X-ray Diffraction Microstructural Analysis of Swelling by Ethylene Glycol in Two Reference Clay Minerals

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Kaolinite and montmorillonite are two clay minerals with different structures: dioctahedral 1:1 without layer charge and dioctahedral 2:1 with low layer charge. X-ray-diffraction microstructural analysis of two fractions of two reference clays (with kaolinite or montmorillonite) from the Clay Minerals Society Source Clay Repository were performed by the Voigt function method to provide microstructural data not available in the baseline studies of this Repository. A rough agreement was found between crystallite sizes determined from X-ray diffraction patterns and from images by field-emission scanning electron microscopy. In addition, the influence of swelling by ethylene-glycol on crystallite size was studied by the mentioned method. Two factors were found to affect the crystallite size variation in ethylene-glycol-treated clay minerals: (i) the increase of the unit cell in [001] direction due to the interlayer absorption of ethylene glycol molecules in the case of swelling minerals and (ii) the physisorption at the surfaces of the crystallites. Both effects operate in the case of montmorillonite, whereas just the latter one is expected in kaolinite.

1. Introduction

Smectites and kaolinites are the main clay minerals constitutive of bentonites and kaolins respectively, both industrial minerals with a wide range of uses [1].

Kaolinites and smectites are two types of clay minerals with different structures, dioctahedral 1:1 without layer charge and dioctahedral 2:1 with low layer charge, that cause very different properties especially in the presence of organic molecules [2]. Only in smectites the absorption of glycerine or ethylene-glycol results in significant interlayer expansion and increases of d_{001} distance, which is commonly used for identification [2].

Near-mine and subsequent processing of clays involves frequently fractionation and treatment of water suspensions of these materials [1].
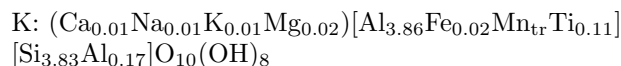
The main aims of this work are (i) to use powder X-ray diffraction microstructure analysis to compare the microstructure of kaolinites and smectites in industrially relevant granulometrical fractions; (ii) to verify the results by direct crystallite thickness measurements by field emission scanning electron microscopy as done by Pardo et al. [3], and (iii) to asses the effect of ethylene-glycol treatment in both minerals at crystallite size level.
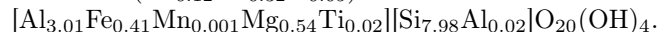
2. Experimental

2.1. Materials

The studied materials (labelled as K and EDS) were two reference clays (Georgia kaolin KGa1 and Wyoming bentonite SWy-1 respectively) of the Clay Minerals Society Source Clay Repository [4].

The corresponding structural formulae [5] of the clays employed are, respectively:

K: $(Ca_{0.01}Na_{0.01}K_{0.01}Mg_{0.02})[Al_{3.86}Fe_{0.02}Mn_{tr}Ti_{0.11}]$ $[Si_{3.83}Al_{0.17}]O_{10}(OH)_8$

and EDS: $(Ca_{0.12}Na_{0.32}K_{0.05})$ $[Al_{3.01}Fe_{0.41}Mn_{0.001}Mg_{0.54}Ti_{0.02}][Si_{7.98}Al_{0.02}]O_{20}(OH)_4$.

2.2. Methods

2.2.1. Sample preparation and mechanical fractionation

Samples of both clays were gently ground with mortar and pestle to powder passing through 230 ASTM sieve, after drying at 65 °C in an air-forced furnace for 12 h.

Water suspensions of each material were prepared by adding 50 g of dry powder to 1 l of distilled water with 10 ml of 1N sodium pyrophosphate. Fractions of equivalent sphere diameters $< 4~\mu$m and $< 20~\mu$m (further labelled as K4, K20, EDS4 and EDS20, respectively) were obtained by sedimentation at settling times calculated with program SediCalc_0_9 (from www.geo.uni-erlangen.de).

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2.2.2. Characterisation methods

Particle size distributions of the fractionated clays were measured with a low-angle laser light Mastersizer 2000 equipment and particle size reported as a volume-equivalent sphere diameter (www.malvern.com/Manuals).

