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Alteration of swelling clay minerals by acid activation

A. Steudel [a,c,*], L.F. Batenburg [b], H.R. Fischer [b], P.G. Weidler [a], K. Emmerich [a,c]

[a] Institute for Functional Interfaces (IFG former ITC-WGT), Forschungszentrum Karlsruhe GmbH, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[b] TNO Science and Industry, De Rondom 1, 5612 AP Eindhoven, The Netherlands
[c] Competence Center of Material Moisture (CMM), University of Karlsruhe, Kaiserstr. 12, D-76131 Karlsruhe, Germany

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ABSTRACT

The bulk material of six dioctahedral and two trioctahedral swellable clay minerals was leached in H_2SO_4 and HCl at concentrations of 1.0, 5.0 and 10.0 M at 80 °C for several hours. Alteration of the clay mineral structures was dependent on the individual character of each mineral (chemical composition and initial particle size). Acid attack dissolved the octahedral sheets by interlayer and edge attack. The number of substitutions by Mg or Fe in the octahedral sheet of the clay minerals promoted the dissolution of these layers and the formation of a silica phase. The dissolution of the octahedral cations occurred in the following order: $Mg > Fe > Al$. The dioctahedral smectites were more stable than the trioctahedral smectites and vermiculites; the behavior of trioctahedral smectites against acid was similar to that of vermiculites. The acid activated smectites displayed still the ability to exchange cations. The obtained materials had a lower layer charge, lower CEC and higher specific surface area than the crude materials but still adsorbed very large organic cations like dodecylammonium ions. The reaction with the acid caused particle splitting within the octahedral sheet. A model of dissolution and particle splitting is proposed.

1. Introduction

Clay minerals like smectite and vermiculite vary in their chemical composition, which influences layer charge, cation exchange capacity, adsorption capacity and morphology. Because of their large variability (e.g. chemical composition) these clay minerals are widely used in many industrial applications like foundry industries, chemical industries and food industries (Bergaya et al., 2006). They are applied in their natural form or after modification (acid, alkali or organic).

Acid attack is a useful method to modify the catalytic behavior of clay minerals (Komadel et al., 1997; Ravichandran and Sivasankar, 1997). Acid activated clay minerals find wide industrial applications as bleaching earth (Siddiqui, 1968; Kaufhold, 2001), catalysts (Adams 1987) or catalyst supports (Rhodes et al., 1991; Rhodes and Brown, 1992) and in carbonless copying paper (Fahn and Fenderl, 1983).

Several studies dealt with acid attack. A number of workers investigated the influence of hydrochloric acid on the structure of smectite (Novák and Číčel, 1978; Komadel et al., 1990; Ravichandran and Sivasankar, 1997; Madejová et al., 1998; Pálková et al., 2003). These authors have primary used FTIR spectroscopy to follow the changes of the acid treated smectites.

Only a few researchers used sulphuric acid for the reaction with smectites (Breen et al., 1995; Komadel et al., 1997; Önal and Sarikaya, 2007). Komadel et al. (1990) used both acids and homoionic (calcium, sodium) exchanged <2 µm samples. In a few of these earlier studies the different influence of sulphuric and hydrochloric acid was noted (e.g. Komadel et al., 1996).

The first step of acid attack is to remove the exchangeable cations by protons. The second effect is the leaching of Al, Mg and Fe from the octahedral and tetrahedral sheet, but the SiO_4 groups of the tetrahedral sheet stay largely intact. Thus, acid attack causes a corrosion of the octahedral sheet; however, it is still under discussion if this process is complete or incomplete.

Contrary to most studies we used bulk material because for most of the industrial applications purification and separation of clay fractions (<2 µm) is too time consuming and too expensive. Several bentonites containing dioctahedral clay minerals and two trioctahedral clay minerals (hectorite, vermiculite) were reacted with acid. A combination of several methods is imperative to monitor structural alteration of all phases in the bulk material.

