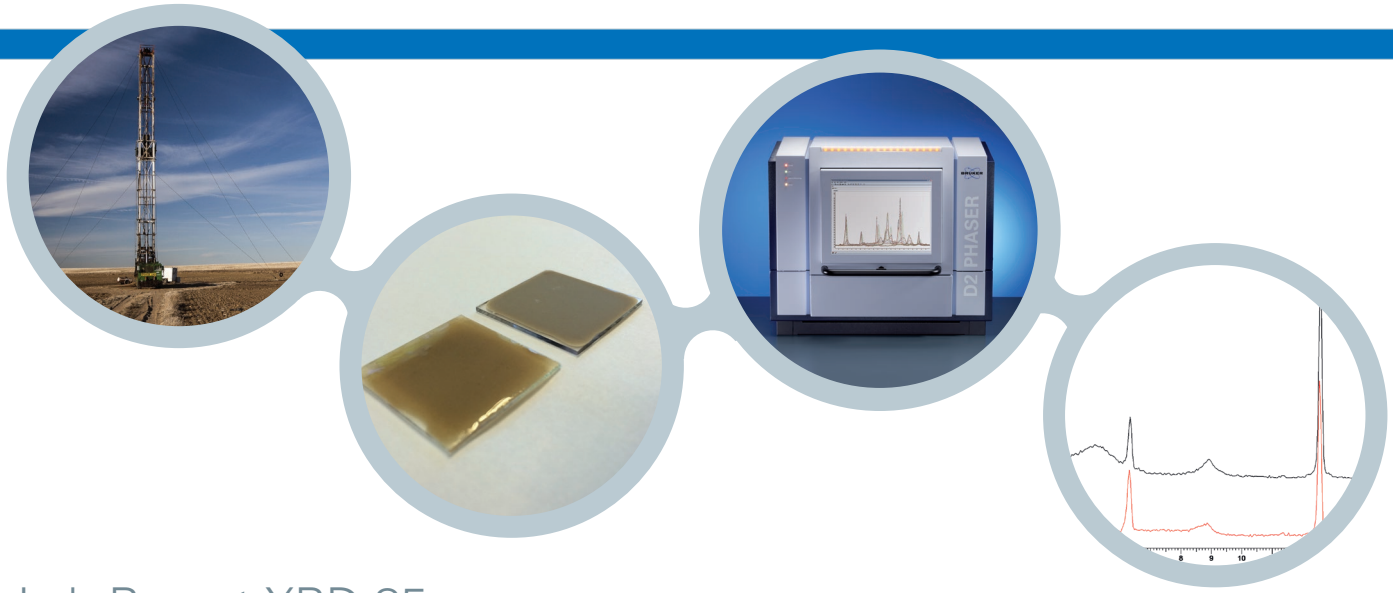

Lab Report XRD 85

X-Ray Diffraction in the Petrochemical Industry
Identification of Swelling Clays with the D2 PHASER

The D2 PHASER is a mobile benchtop X-ray diffractometer (XRD) used in the identification of both bulk and clay minerals within geological samples. In this report, we describe the analysis of clay samples using oriented mounts. Diffraction studies enable the differentiation between swelling and non-swelling clays by observing the shifting of diffraction peaks due to expansion in swelling clays.

Introduction

Clay minerals comprise a large class of fine-grained, layered silicates that result from the weathering of bulk minerals. Clays are of particular interest for the mining and drilling industries due to the physical properties they impart on surrounding geological formations. Here, we discuss the qualitative analysis of clays by X-ray diffraction (XRD) with the D2 PHASER benchtop diffractometer (Figure 1), specifically towards identifying swelling clay species.

Although there are quite a number of discrete clay species and interstratifications, clay minerals can be roughly arranged into three major groups: kaolinite, illite, and smectite. Vermiculites are often considered as a fourth classification. Other phyllosilicate minerals of interest include micas and chlorites, which are sometimes included in the analysis of clay minerals, though neither are explicitly clays.

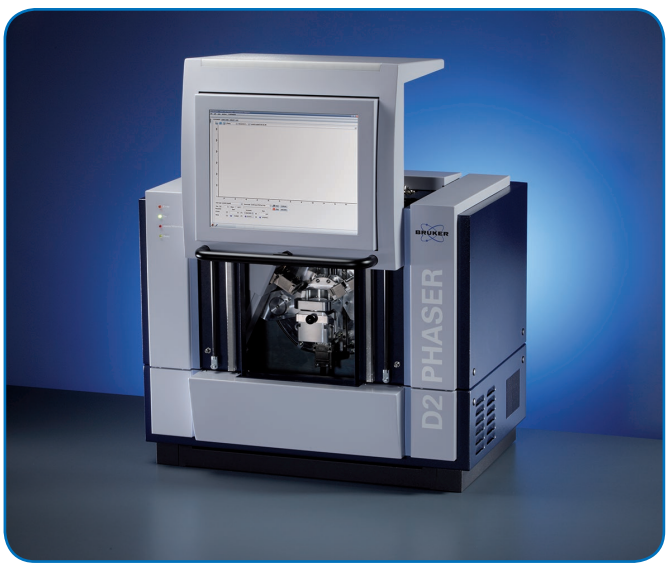

Figure 1. The D2 PHASER benchtop diffractometer.

