TIM BAUSE
University of Mining and Technology, Freiberg, Germany

X-RAY DIFFRACTIONAL STUDIES FOR CRYSTAL – CHEMICAL CHARACTERIZATION AND QUANTIFICATION OF SMECTITES

To evaluate the quality of bentonites and its suitability for industrial applications, an accurate determination of the smectite content is required. Up to now it was not possible to use the standard Rietveld method for quantitative phase analysis of smectite-containing samples because of the turbostratic disorder of many natural occurring smectites. The article proposes a model allowing a description of under room condition measured X-ray diffraction powder patterns of montmorillonitic samples.

Для оценки качества бентонитов и их промышленного использования необходимо точно определить содержание в них смектита. До настоящего времени было невозможно использовать стандартный метод Ритвелда для количественного фазового анализа смектит-содержащих образцов из-за турбостатического беспорядка большинства природных смектитов. Предлагается модель, позволяющая описать порошковые дифракционные рентгенограммы образцов монтмориллонита, полученные в комнатных условиях.

1. Introduction

Smectites are 2 : 1 phyllosilicates with a layer structure consisting of an octahedral sheet sandwiched between two siliceous tetrahedral sheets. Isomorphic substitutions in either tetrahedral or octahedral sites induce a permanent negative layer charge, which is compensated for by the presence of cations in the interlayer.

Dioctahedral aluminous smectites are represented by the montmorillonite-beidellite series according to the structural formula $(Me_{x+y})(H_2O)_n(Al_{2-y}Mg_y)(Si_{4-x}Al_x)O_{10}(OH)_2$. The amount of Me represents the interlayer cation, y and x the octahedral and tetrahedral substitutions, respectively. Smectites with $y > x$ are called montmorillonites and those with $y < x$ beidellites. Montmorillonites are commonly the main constituents of bentonite rocks whereas beidellites are frequently found in soils as weathering products of detrital micas. Dioctahedral smectites with iron as main substituent are called nontronites (Guven 1988).

As mentioned above, smectite minerals are constituents of soils and the main components of bentonite rocks. Bentonites are used in various fields of technical applications in civil engineering (e.g. construction, drilling, foundry industry), as well as in the food, chemical, and pharmaceutical industry. Most of the bentonite deposits developed from volcanoclastic rocks by weathering.

To evaluate the quality of bentonites and its suitability for industrial applications, an accurate determination of the smectite content is required. Up to now it was not possible to use the standard Rietveld method for quantitative phase analysis of smectite containing samples because of the turbostratic disorder of many natural occurring smectites. Turbostratic disorder of layered structures can be described as a random rotation and/or translation of the individual layers relative to each other (Warren 1941). In the «ideal» turbostratic case of layer stacking, no correlation between translations/rotations of consecutive layers occurs. In X-ray diffraction powder patterns of smectites, this kind of disorder can be identified by the presence of extremely asymmetric peaks close to the position of the hk0-reflections (Figure 1). Three-dimensional peaks (h, k, and $l \neq 0$) are missing; their positions lie in the tails of the hk-bands. To describe the uncorrelated turbostratic case in compatibility with the Rietveld method Ufer et al. (2004) proposed the so-called single layer approach. In this model, the asymmetric hk-bands indicating turbostratic disorder are

