

Bulk- and Clay-Mineral Quantification in the Upper Cretaceous Emscher Formation – Evaluating a Potential Hydraulic Barrier During Mine Water Rebound in the Ruhr District

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Abstract

Combined mineralogical, geophysical and petrophysical methods are necessary to determine the hydraulic conductivity and the so-called healing potential of fractures within “Emscher-Formation” which acts as a cap rock during rebound. From the mineralogy and especially the clay-mineralogy of the “Emscher-Formation” one can infer key aspects of hydraulic behaviour of the rock. Due to their small grain size, the large surface area and their interactions at the molecular level, the amount of clay minerals and their different phases influence the petrophysical behaviour. X-ray diffraction analyses, using different approaches and sample preparations to determine and quantify the mineral composition has been used.

Keywords: Clay Mineralogy, XRD, Rietveld, Cap Rock

Introduction

Cuttings and core material from monitoring well “Waltrop 2”, which was spudded in July 2018, was analyzed for special clay mineral analysis using a combined X-ray diffraction (XRD)-Rietveld post-processing approach. Well site “Waltrop 2” is situated 15 km north of the city of Dortmund, Ruhr District, North Rhine Westphalia, Germany. The closest mine shaft called “Waltrop 3” is located 6 km south of the monitoring well (Fig. 1). The sampled section ranges from 40 m to 488 m TVD. The Emscher-Formation (Upper Santonian – Middle Coniacian) consists of clayish to marly dark grey monotonous bioturbated sediments (Hiß *et al.*, 1995). The Emscher-Formation generally acts as a regional hydraulic barrier. Within the mine water rebound process associated with the former hard coal mining region of this area, it is regarded as an important natural barrier protecting regional drinking water reservoirs. To estimate the self-sealing potential of the Emscher Formation the amount of clay mineral content and especially the amount of swelling clay minerals (smectite) have been evaluated in ten cutting-samples taken every 20 m of the analysed core section. In addition

to the cutting-samples, 16 core-samples of the lower section where analysed as bulk powder samples.

Clay minerals are hydrous aluminium phyllosilicates, are mostly part of the grain size fraction $<2 \mu\text{m}$ and can be classified in four different groups due to their internal layer structure. These groups are: kaolinites, chlorites, illites and smectites. Clay minerals exhibit a high surface area, have the ability of cation exchange and in particular the smectite group has the ability to incorporate water within its layers and has the ability to swell by incorporating water molecules in the lattice (Moore & Reynolds, 1997). The proportion of swelling clays compared to the overall amount of clay minerals present in the rock matrix was determined to estimate the amount of plastic behavior and crack healing potential of the marls and marly carbonates.

Methods

Drilled cores (depth 15 m-71 m) from the drilling “Waltrop 1” (Genth *et al.*, 2021) and the cores of the drilling “Waltrop 2” (depth 440 m – 611 m) have been described using classic protocols for visual and lithological core inspection on the site of the Geological Survey of North Rhine Westphalia (GD

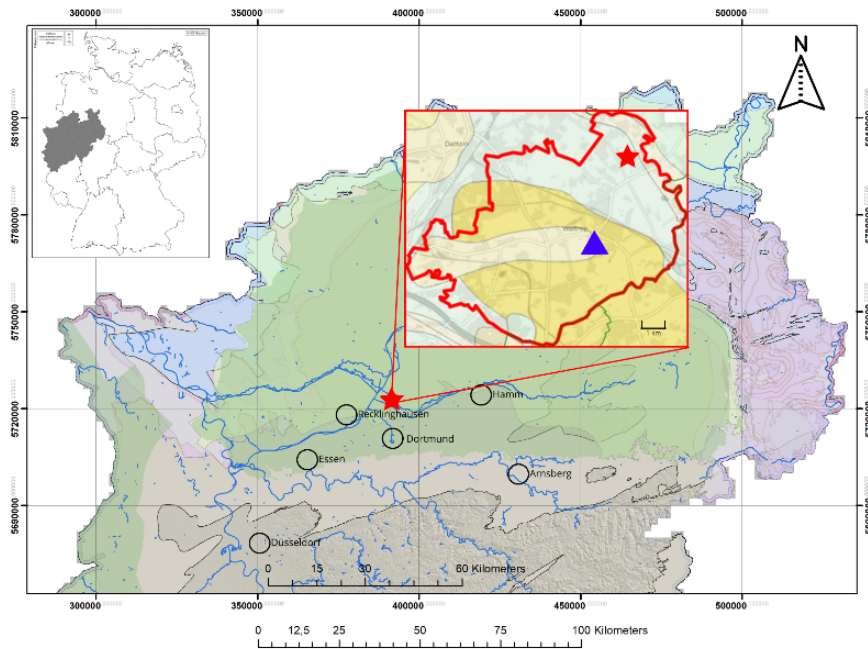


Figure 1 Bedrock geology map of the Muensterland Basin and Rhenish Massif, North Rhine Westphalia, Germany, Quaternary and Tertiary strata removed, sample material/drill cores from drill site (marked by red star); close up map: district borders (red line)

NRW). The analysed samples are cuttings from the drilling “Waltrop 2” (40 m – 430 m TVD) in the text named as “cutting-samples” and an additional core sample set named as “core-samples”. The core sample set is taken close to the lithostratigraphic transition to the underlying “Erwitte Formation” (434.8 m – 487.9 m TVD) which is called locally calcareous to marly transition beds. The wells “Waltrop 1” and “Waltrop 2” are located in the same area, with a distance of pprox.. 25 m to each other. All samples were cleaned to be free of drilling fluid.