Unoriented powder (with randomly distributed crystals) of whole sample [6] and oriented aggregates of fractions [5] were prepared for analysis by powder X-ray diffraction (XRD) to obtain patterns of non-oriented powder of whole sample and well as of pure and ethylene-glycol-oriented aggregates of $< 4 \ \mu m$ and $< 20 \ \mu m$ fractions using a Bruker D8 Advance diffractometer, with LynxEye detector, at 40 kV and 30 mA, with Cu K_α radiation. The Eva program of Diffrac Plus system was used for identification.

Simplified microstructural analysis was performed from 001 reflections by the Voigt function method [7, 8] using instrumental profiles produced from LaB$_6$ standard (NIST SRM660a). In this method, the diffraction profile is assumed to be Voigtian (convolution of Cauchy and Gaussian profiles) and the Cauchy and Gaussian components of the measured profiles are related to the microstructural parameters (size and strain) of the diffracting sample. The formula used for the size parameter is

$$\langle D_v \rangle = \lambda / \beta_{\rm cf} \cos \theta,$$

where $\langle D_v \rangle$ corresponds to the crystallite size, $\beta_{\rm cf}$ is the integral breadth of the Cauchyan component of the real profile expressed in rad, λ is the wavelength used, and θ is the Bragg angle for the $\alpha 1$ component.

Field emission scanning electron microscopy (FESEM) images were performed in a HITACHI S4800 microscope as in [3], using Image J software for image treatment and measurements (http://imagej.nih.gov/ij/docs/guide/user-guide.pdf).

3. Results and discussion

3.1. Particle size

Figures 1 and 2 show the frequency and cumulative particle size distributions of fractions $< 4 \ \mu m$ and $< 20 \ \mu m$ of samples K and EDS. It can be observed that the fractionation was more effective in K sample, where 90% of particles of fraction $< 4 \ \mu m$ was effectively under that size (80% in the case of EDS); and just a 3% of particles of fraction $< 20 \ \mu m$ were over that size (10% in the case of EDS, including sizes up to 70 μm).
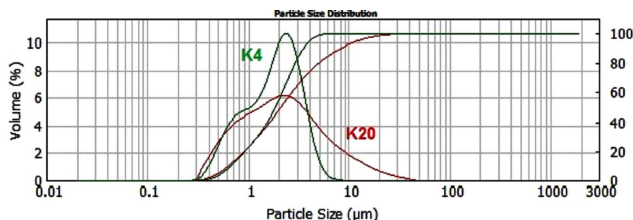
Fig. 1. Frequency and cumulative particle size distributions of K4 and K20 fractions.
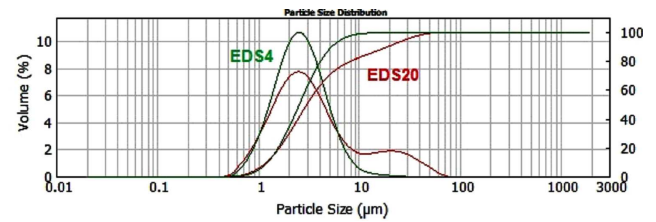
Fig. 2. Frequency and cumulative particle size distributions of EDS4 and EDS20 fractions.