The focus of this study was to prepare materials by acid attack which retain the layered morphology but develop a high specific surface area and still have the ability to adsorb organic molecules. These materials may preferentially be used as precursor for clay-polymer-nanocomposites.

Special attention was drawn on the dissolution kinetics of the octahedral sheet with respect to Mg, Fe and Al.

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* Corresponding author. Institute for Functional Interfaces (IFG former ITC-WGT), Forschungszentrum Karlsruhe GmbH, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany. Tel.: +49 7247826805; fax: +49 07247823478.
E-mail address: annett.steudel@ifg.fzk.de (A. Steudel).

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2. Materials

Six bentonites with a high content of dioctahedral smectites, a hectorite and a vermiculite were used (Table 1). The clay minerals differ in their layer charge, particle size and morphology.

In contrast to the other crude materials vermiculite had a very low content of the fraction <2 µm, <10 mass-% by particle size separation. Therefore particle size was reduced by gentle grinding in a CGS 10 (Netzsch — Condux Mahltechnik GmbH).

3. Methods

3.1. Acid activation

Samples of 4 g were dispersed in 400 ml of 1, 5, and 10 M H_2SO_4 (prepared from H_2SO_4 98%, p.a., Merck) or HCl (prepared from HCl 37%, p.a., Merck) at 80 °C for several hours (up to 96 h).

The samples were dispersed in 100 ml deionised water, 300 ml of depleted acid were added to adjust the final concentration. During the preparation and reaction steps the dispersions were stirred continuously. Subsequently the dispersions were heated to 80 °C. Reaction kinetics of the 5 M H_2SO_4 treatment at 80 °C were investigated in more detail (Table 2). The reaction times were adjusted according to degree of corrosion of the starting material after preliminary tests at 20 h. The reactions were terminated by cooling for 5 to 10 min in an ice bath.

The samples were centrifuged and the remaining solid was washed with deionised water until the conductivity of the supernatant solution was below 5 µS/cm (conductivity of the deionised water at our laboratory). The dispersions were then freeze-dried.

3.2. Characterization

The mineralogical composition of crude and acid activated materials was determined by X-ray diffraction analysis (Siemens D5000 diffractometer, CuK_α radiation, graphite secondary monochromator, 5 s counting time per 0.02° 2θ step, divergence and antiscatter slit at 1 mm, detector slit 0.1 mm).

Quantitative analysis was performed using the Rietveld program “Autoquan” (Agfa NDT Pantak Seifert GmbH_CO.KG, Version 2.7.0) (Kleeberg and Bergmann, 2002). An internal standard (ZnO) was used to quantify amorphous SiO_2. For these measurements the powdered samples were mixed with ZnO in the ratio of 9:1.

The chemical composition of the natural and acid treated materials was determined with X-ray fluorescence analysis (XRF). The analyses were performed on a MagiXPRO spectrometer (Phillips), equipped with a rhodium X-ray tube running at 3.2 kW, using air dry powdered samples fused with lithium tetraborate (mixing ratio 1:7). The loss of ignition was determined separately at 1000 °C (2 h). The content of lithium in the octahedral sheet of the hectorite was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). The sample was dissolved with nitrohydrochloric acid and with a mixture of hydrofluoric and nitric acid, using a microwave (Multiwave 3000, Anton Paar).

Table 1
Origin and the suppliers of samples.

Sample	Product name	Main phase	Provenance	Supplier
1_Calci	Bentonite Calcigel	Smectite (di)	Bavaria, Germany	Südchemie AG, Germany
2_EXM757	Bentonite EXM757	Smectite (di)	Germany	Südchemie AG, Germany
3_SWy-2	Bentonite SWy-2	Smectite (di)	Wyoming, USA	Source Clay Repository of the Clay Mineral Society
4_Vol	Bentonite Volclay	Smectite (di)	Wyoming, USA	Südchemie AG, Germany
5_WYO	Bentonite	Smectite (di)	Wyoming, USA	Sampled touring excursion
6_IndBent	Bentonite	Smectite (di)	India	F. Wolters, Düsseldorf, Germany
7_Nhec	Hectorite	Smectite (tri)	USA	Elementis, USA
8_Verm	Vermiculite	Vermiculite	Russia	S. Dultz, Uni Hannover, Germany

Table 2
Reaction times of clay suspensions with 5 M H_2SO_4 at 80 °C.

