XRD Texture Measurements of Clay Aggregates – A Quantification Tool

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Abstract. The preferring orientation (texture) of clay minerals is one of the important factors control XRD intensities, especially in oriented clay aggregates. Texture (\(\sigma^*\)) is a potentially large source of error in any attempt of quantitative XRD-analysis, since it can not be assumed to be constant among minerals and may vary as a result of pretreatment.

Introduction

Clay mineral quantification is traditionally based on XRD, although usually additional information of other analytical techniques is required. The preferred orientation (texture) of clay minerals is one of the important factors that control the XRD intensity. “The parameter \(\sigma^*\) is the standard deviation of the tilt angles of 00l planes of the crystallites about their mean position, which is parallel to the surface of sample [5]”.

The degree of preferred orientation depends on both type and morphology of the respective clay mineral. In order to increase the XRD detection limit the preparation of XRD texture slides produced by sedimentation on glass or ceramic slides (oriented clay aggregates) is frequently used. Ideally, oriented aggregates should exhibit perfect orientation of the clay mineral flakes parallel to the refracting plane. In this case, the standard deviation of the tilt angles of the crystallites about the mean crystallite orientation (“preferred orientation”), \(\sigma^*\) would be close to zero.

Empirical considerations have led [4] to propose a default value of \(\sigma^* = 12^\circ\) for such instances where recorded diffraction intensities suggest preferred orientation to be typical for oriented aggregates. However, peak intensity is proportional to \((1/\sigma^*)^2\), so the estimated limiting values for the reported \(\sigma^*\)-range from 4 \(^\circ\) to 30 \(^\circ\) [3] will produce a 56-fold difference in basal or 00l intensities. A number of authors [7, 2, 6] have reported on preferred orientation of kaolinite varying between 8 \(^\circ\) and 20 \(^\circ\) for oriented aggregates and between 18 \(^\circ\) and 44 \(^\circ\) for powder samples. The changes in preferred orientation cause very large differences in intensities. Therefore the use of “Mineral Intensity Factors” as discussed in [1] is confirmed to be insufficient for the quantification of clay minerals in oriented aggregates.
Experimental

68 mg of clay sample were dispersed in 1.5 ml of deionised water by ultrasonic treatment for 3 minutes at three different ultrasonic steps (32, 47, and 82 J s\(^{-1}\)). For the preparation on glass slides the clay suspension deposited on roughened, circular glass slides with a diameter of 2.4 cm. The drying time was varied from several hours to 2 days. Ceramic slides were circular as well with identical diameter and a thickness of 3 mm. The suspension was filtered through the tile using a vacuum filter apparatus. Ingestion time of the liquid varied between 1 and 30 minutes. For the measurements we used a Seifert 3003 TT diffractometer with an open Eulerian cradle, a 0.2 mm primary hole slit, a position sensitive detector (PSD) and Cu K\(\alpha\) radiation. The variation of diffracted intensity with changing tilt angle (\(\chi\)) was recorded using the "PSD Data Reduction" routine of the software "Seifert-analyze". The samples were rotated in \(\phi = 90^\circ\) increments, while \(\chi\) was varied in 5 \(^\circ\) increments (70 \(^\circ\) maximum). XRD-scans were obtained for every \(\phi\)-position, yielding a total of five scans (\(\phi = 0^\circ; 90^\circ; 180^\circ; 270^\circ; 360^\circ\)) per increment of tilt angle. We could prove that according to expectation there was no significant variation in intensities by variation of \(\phi\).

Results and Discussion

Pure Na\(^+\) exchanged illite (< 2 µm) and Ca\(^{2+}\) exchanged kaolinite (< 2 µm) were used as standard materials. The standard deviation of \(\sigma^*\) determination was calculated to be 2 \(^\circ\) (3 sigma; \(n = 36\)). The \(\sigma^*\) values of the illite (\(\sigma^* = 14 \pm 15 \(^\circ\)\)) and kaolinite (\(\sigma^* = 18 \pm 19 \(^\circ\)\)) standard on ceramic and glass slide at different ultrasonic treatments are approx. the same. This leads to the conclusion that the ultrasonic treatments had no influence on the preferred orientation of these two pure clay minerals. Furthermore it is evident that there is no significant difference for the \(\sigma^*\) values after preparation on glass or ceramic slide.

In the next step these standards were mixed (80 wt % illite and 20 wt % kaolinite). Clay suspensions were prepared of glass and ceramic slides. Results indicate that there is no dependency of the \(\sigma^*\) values for kaolinite and illite for the type of slide used (table 1).

However, there is a pronounced difference between the \(\sigma^*\) value of pure kaolinite (\(\sigma^* = 19 \(^\circ\)\)) and the \(\sigma^*\) value of kaolinite in the mixture (\(\sigma^* = 11 \(^\circ\)\)). The presence of illite influences the preferred orientation of kaolinite in a way, that kaolinite is forced to have a better orientation. The measurements were confirmed by scanning electron microscopy (SEM). The SEM images show side views of broken ceramic slides with clay films of the illite/kaolinite mixture and of the pure kaolinite standard. Fig. 1 a) shows the mixture illite/kaolinite on ceramic slide with an explicit parallel texture. The clay film of the pure kaolinite (fig. 1b) shows a more random orientation of the kaolinite minerals.

| Table 1: \(\sigma^*\) values of illite, kaolinite, and illite/kaolinite mixture on glass and ceramic slides |
|---|---|---|
| glass slide | ceramic slide |
| kaolinite (pure) | 18 | 19 |
| kaolinite (mixture) | 11 | 11 |
| illite (pure) | 14 | 15 |
| Illite (mixture) | 13 | 14 |
Conclusions

Pure illite has a $\sigma^*$ value of 14° whereas pure kaolinite showed a more random orientation ($\sigma^* = 19°$). As expected parallel orientation of 20 wt % kaolinite mixed with 80 wt % illite increased. This likely can be explained by larger oriented illite flakes that force the smaller kaolinite flakes between their lamellar interparticle spaces. However, this does not explain why the degree of preferred orientation of kaolinite ($\sigma^* = 11°$) in this mixture is even better than that of illite which is unchanged in the mixture. In conclusion with respect to orientation in mixtures and therefore it is important to know the degree of preferred orientation of all clay minerals in a sample for quantitative analyses.

The ultrasonic energy employed to disperse clay particles could not be related to preferred orientation. This means that, within the applied energy range, an increase in energy input does not lead to a better orientation of XRD specimen.

In frameworks of this study we observed no significant differences in the preferred orientation of the clay minerals on ceramic- or glass-slides.

References