Of the three major groups, smectites are distinguished by the ability to absorb moisture and the concomitant demonstration of volumetric expansion. As such, members of the smectite group, like montmorillonite, are often referred to as swelling clays.

As mentioned previously, clay minerals are a key concern in many drilling applications. For example, in the hydraulic fracturing industry, high concentrations of clays indicate higher ductility and can lead to poor fracture formation. Additionally, the presence of swelling clays can lead to water-induced swelling during the initiation process or negative effects, such as self-healing, during production stages. The identification of these minerals is essential for developing tailored solutions for additives and stabilizers.

In this report, we demonstrate the identification of swelling clays using a mobile, benchtop diffractometer and a few simple pieces of laboratory equipment.

Overview and Experimental

Samples were prepared as air-dried and glycolated oriented mounts according to the procedure outlined by the U. S. Geological Survey (USGS).[1] The oriented mount causes the plate-shaped clay mineral particles to lie flat along the substrate surface allowing the basal diffraction peaks to be probed using XRD symmetric scans in reflection geometry. The basal plane spacing (or d-spacing) can be calculated by determining the diffraction peak angle (in degrees 2Theta) of a diffractogram. The initial d-spacing and the degree of expansion or contraction, after certain treatments such as glycolation, allows the identification of clay minerals including swelling clays. For example, the addition of glycol to smectite clays results in expansion of the basal planes as polyol molecules intercalate between atomic layers, forcing them apart. The associated reflection in diffraction data will shift to a larger d-spacing and smaller diffraction angle as predicted by Bragg's Law. Non-swelling clays will not demonstrate this lattice expansion. As such, the associated diffraction peaks will remain in the same location both before and after glycolation.

A bulk sample of shale rock was ground using a micronizing mill and dispersed in water via sonication (Figure 2). A small amount of sodium hexametaphosphate, a dispersant, was added to aid in breaking up flocculated clay particles and agglomerates. Bulk minerals were allowed to settle for one hour prior to collecting the clay minerals (Figure 2). The supernatant with the clay fraction was separated by decanting and set aside for the preparation of oriented mounts. Although this can be done gravimetrically, the use of a centrifuge can rapidly speed up the process.

Oriented mounts were prepared by depositing the dispersed clay particles onto glass slides and allowing the suspension to dry. Additional sample was added dropwise until an opaque film was acquired. The dried oriented mounts were analyzed via XRD and then modified by glycolation. This was done by carefully applying a small drop of ethylene glycol to the surface of the clay and allowing it to absorb (Figure 3). Multiple clay mounts can be batch-processed by placing in a warm desiccator filled with a small amount of ethylene glycol for several hours. A second diffraction scan was collected after treatment for comparison to the original oriented mount. Additional mounts were prepared from several commercially available clay standards for demonstration purposes.

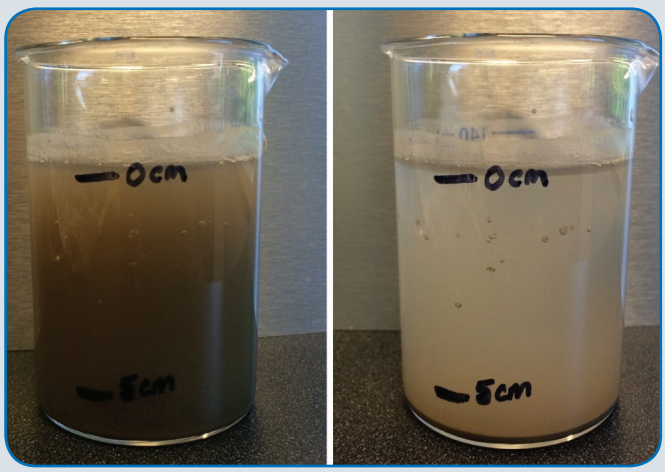

Figure 2. Finely ground geological samples are dispersed in water via sonication (left). The bulk and clay mineral fractions are divided by gravimetric separation (right), and the clay minerals are collected by decanting. The markings on the beaker are for tracking the progress of separations.

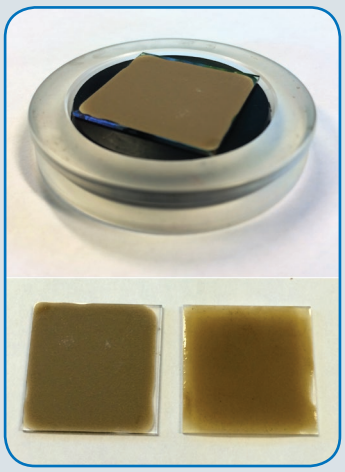

Figure 3. Prepared clay slides are placed in a sample holder with adjustable height (top) for accurate positioning within the diffractometer. Clay specimens are analyzed as a dry oriented mount (bottom left) and again following the addition of ethylene glycol (bottom right).

