Extraction and identification of clay fractions by X-Ray powder diffractometry

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Introduction

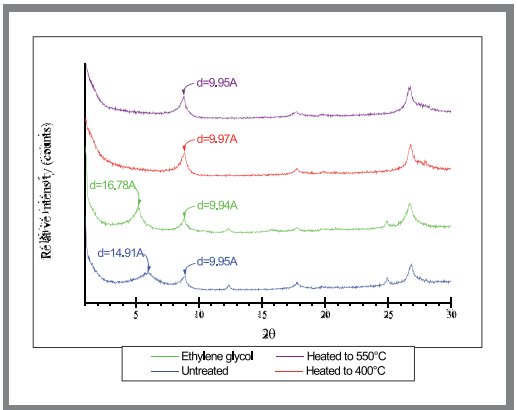
Clays are one of the oldest materials used by humans, and are present in many modern industrial processes such as: cement production, chemical filtering and paper processing. Its main attribute is its ability to tune the mechanical properties of a material (increase its hardness, improve its fire resistance, etc.).
Previously, the CDHL had no method to analyse this kind of material. The aim of my work was to develop and optimise the different stages of a method to analyze clay.
The principal treatment applied to the raw sample was a purification step: an extraction of associated compounds, which can give a signal during analyses, and shadow the clay fingerprint.
First, carbonated compounds (calcite, dolomit, etc.) were removed from the clay sample. Then, organic fractions were extracted and removed as well. Following purification, clay samples were identified by X-Ray powder diffraction.

Experimental Conditions

Once extracted, the clay sample was put into a solution and placed on a fine plate of glass. The evaporation of water created a deposit, and sedimentation activity induced a preferential orientation of the clay layers.
First the sample was analysed with a Bruker D8 X-Ray diffractometer between 1 and 30° 2θ; using copper radiation, variable slits (V4), a position sensitive detector (PSD) with a 3° opening, a time scale of 2, and spinning of the sample.
Next, the sample was placed into an ethylene glycol environment: the aim was to introduce molecules of ethylene glycol between clay layers. The sample was analysed a second time by X-Ray diffractometry, in the same conditions as previously.
After that, another treatment was applied to the sample, it was heated for 45 minutes in an oven at 400°C, so as to remove any molecules present between the layers (for example solvent molecules). After cooling, the sample was again analysed as in the previous conditions.
The last treatment was the same as the previous one, but with a temperature of 550°C. The sample was analysed for the fourth time in the same conditions as the others.

Results and discussion

When all the analyses were done, the comparison of all 4 diffractograms was necessary to allow a characterization of clay types present in the sample.
The diffraction peaks at low angles can directly be related to the distance between two clay layers (d) by using Bragg's law : $2.d.\sin\theta=\lambda$
The angular variation of the d values for the major peaks on the 4 diffractograms, were then used for clay identification with a flow diagram.
A typical sample analysis was showed in the following Figure: The untreated sample diffractogram displayed a major peak at d=14.91Å. After the treatment with ethylene glycol, this peak shifted to d=16.78Å; it then collapsed to d=9.97Å following heating at 400°C. The peak maintained a d=9.95Å, after treatment at 550°C. These 4 values were used within the flow diagram and further identified the clay fraction as MONTMORILLONITE.



X-Ray diffractograms of a clay sample: before treatments, after an ethylene glycol treatment, after a heating at 400°C and another at 550°C

Conclusion

The identification of clay fraction contained in ground samples can be achieved quite routinely and reliably by X-ray powder diffraction. The success of this analysis lies on a careful extraction and purification of the sample.
As often with powder diffraction, the handling and preparation of the samples were critical for the results. That is why a detailed protocol was written, so these manipulations can be as reproducible as possible.
The elaboration of the flow diagram allowed for quick identification of the clay fraction, after the acquisition of the 4 powder patterns. The main limitation was for samples made of a mixture of different clays.

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