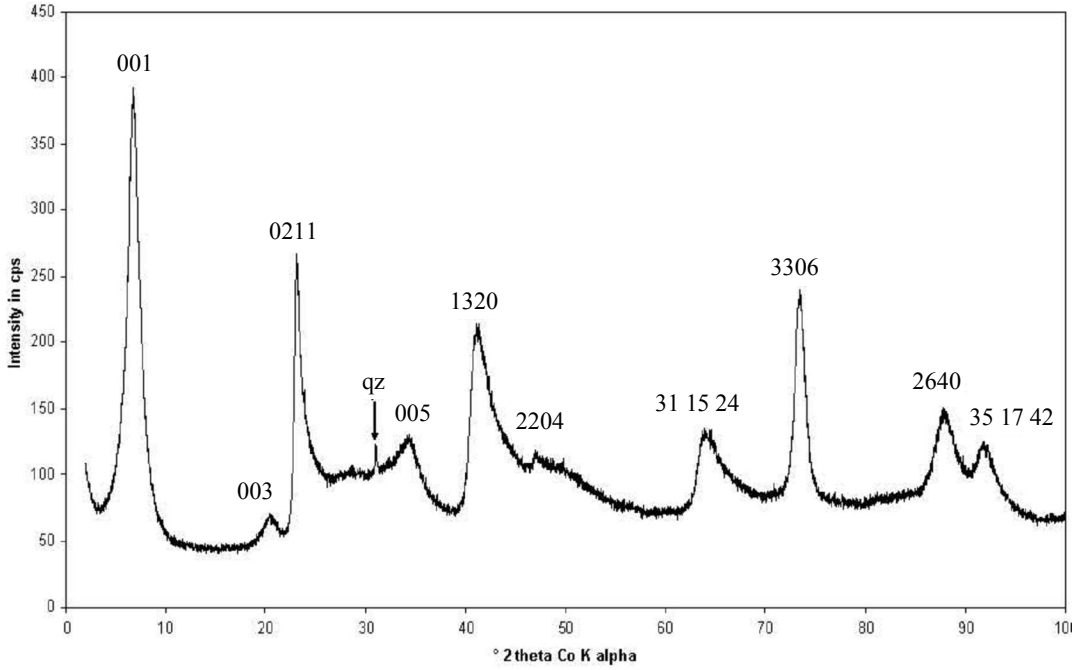

Figure 1: X-ray diffraction powder pattern of a dioctahedral smectite showing turbostratic disorder (sample RoTo43_Ca, < 2 μm size fraction, contains montmorillonite and traces of quartz (qz)). The two types of characteristic reflections were indicated: oo1-reflections (bold) and hk-bands (in dashed boxes)

contributed by the calculation of the diffraction intensity of a single 2 : 1 layer in a partly filled supercell showing a ten fold elongation of the unit cell in c direction. In contrast, the 00l-reflections are calculated from the subcell. Based on this approach, a real structure model suitable for Rietveld refinement of smectites was developed. The aim of this study was to investigate whether it is possible to describe X-ray powder patterns of several smectite samples with the proposed structure model. Furthermore, on capable samples it was tried to refine some of the model's as yet fixed parameters, e.g. mean octahedral occupancy and interlayer content. Because of the strong correlation between these parameters and the intensity ratio of the 00l-reflections, 00l-reflection series rational as possible were required. Diffraction tests for each sample with different interlayer occupancies measured at different relative humidities were performed in order to find conditions for rational 00l-series.

2. Materials and methods

2.1. Samples and preparation

The following samples were taken from the mineralogical laboratory collection of the Institute of Mineralogy (University of Mining and Technology Freiberg):

- RoTo43 – light green bentonite (Budateteny, Hungary),
- Seneg – white-yellowish bentonite (Morocco),
- RoTo212 – yellow-green nontronite rich clay (mine Red Bear, St.Andreasberg, Germany.

At fist size fractionation was performed by wet sieving and settling (Atterberg method) to obtain the < 2 μm size fraction. Then cation exchange was performed to occupy the interlayer with Ca, Mg, Na and Li cations, respectively. For this purpose, 1 mol/1 aqueous solutions of Ca and Mg chlorides and 0.1 mol/1 aqueous solutions of Na and Li chlorides were used. The suspensions of solid and saline solutions were shaken mechanically before separation by centrifugation and addition of fresh saline solution. These steps were repeated three times in order to ensure a complete cation exchange. Removal of axcess chloride was performed by washing the solid in distilled water at least three times. For the following X-ray diffraction tests the air dried solids were sieved < 20 μm.

2.2. Methods

2.2.1. Chemical analysis and structural formula calculation

All samples with Ca cation occupance were analyzed chemically by X-ray fluorescence spectroscopy (XRF). It was performed by using in combination a Philips PW 1480 (Cr radiation) and a Philips PW 2400 (Rh radiation) spectrometer. In addition cation exchange capacity (CEC) was determined by the Cu(II)-triethylenetetramine method after Meier and Kahr (1999).

For the analyses a UV-VIS spectrometer was used at 578 nm with water as blank. Under the consideration of the CEC, chemical compositions were transformed into structural formulae. Details of the calculation are given in Koster (1977).

2.2.2. X-ray diffraction tests on oriented aggregates

Oriented slide mounts were prepared for each sample by air drying at room temperature a pipetted clay slurry covering a round glass slide ($\Leftrightarrow$ 24 mm). X-ray diffraction patterns were recorded using a Seifert 3003 TT diffractometer (Cu-Kα radiation, 45 kV, 30 mA) equipped with a General Eastern C-1 RH humidity control device coupled to a MRI humidity chamber. Scanning parameters were 0.04 °2θ as step size and 6 s as counting time per step over an angular range from 2 to 50 °2θ. For all samples X-ray diffraction patterns were recorded following the sequence 30, 40, 60, and 20 % relative humidity. In order to estimate the rationality of a series of 00l-reflections, the variation coefficient (VC) was determined. The VC is a measure of the regularity of the stacking along the c-axis. It is defined as the relative standard deviation of the mean value of basal spacings calculated from a series of 00l-reflections (Moore & Reynolds 1997).

