ALUMINIUM RELEASE RATES FROM ACIDIFIED CLAY STRUCTURES: COMPARATIVE KINETIC STUDY
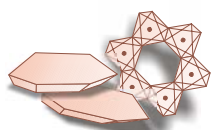
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Abstract: Dissolution rates of several clay materials (reference kaolinite samples, natural kaolinites of different origin, illitic clays, halloysite) in 0.5 and 5 M sulphuric and 1 M hydrochloric acids were determined by measuring the release rate of aluminium into solution. The X-ray powder diffraction and X-ray fluorescence methods have been employed for mineralogical and chemical analyses of clay samples, respectively. The surface area of the samples was determined by a N_2 adsorption technique (BET). The dissolved Al concentration was determined by spectrophotometry. The dissolution rate of kaolinite in 0.5 M sulphuric acid at 25 °C is approximately three times higher than in hydrochloric acid of formally equivalent H^+ concentration. The dissolution in 5 M sulphuric acid is eight times faster if the solid phase is periodically separated from the acid solution, washed by distilled water and dried. The aluminium release rate decreases with the increasing amounts of clay micas in kaolinitic clays and is affected by the concentration of Al in the mineral structure. Crystallinity, as a factor reflecting the quality of the crystal structure, influences significantly the aluminium release rates during dissolution by acids.

Key words: kaolinite, illite, halloysite, aluminium release rates, sulphuric acid, hydrochloric acid.

Introduction

Acid-sensitive surface and soil waters are characterized by insufficient neutralizing capacity to compensate for increases in acid input, for example due to acid rain or acid main drainage, leading to dissolution of aluminium-containing clay minerals. Since the residence time of the surface waters is not sufficient for attaining chemical equilibrium with the solid phase, the kinetics of its dissolution may be crucial for the development of weathering profiles and for aluminium mobility.

It has been suggested by many authors (e.g. Carroll-Webb & Walther 1988; Carroll & Walther 1990; Nagy et al. 1991; Wieland & Stumm 1992; Xie & Walther 1992; Ganor et al. 1995; Devidal et al. 1997; Huertas et al. 1998 and 1999) that the dissolution rate of kaolinite, as well as other sparingly soluble silicates, in acid solutions is governed by the presence of surface complexes at Al hydroxyl sites. Therefore, the dissolution rate should be related to the accessibility of hydroxyl groups on the basal octahedral and edge surfaces of the clay mineral.

If the reaction is far from equilibrium, the reaction rate R (mol $m^{-2}s^{-1}$), defined as the release rate of the selected element (e.g. aluminium) per unit surface area of the solid phase, has a direct relation to pH (or activity of protons), given, for example, by Stumm (1990) as:

$$\log R = \log k - b\,\mathrm{pH} \qquad (1)$$

where b is the reaction order and k is the reaction constant. Various authors give significantly different values of the reaction order b, for example, for kaolinite and pH < 4 as 0.5 (Ganor et al. 1995) or 0.38 and –0.02 (Wieland & Stumm 1992) or

0.09 (Carrol & Walther 1990). Therefore, other factors probably affect the dissolution kinetics. The chemical composition of the solution and the physico-chemical properties of the solid phase should be taken into consideration. For example, Ridley et al. (1997) found that dissolution of gibbsite in acidic low-temperature solutions is significantly enhanced by the presence of sulphate ions, in comparison to chloride ions. When all other parameters are fixed, gibbsite dissolves ten times faster in 0.005 M H_2SO_4 solution than in 0.01 M HCl solution. Moreover, natural samples of minerals of the same chemical composition, such as kaolinites, exhibit different dissolution rates under the same experimental conditions (Hradil & Hostomský 1999) and the dissolution process can be substantially faster for minerals of lower crystallinity (Soukupová et al., in press). One may also ask what is the difference in reactivity of a mineral surface if so-called 'external' hydroxyls, which are typical for the structure of kaolinites, are absent in 2 : 1 clays, such as mica and smectite.

