montmorillonite is expected to be approximately 1000 times greater than that of nontronite. Comparing the real dimensions of particles of both minerals we can see that they are approximately of the same size. Thus, we can suppose that differences in particle size are contributing to the scattering of the measured data but are not of primary importance.

Different kinds of defects, such as cleavage, irregularities in distribution of central atoms in the structure and vacancies usually are present in smectites. In these spots the process of leaching of the octahedral layer could be identical with that taking place on the grain boundaries. Then the decomposition rate would depend on the quantity of such defects. Their number should increase with an increasing number of central atoms of Mg and Fe in the structure of the mineral. Since there is no possibility of determining the number of defects in individual crystals, it is rather difficult to say whether the number of imperfections increases with an increasing rate of dissolution.

The assumption that the number of imperfections increases in some proportion to the number of the substituted central atoms in octahedra in montmorillonite is acceptable until approximately one half of the Al atoms are replaced by Fe. Beyond this limit a new stable structure is formed. It is nontronite and the increasing number of Fe atoms leads to a more stable and perfect structure while the number of defects is decreasing. If this is true, then the structural defects cannot be responsible for the acceleration of the decomposition of smectites, which increased by as much as three orders of magnitude, when comparing nontronites with montmorillonites.

The change in the dissolution rate of smectites could be explained by a lowering of the stability of the octahedral layer as a consequence of a successive substitution by iron and magnesium for aluminum. With regard to the greater ionic radius of trivalent iron and bivalent magnesium, when compared with aluminum, the octahedra of the layer are flattened, more distorted (Donnay et al., 1964) and the tension in the structure is increasing. This can support the more rapid release of central atoms from the structure despite the nearly constant apparent activation energies for the samples within the whole range of substitutions (Osthaus, 1956; Turner, 1964; Gregor et al., 1966).

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Резюме- Было проведено изучение корреляционной зависимости между кристаллохимическими данными 15 образцов смектита и половиной времени их растворения (t_{05}) в 6N соляной кислоте при 96°C. Отсюда было получено следующее соотношение: $\ln t_{05}=3.95-1.96Fe^{VI}-2.30Mg^{VI}$. Оно показывает примечательную зависимость удельной скорости растворения октаэдрического слоя смектитов от замещения Al^{+3} катионами Fe^{3+} и Mg^{2+} в октаэдрической позиции.

Kurzreferat- Eine Korrelation kristallchemischer Daten von 15 Smektiten mit den Halbwertszeiten der Auflösung (t_{05}) in 6N HCl bei 96°C wurde aufgestellt.Daraus wurde die Gleichung: $\ln t_{05}=3,95-1,96\ Fe^{VI}-2,30\ Mg^{VI}$ abgeleitet. Es zeigte sich eine bemerkenswerte Abhängigkeit der scheinbaren Auflösungsrate der oktahedrischen Schicht der Smektiten von der Substitution von Fe(III) und Mg(II) für Al(III) in der oktahedrischen Position.

Résumé-Une corrélation a été établie entre les données cristallochimiques de quinze smectites ayant un demi-temps de dissolution(t_{05}) dans l'acide hydrochlorique 6N à 96°C.La relation suivante a été développée: $\ln t_{05} = 3.95-1.96\ Fe^{VI}-2.30\ Mg^{VI}$
Elle montre une dépendance remarquable de la vitesse apparente de dissolution du feuillet octaèdral des smectites de la substitution de Fe^{3+} et Mg^{2+}à Al^{+3} dans la position octaèdrale.