2.2.3. X-ray diffraction tests on powder packs

X-ray diffraction powder patterns of selected samples were recorded for refinement tests. Sample powder (< 2 μm fraction, < 20 μm sieved) was prepared in an aluminium cuvette by side loading. The measurements were performed under room conditions (≈ 35 % relative humidity) using a Seifert-FPM URD6 diffractometer (Cr-Kα radiation, 40 kV, 30 mA). Scanning parameters were 0.02 °2θ as step size and 20 s as counting time per step over an angular range from 2 to 100 °2θ.

2.2.4. Refinements

The Rietveld code BGMN (Bergmann et al. 1998) was used for the calculations. At the beginning only the lattice parameters and the cation distribution over cis- and trans-octahedra were refined whereas the parameters interlayer content and mean octahedral occupancy were kept fixed according to the results of the chemical analysis. Then it was tried to refine the before fixed parameters stepwise. The temperature factors were estimated. It was not tried to refine atomic coordinates (they were taken from Tsipursky and Drits (1984)).

3. Results and discussion

3.1. Calculation of the structural formulae

Based on the data of the chemical analyses, the structural formulae of all samples were calculated (Table 1). According to this, the samples RoTo43 and Seneg can be described as montmorillonites. Nevertheless both samples show a beidellitic character because of the noticeable aluminium amount in the tetrahedral sheet. The presumption that the sample RoTo212

Table 1: Structural formulae, cation exchange capacities (CEC) and calculated layer charges (each sample with Ca occupancy)

	CEC in		Interlayer cations			Octahedral cations				Tetrahedral cations			
sample	meq/100 g	c/huc	Ca^{2+}	Na^{+}	K^{+}	Al^{3+}	Fe^{3+}	Mg^{2+}	∑Okt	Si^{4+}	Al^{3+}	Fe^{3+}	O_2
Seneg	112	0,396	0,223	0,007	0,009	1,483	0,207	0,197	1,886	3,681	0,319		11
RoTo43	104	0,368	0,211	0,001	0,013	1,382	0,205	0,337	1,923	3,762	0,238		11
RoTo212	77	0,322	0,242	0,002	0,003	0,027	1,870	0,012	1,909	3,474		0,526	11

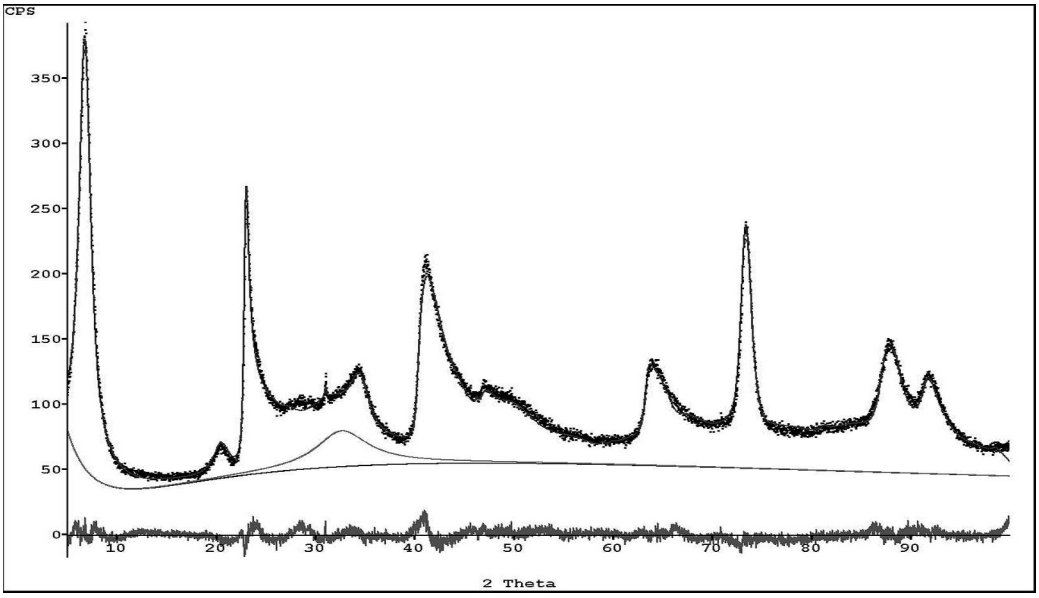

Figure 2: Rietveld plot of the montmorillonite sample Seneg (with Ca occupancy).
An amorphous phase was included, which was simulated by the bottom peak