The aim of the present study is to compare dissolution rates of different clay minerals and to study the influence of structural properties of the samples, their crystallinity and aluminium content, as well as the effect of the presence of complexing agents (sulphates) in solution. Furthermore, the dissolution kinetics of kaolinite and halloysite with a variable content of clay micas is investigated.

Materials and methods

Two samples of pure kaolinite which differ significantly in crystallinity (KGa-1b and KGa-2, Georgia; USA) have been used as reference materials (Fig. 1). Dissolution rates of both
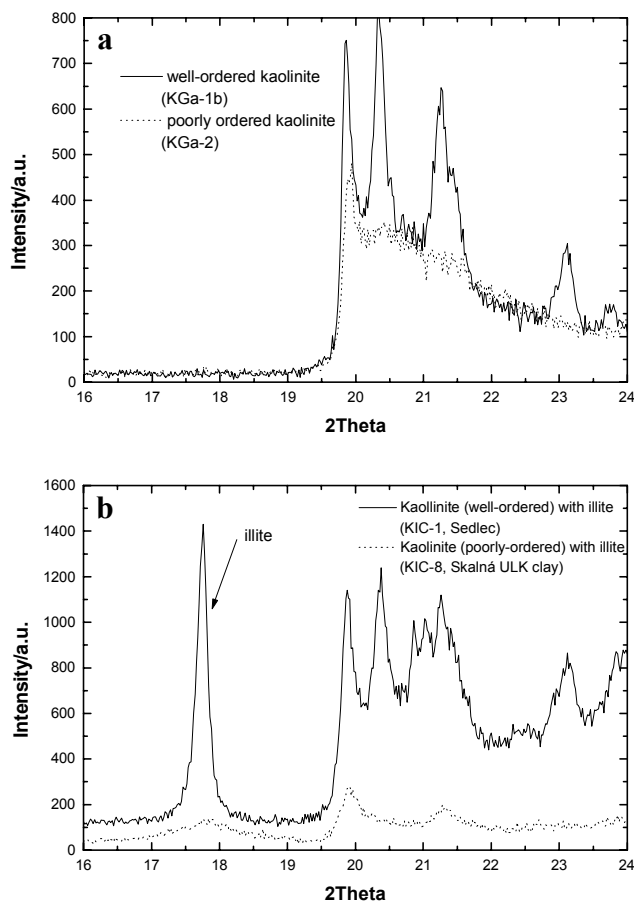
Fig. 1. Powder diffraction patterns of well and poorly ordered kaolinites. **(a)** — reference clays KGa-1b vs. KGa-2, **(b)** — illite-rich kaolins KIC-1 vs. KIC-8.

materials were measured by Sutheimer et al. (1999) at pH 3 in nitric acid solutions and by Hradil & Hostomský (in press) at pH 0.65 in sulphuric acid solutions, respectively. KGa-1b is classified as 'well-ordered' and KGa-2 as 'poorly-ordered' kaolinite by Van Olphen & Fripiat (1979) using the Hinckley index, defined as the ratio of the sum of the heights of ($1\ \bar{1}\ 0$) and ($1\ \bar{1}\ 1$) diffraction peaks measured from their base and the height of ($1\ \bar{1}\ 0$) peak measured from the background of the whole diffraction record. Sutheimer et al. (1999) described the grains of KGa-2 kaolinite as more rounded than KGa-1b, with curved edge steps (as analysed by atomic force microscopy). According to Konta (1994), the structural disorder is a consequence of the turbostratic structure, which is manifested by a sheet translation in the *b*-axis direction.