Sample	Reaction time (h)				
	1.5	5	20	72	96
1_Calci	X	X	X	X	X
2_EXM757	X	X	X	X	X
3_SWy-2			X		X
4_Vol	X	X	X	X	X
5_WYO			X		X
6_IndBent	X	X	X		X
7_Nhec	X	X	X		X
8_Verm	X	X	X		

The cation exchange capacity (CEC) was measured with 0.01 M Cu-triethylentetramine (Meier and Kahr 1999). The CEC of vermiculite and acid treated vermiculite was determined with the ammonium acetate method according to MacKenzie (1951) and Emmerich (2000). Additionally, the decrease of the charge density was proven by the exchange with large molecules like alkylammonium ions while measuring layer charge (Lagaly and Weiss, 1970; Lagaly, 1989 and 1994; Wolters, 2005).

The structural formula of clay minerals was calculated from the chemical composition of the fractions <2 µm or <0.2 µm with consideration of the measured layer charge (Köster, 1977; Olis et al., 1990; Lagaly, 1994; Wolters et al., 2008). The fraction <2 µm was obtained by sedimentation from the purified samples (Tributh and Lagaly, 1986) and the <0.2 µm fraction by centrifugation ($T=20$ °C, 4500 rpm, $h=6$ cm, $t=25$ min).

The Fourier Transform Infrared Spectroscopy (FTIR) and diffuse reflectance (DRIFT) was used to investigate the short range of structural changes which were caused by the acid attack. For a better discrimination of the bands in the Si–O stretching region (1200–800 cm^{-1}) a diffuse reflectance accessory from Spectra-Tech Inc. (DRIFT) was used. Random orientation of the clay particles was obtained by mixing 2.5 mg of a sample with 500 mg KBr (for IR spectroscopy, Merck). The FTIR spectra were recorded on a Bruker IFS66/S spectrometer equipped with a deuterated triglycinesulphonate detector (DTGS). 64 scans were recorded between 4000 and 400 cm^{-1} (resolution of 4 cm^{-1}, scanner velocity of 4 kHz, lens aperture of 12 mm). Prior to the measurement each sample was flushed with nitrogen for 2 min. Pure KBr powder was used for measurement of the background.

Raw DRIFT data were transformed by a Kubelka–Munk function. The PeakFit program 4.0 (Jandel Scientific) was used for single line peak fitting using Gauß function. Those data were compared with the adjusted amount of the unreacted octahedral cations like Al Mg and Fe which were measured by XRF.

ICP-OES was used to determine the amount of Si, Al, Fe, Mg, Na, Ca, K in the supernatant reaction solutions.

Changes in particle morphology were observed with an Environmental Scanning Electron Microscope (ESEM) (Philips ESEM XL 30 FEG). A chamber atmosphere of 1 Torr and an acceleration voltage of 20 kV was applied. The used holder consists of Al, which was laminated with an adhesive carbon foil. Very small amounts of the powdered samples were dispensed onto the foil.

The specific BET surface area was measured by Nitrogen adsorption (Quantachrome Autosorb-1 MP) (Brunauer et al., 1932; Gregg and Sing, 1991). A number of 11 adsorption points in the range of p/p0 from 0.05 to 0.32 were used for BET evaluation. The samples were outgased 24 h under vacuum at 95 °C. The *t*-plot according to De Boer et al. (1966) was applied to estimate the external specific surface area (A_E) and the micro-pore area (A_{MP}).