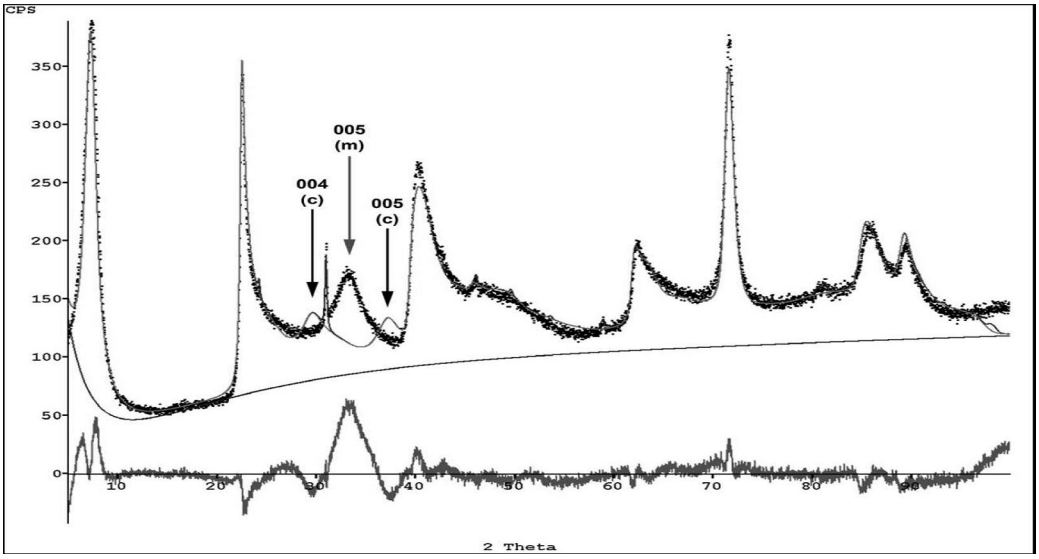

Figure 3: Rietveld plot of the nontronite sample RoTo212 (with Ca occupancy).
Black arrows mark 00l-reflections, which were calculated based on the proposed model.
The gray arrow indicates a measured 00l-reflection

mainly contains of Nontronite was confirmed by the high iron amount in both the tetrahedral and the octahedral sheet.

3.2. X-ray diffraction tests on oriented aggregates

The montmorillonitic samples occupied with Ca or Mg showed the most rational series of 00l-reflections. Their parameters laid over a wide range of relative humidites (20 – 60 %) within the limits, which according to Ferrage et al. (2005) indicate homogeneous hydration domains (width at half maximum intensity of the 001-reflection (FWHM) < 1.1 °2θ Cu-Kα and variation coefficient (VC) < 0.4 A). Therefore it was decided to obtain the diffraction data for refinement test from samples measured at standard laboratory conditions and occupied with Ca and Mg, respectively.

3.3. Results of the refinement tests

Refinement tests were performed on the montmorillonitic samples RoTo43 and Seneg (each with Ca Mg occupancy, respectively) as well as on the nontronite sample RoTo212 with Ca occupancy.

The two montmorillonitic samples showed similar results. First of all, the Rietveld plots showed a good profile match during all refinement tests (e.g. Figure 2). Always a more cis-vacant octahedral sheet was refined. The parameter ptrans was in the range from 0.75 to 0.9 (ptrans = 1 indicates a cis-vacant octahedral sheet whereas ptrans = 0 stands for a trans-vacant layer). The Fe-Al ratio in the octahedral sheet could not be refined. The calculated Fe^{3+} amounts were too high compared to the analyses results whereas the calculated Al amounts were too low. It seems that the implied model for the hydration complex around the cation in the interlayer interferes this calculation. The Mg-Al ratio in the octahedral sheet could not be refined as well. This was partly expected because of the similar atomic scattering factors of Mg and Al, which it makes difficult to differentiate between them by X-ray diffraction. The calculated amount of interlayer cations varied differently but showed results similar to the analyses data. It seems to remain an influence of irrationality caused by the complex hydration behavior of smectites, which also could not be excluded by measurements at fixed relative humidities.

In the Rietveld plot of the nontronite sample RoTo212 (Figure 3) a larger variation between calculated and measured profile can be observed, especially in the range from 30 to 40 °2θ. For it, several reasons have to be considered. First of all, the proposed start model was customized to a montmorillonitic composition. To improve the profile match the model has to be further corrected to meet more of the Nontronite structure. But the larger problem in this case was the complex hydration behavior of Nontronite and the consequential irrationality of the series of the 00l-reflections. This could not be handled by the proposed model, which presupposes rational series of 00l-reflections.

4. Conclusion

The proposed model allowed an almost fitting description of under room condition measured X-ray diffraction powder patterns of montmorillonitic samples. In order to improve refinements further adjustments on structure parameters is still needed. It was shown that a transfer of the model to other smectite compositions is possible, but more customization is needed to describe another smectite structures accurately. Because of the rational series of 00l-reflections required by the proposed model future work should consider other possibilities to assure a constant layer spacing (e.g. vacuum measurements or the introduction of intercalation compounds in the interlayer).

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