Other natural samples from different sources were pre-treated by sedimentation in distilled water and the < 4 µm fraction was separated. X-ray powder diffraction has been employed for mineralogical analyses using a SIEMENS D-5005 instrument under the following measurement conditions: CuKα radiation, secondary monochromator, voltage 40 kV, current 30 mA, degree range 2θ 3–90°, step 0.02° per 8 seconds. The raw data were processed by the ZDS for Windows program (Ondruš 1997) employing the diffraction pattern database (JCPDS 2000). In addition, mineral compositions were calculated from

quantitative chemical analyses obtained by X-ray fluorescence (Vacuum X-ray spectrometer PHILIPS PW 1404/10). Ideal formulas of the mineral phases given by Deer et al. (1992) and Velde (1992) were used; volatile compounds were excluded from the calculation. The surface area of the samples was determined by a N_2 adsorption technique (BET; Brunauer et al. 1938) using a Coulter SA3100 device. The physical parameters and mineral and chemical compositions are listed in Table 1.

The following dissolution experiments were performed at 25 °C:
— Continuous dissolution of samples suspended in 0.5 M and 5 M H_2SO_4 and in 1 M HCl;
— Discontinuous dissolution of samples in 5 M H_2SO_4.

In a continuous experiment, 100 cm^3 polyethylene bottles were filled with 70 cm^3 of the acid solution and 0.7 g of the solid material was added. The bottles were placed into a constant temperature shaking bath. At each predetermined time interval, a bottle was taken off and the solid phase was separated by centrifugation.

In the discontinuous experiment, only one reaction vessel was used. The solid to solution ratio was the same as in the continuous experiments, that is 0.01 g cm^{-3}. At each sampling, the whole volume of suspension was centrifuged. After decantation of the solution, the solid residue was washed three times with distilled water and dried in air at 90 °C. Then it was redispersed in the appropriate amount of the fresh acid solution to restore the solid/liquid ratio (0.01 g cm^{-3}) and to start the next dissolution step.

The dissolved Al concentration was determined by spectrophotometry (Spekol, Carl Zeiss Jena, Germany) using the Al complex with Chromazurol S after masking Fe by ascorbic acid (Malát 1973).

Results and discussion

Effect of sulphates and acidity

The dissolution rate of the well-ordered kaolinite KGa-1b, defined as the release rate of Al per unit surface area of the solid phase, in 0.5 M H_2SO_4 solution is three times higher than in 1 M HCl (Table 2).

In 5 M H_2SO_4, aluminium release rates differ significantly for continuous and discontinuous experiments. If samples are washed and dried periodically, their resulting dissolution is much faster both for the pure kaolinite KGa-1b and for the illite-rich clay IMt-1 (Table 2 and Fig. 2).

The dissolution rate R_{Al} (mol m^{-2}s^{-1}), of the pure, well-ordered kaolinite KGa-1b in continuous experiments in the concentration interval 0.5 M < c_A < 5 M may be approximated by the equation:

$$R_{Al} = 6.32 \times 10^{-12} \cdot c_A^{0.69} \qquad (2)$$

which was obtained using two experimental points given in Table 2.

Taking into consideration that the reaction order (with respect to c_A) in the acid concentration interval 0.05 M < c_A < 0.5 M calculated for different kaolinites is always close to 0.5 (Hradil &

Table 1: Composition and properties of studied clay samples.