3.2. Powder X-ray diffraction

The mineral compositions of K and EDS materials were studied from X-ray diffraction patterns of unoriented powders of whole samples. Kaolinite (ICDD 01-083-0971), impurities of illite (ICDD 00-015-0603), muscovite (ICDD 01-077-2255), anatase (ICDD 1-071-1167), and quartz (ICDD 00-005-0490) were recognized in K samples. Montmorillonite (ICDD 00-012-0232) and impurities of quartz (ICDD 00-005-0490), feldspars as microcline (ICDD 00-019-0932), orthoclase (ICDD 00-002-0534), albite (ICDD 00-002-0515), illite (ICDD 00-015-0603), muscovite (ICDD 01-077-2255), calcite (ICDD 01-072-1214), dolomite (ICDD 00-036-0426) and cristobalite (ICDD 01-076-0941) were recognized in EDS samples. Figure 3 illustrates powder XRD patterns of obtained fractions.
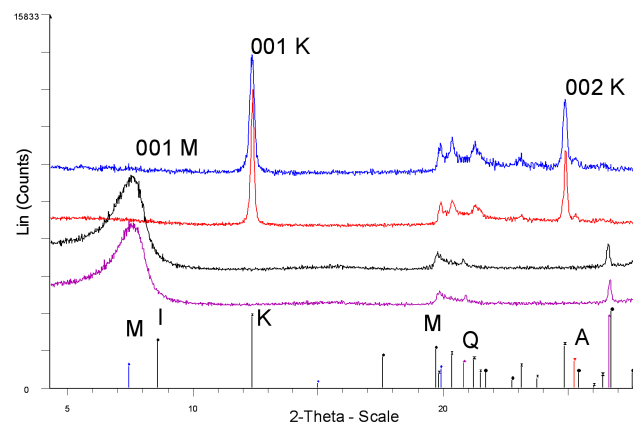
Fig. 3. X-ray diffraction patterns from unoriented powders of the studied fractions (EDS4 — bottom, EDS20, K4, K20 — top); labels are given for identifying lines from different ICDD files of present minerals: M — montmorillonite, I — illite, K — kaolinite, A — anatase, Q — quartz.

Pure and ethylene-glycol-oriented aggregates of both materials were studied with X-ray diffraction. No swelling effect in direction normal to (001) planes was observed for kaolinite in samples K. The change of interplanar spacing d_{001} of montmorillonite from 1.25 nm to 1.70 nm was observed in EDS fractions, due to the swelling effect of interlayer absorption of ethylene-glycol molecules. The value of d_{001} found for untreated montmorillonite in EDS4 was in the range of that found for

calcium-saturated montmorillonite of fraction < 2 μm in the SWy1 reference clay with up to 20% humidity [9]. Table I includes main XRD profile fitting parameters and crystallite sizes calculated for the fractions of samples K and EDS in the pure and ethylene-glycol-oriented aggregates.

XRD profile fitting parameters: reliability (Rel.), position (2θ), 001 interplanar spacing (d_{001}), full width at half maximum (FWHM) and crystallite size ($\langle D_v \rangle$) for two fractions of samples K and EDS, obtained in profile fitting of 001 peaks of untreated aggregates (K4, K20, EDS4, EDS20) and ethylene-glycol-oriented aggregates (K4E, K20E, EDS4E, EDS20E).

Ref. -sample	Rel. [%]	$2\theta°$ (Cu K_α)	d_{001} [nm]	FWHM	$\langle D_v \rangle$ [nm]	$\langle D_v \rangle / d_{001}$
K4	2.2	12.36	0.716	0.136	65	91
K20	2.0	12.35	0.716	0.150	65	91
EDS4	2.1	7.06	1.252	1.600	4	3.2
EDS20	1.8	7.08	1.248	1.663	4	3.2
K4E	2.6	12.31	0.718	0.135	77	107
K20E	1.4	12.34	0.717	0.137	73	102
EDS4E	0.9	5.16	1.710	0.365	15	8.7
EDS20E	2.6	5.20	1.698	0.344	16	9.4

Crystallite size for kaolinite in K fractions was smaller than that previously found (79 nm) in the untreated sample of the same reference clay [3]. EDS samples presented smaller montmorillonite crystallite size values than K (kaolinite) samples. An increase of the crystallite size of ethylene-glycol-treated minerals is observed for both materials, being of special importance for both fractions of EDS (from 4 nm to 15 nm). The observed values for crystallite size of minerals in untreated EDS fractions were smaller than those reported for other Wyoming smectites [10] with MudMaster program [11], and in the range of those found for other montmorillonites in a more simplified way [12]. No difference in crystallite sizes of both fractions in either kaolinite or smectite was found. The differences in crystallite size of pure and ethylene-glycol-treated fractions were not significant (less than 10%) for both materials, as well.