Data was collected in reflection geometry using the D2 PHASER equipped with a high-speed linear detector (LYNXEYE), which is essential for rapid data collection. The D2 PHASER is capable of being operated in a mobile lab environment, featuring an on-board cooling system, integrated computer, and operating with standard domestic power. The scanning range should start at ≤ 3 ° 2θ in order to ensure that the clay peaks of interest are fully and properly observed. Total data collection time for these two scans is 10 minutes each. Total processing time for each sample is about 3 hours, mostly unattended during separation and drying steps.

Discussion

Two scans were collected on each prepared sample. The first scan was collected on the untreated oriented slide. The second scan was collected on the fully swelled and glycolated slide.

Low angle diffraction data for two clay samples is shown in Figure 4. A dramatic shift to a larger d-spacing is observed for the bentonite sample, indicating sample swelling. The kaolinite reflections are unaffected.

For the collected clay fraction, several mineral species were observed, as shown in Figure 5, including strong reflections from chlorite and muscovite. Although the smectite reflection is severely broadened in the oriented mount – to the point of being difficult to confirm visually – the swelled mount displays a very clear shifted reflection centered around 17.4 Å, confirming the presence of swelling clays in this sample.

Conclusions

In this report, we have demonstrated the ability of using the mobile D2 PHASER X-ray diffractometer to identify the presence of swelling clays. Sample preparation involves a straightforward approach with grinding, dispersal in water, separation, and depositing onto glass slides. Samples are analyzed as oriented mounts in reflection geometry; once as deposited and air-dryed, and a second time following the addition of ethylene glycol. This process can be sped up dramatically with a small centrifuge and a warm drying oven.

The focus of this report is the identification of smectite clays. More detailed clay speciation is achievable with the D2 PHASER with additional sample processing (e.g., multiple heating cycles) beyond the scope of this study. Additional information is available in the excellent report by the U.S. Geological Survey.

References

[1] Poppe, L.J.; Paskevich, V.F.; Hathaway, J.C.; and Blackwood, D.S. *A Laboratory Manual for X-Ray Powder Diffraction*; U.S. Geological Survey Open-File Report 01-041; Woods Hole, MA, 2001.

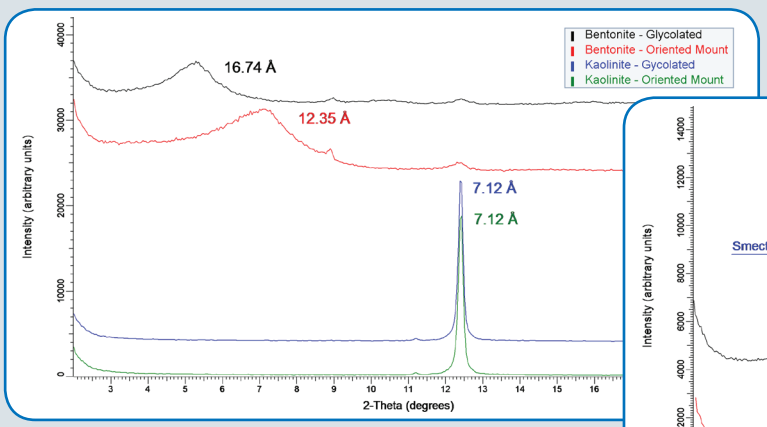

Figure 4. Diffraction data for two clay samples – bentonite and kaolinite – as both oriented mounts and glycolated specimens. The clear shift in low angle data for the bentonite sample indicates expansion along the c-axis. The kaolinite sample does not swell with the addition of glycol; consequently, the reflection is observed at the same location.

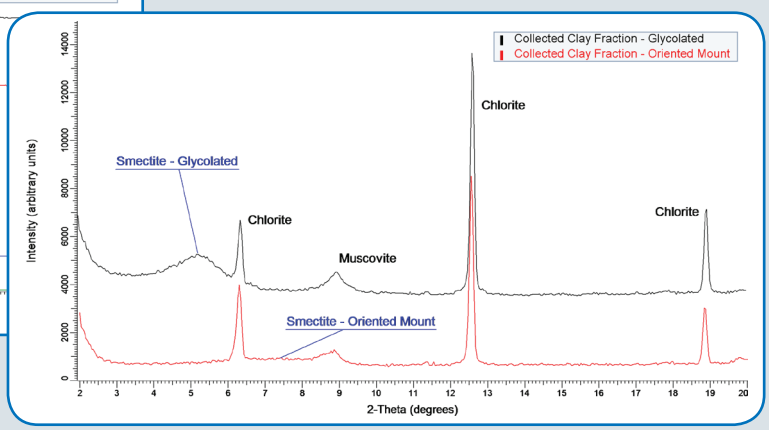

Figure 5. Diffraction data for a clay fraction collected from shale rock. Chlorite and muscovite reflections are easily detected and do not shift upon glycolation. The broad smectite reflection is difficult to observe in the oriented mount but appears as a stronger, shifted reflection after the addition of ethylene glycol.

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