Sample:	KGa-1b	KGa-2	KIC-1	KIC-8	IMt-1	HAL-1	KAO-6
Locality and origin:							
	Washington County, GA, U.S.A. (clay)	Waren County, GA, U.S.A. (clay)	Sedlec, Czech Rep. (clay)	Skalná -ULK clay, Czech Rep. (clay)	Illinois, U.S.A. (clay)	Michalovce, Slovakia (clay)	Hamr, Czech Rep. (sandstone matrix)
Mineralogical composition (wt. %):							
kaolinite	98	96	78	59	11	0	80
halloysite	0	0	0	0	0	95	0
illite	traces	0.5	19	34	72	0	traces
quartz	0	0	2	1	9	3	2
other phases	2	3.5	1	6	8	2	17.5
Content of Al_2O_3 (wt. %)	39.7	38.5	36.2	33.9	24.3	36.4	35.1
Physical properties:							
BET surface area (m^2/g)	10.1	23.5	15.5	21.3	33.8	37.7	10.1
Grain size (μm)	<2	<2	<2	<4	<2	<2	<63
References:	Van Olphen & Fripiat (1979)	Van Olphen & Fripiat (1979)					Hradil & Hostomský (1999)
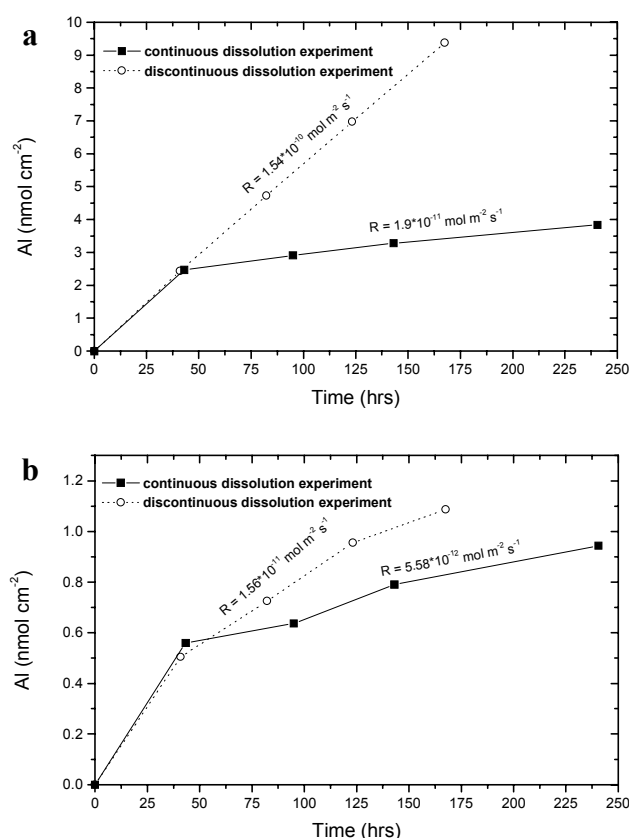
Fig. 2. Aluminium release in 5 M H_2SO_4 solution in two experimental arrangements for **(a)** pure kaolinite (KGa-1b); **(b)** illite-rich clay (IMt-1).

Table 2: Aluminium release rates of reference well-ordered kaolinite KGa-1b in different dissolution regimes and 25 °C.

Solution	Regime	Duration (hours)	R_{Al} (mol $m^{-2}s^{-1}$) (percentage of the previous value in parentheses)	$log\ R_{Al}$
0.5 M H_2SO_4	Continuous	235	3.73×10^{-12}	−11.43
1 M HCl	Continuous	167	1.40×10^{-12} (35%)	−11.86
5 M H_2SO_4	Continuous	240	1.90×10^{-11}	−10.72
5 M H_2SO_4	Discontinuous	168	1.54×10^{-10} (810%)	−9.81

Effect of composition of structural layers

In order to compare different clay minerals from the point of view of the aluminium release rate, the Al concentration in the solid sample should be taken into account. The difference becomes important in minerals relatively poor in aluminum. In the Fig. 3, differences in rates related to the value of the dissolution rate of the reference kaolinite (KGa-1b) in 0.5 M H_2SO_4 solution are shown. Well-crystallized sedimentary clays (KGa-1b, KIC-1, IMt-1 — solid circles), which differ in illite concentration (Table 1) and, therefore, also in Al concentration, exhibit significant differences in their aluminium release rates; the dissolution rates decrease with increasing content of illite (Hradil & Hostomský, in press). We suggest that these differences are caused partially by the different content of aluminium (Fig. 3) and probably by the absence of 'external' hydroxyls in 2 : 1 structures of clay micas.