Table I shows no expansion of kaolinite interplanar spacing d_{001} but a slight increase of crystallite size (of 12–18%) in ethylene-glycol-treated kaolinites. On the contrary, both the spacing d_{001} and average apparent crystallite size increased (37% and 400%, respectively) in ethylene-glycol-treated smectites.

3.3. FESEM

FESEM images allowed the recognition of prevailing face to face aggregations of crystallites in kaolinite K4 (Fig. 4), edge-face aggregation in smectite EDS4 (Fig. 5). Crystallite thicknesses of average values of 73.5 nm for K4 and 7.5 nm for EDS4 were obtained from FESEM images. A rough correspondence could be found between crystallite thicknesses measured from FESEM images and

apparent crystallite sizes calculated from X-ray diffraction data. These results were similar to those reported of 62.5 nm for unmilled kaolinite KGa1 [3] and of 8.2 nm for Na-smectite [13].
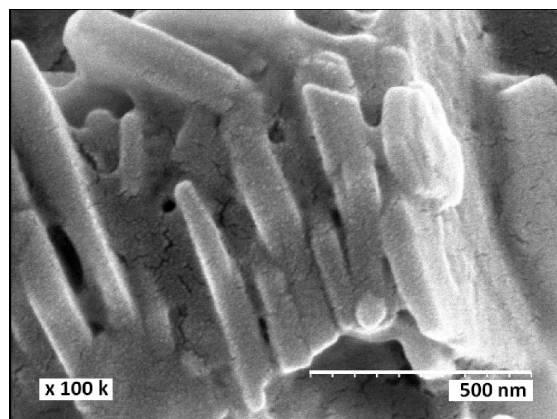

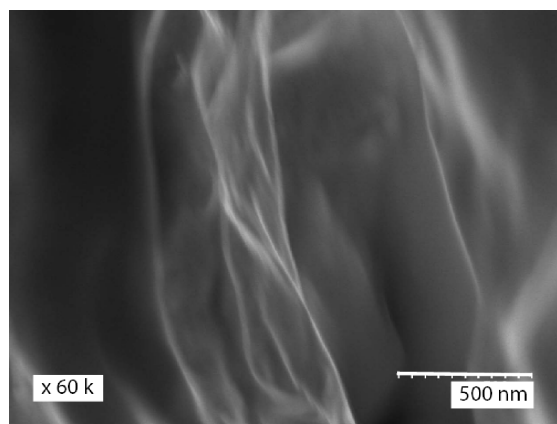Fig. 4.   FESEM image of kaolinite in K4 fraction.

Fig. 5.   FESEM image of smectite in EDS4 fraction.

4. Discussion

The smectites show smaller average apparent crystallite size than the kaolinites as shown by $\langle D_v \rangle$ values calculated from X-ray diffraction data in a rough correspondence with the FESEM measurements on untreated samples.

Table I shows that in the direction normal to (001) faces of the smectite, crystallites consisted of 3.2 unit cells on average before swelling and of 8.7 or 9.4 expanded unit cells after swelling. The differences to integer number of cells must have been caused by adsorption of water from the environment or of ethylene-glycol on the surfaces of crystallites in untreated or in treated samples. This effect coincides with the interlayer absorption in smectite cells producing the expansion of the interplanar distance d_{001} from 1.25–1.24 nm to 1.71–1.69 nm. In the case of kaolinite, only a slight increase of the average crystallite size is observed as well as insignificant d_{001} interplanar distance expansion, evidencing no ethylene-glycol absorption.

5. Conclusions

The microstructural characteristics of the studied materials show the wide range of crystallite size in sheet silicates, being in kaolinite much greater than in smectite. At the same time no difference was found for average apparent crystallite sizes in the two studied fractions of the same mineral, which may be relevant for industrial processing.

Two factors affect the crystallite size variation in ethylene-glycol-treated samples. The first one is the increase of unit cell in 001 direction in the case of swelling minerals (like smectites) due to the interlayer absorption of ethylene glycol molecules and the second is physisorption at the surface of the crystallites. Both effects operate in the case of EDS samples, while just the latter one (much more weaker) is observed in K samples.

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