Effect of structural order

Crystallinity' is a term describing broadly the structural perfection of a crystalline phase. One may assume in general that a 'poorly-ordered' phase is more easily dissolved than a 'well-ordered' material. In the case of kaolinite group minerals, 'crystallinity' decreases in the succession kaolinite–hal-
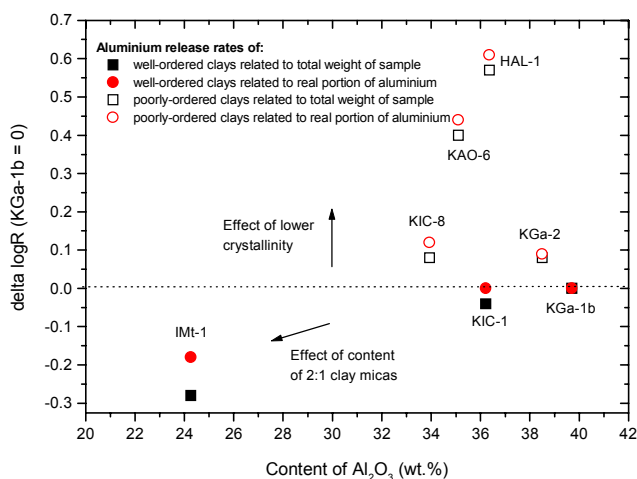
Hostomský 1999), one can conclude that the dissolution rate at the highest acid concentrations (0.5 M < c_A < 5 M) increases with increasing acidity even more steeply than in the concentration interval 0.05 M < c_A < 0.5 M.

Fig. 3. Relative aluminium release rates for different clay samples in 0.5 M H$_2$SO$_4$ solution; effect of sample crystallinity and Al concentration in solids (related to the dissolution rate of KGa-1b kaolinite as the reference value).

loysite–allophane (amorphous). All these phases are nearly of the same chemical composition; halloysite has a tubular structure of rolled sheets instead of typical hexagonal flat sheets of kaolinite and its particles are in general smaller. Even among kaolinite samples, well- and poorly-ordered materials may be identified, but their structural difference is not as significant as is the difference between kaolinite and halloysite samples. In Fig. 1, diffraction patterns of the well- and poorly-ordered kaolinites (reference materials KGa-1b vs. KGa-2 and illite-rich kaolins KIC-1 vs. KIC-8) are compared. As can be seen in Fig. 3, the aluminium release rates of poorly-ordered structures (open circles and squares) are always higher than those of well-ordered materials (solid circles and squares). Extremely reactive kaolinite KAO-6 (with the dissolution rate similar to that of halloysite), has been formed by alteration processes in sandstones of Cenomanian age related to later volcanic activity in the Tertiary, in the area of uranium underground leaching (Stráž pod Ralskem, Czech Republic); this is in contrast to other samples of sedimentary origin.

It may be concluded that crystallinity, which in some way refers to the clay's origin, plays an important role as a factor affecting the mineral's reactivity and, specifically, its dissolution rate.

Conclusions

— The dissolution rate of kaolinite in 0.5 M sulphuric acid at 25 °C is aproximately three times higher than in hydrochloric acid of formally equivalent H$^+$ concentration. The dissolution in 5 M sulphuric acid is eight times faster if the solid phase is periodically separated from acid solution, washed by distilled water and dried.
— Aluminium release rate decreases with the increasing concentrations of 2:1 clays (illites) in kaolinitic clays.
— The dissolution rate defined as the release rate of aluminium per surface area of the solid phase is affected by the con-

centration of Al in the mineral structure. It should be taken into account if clay minerals with the different Al content are compared.
— Crystallinity, as a factor reflecting the quality of the crystal structure, influences significantly the aluminium release rates in dissolution by acids. Halloysite and poorly-ordered clays formed by authigenic alteration processes are extremely reactive in comparison with well-ordered sedimentary clays.

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