Prior to X-ray diffraction (XRD) preparation bulk samples were analysed for its inorganic and organic carbon content using thermal elemental analyser SoliTOC at GD NRW. The XRD measurements for quantification of wt.% of mineral content were conducted at the German Mining Museum Bochum (DBM) using a Panalytical X’pert Pro instrument. Diffraction parameters were as follows: Wavelength CuK α =1.541 Å; tube voltage=40 kV, tube current=45 mA; primary/secondary soller slit=0.04 rad; beam mask=10 mm; anti scatter slit=variable; measuring

range=5-70 $^{\circ}$ 2 Theta; step size=0.0167 $^{\circ}$ 2 Theta; scan speed=20 seconds/step. Twenty-two bulk cutting-samples were measured with an automatic divergence slit. Half of the bulk cutting-samples were de-carbonated, ground using a ball mill and then measured with 0,25 $^{\circ}$ divergence slit. In addition 19 bulk core-samples were measured with a 0.25 $^{\circ}$ divergence slit. The amounts were quantified by Rietveld refinement method using the software “Profex”(Doebelin & Kleberg, 2015).

For further clay mineral identification, oriented cutting-samples were prepared. To minimize the amount of non-clay minerals, the cutting-samples were separated in to the <2 μ m grain section. The separation was done by using classical Stokes law procedure. The sample was brought in suspension using a ULTRA-TURRAX dispersing tool and 10 mg of tetra-sodium pyrophosphate. The separation process was conducted, by using a centrifuge with a sample volume of 100 ml (Poppe *et al.*, 2001). After drying and cleaning from dispersing agent, the samples were brought in suspension again. A vacuum apparatus with a Millipore 0.45 μ m pore size

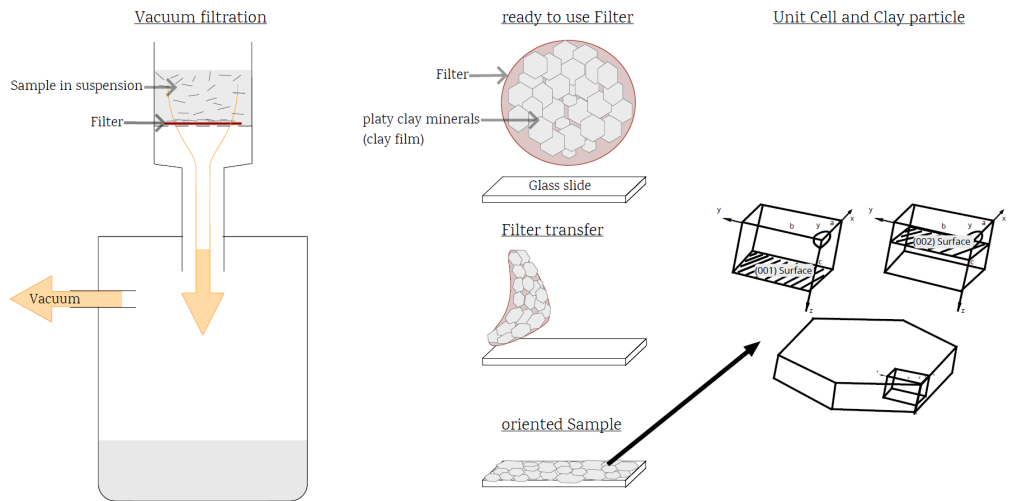


Figure 2 Making the oriented texture sample in order to oriented the clay minerals perpendicular to the c-axis

filter was used for orientation of the clay minerals perpendicular to their c axis. The “wet” filter was then transferred to regular glass slide, by pressing the filter slightly on to it (Fig. 2).

Ten de-carbonated cutting-samples were grain size separated including the $<2 \mu\text{m}$ clay fraction. The samples were measured using a 0.5° divergence slit after certain separate treatments: air dried, glycolated and heated to 550°C . By comparison of the different oriented samples, the ordering type and the ratio of illite/smectite(I/S) mixed layer clays as well the amount of chlorite were determined (Moore & Reynolds, 1997). The results of the inorganic carbon content combined with the XRD wt. % results were plotted vs. depth. A lithological classification scheme based on DIN 22015 (1993) was used.

Results

The carbonate content analyses of the cutting-samples exhibit an average amount of $\text{CaCO}_3 = 38.26 \text{ wt. \%}$. It ranges between a minimum of 24.20 wt. \% and a maximum of 56.70 wt. \% in the analysed section (Fig. 3). The measured CaCO_3 content consists entirely of calcite and increases with depth. Every cutting-sample contains well quantifiable amounts of the following minerals: calcite, quartz, I/S mixed layer clays, illite/muscovite and kaolinite.

Accessory minerals were chlorite, pyrite and feldspars. Within the de-carbonated random powder cutting-samples, the large amounts of quartz, I/S mixed layer clays, and illite/muscovite were verified. The average amount of minerals within the entire random powder cutting-sample set in decreasing wt. % order are: calcite (38.26 wt. \%), quartz (23.63 wt. \%), I/S mixed layer clays (18.39 wt. \%), illite/muscovite (15.18 wt. \%), kaolinite/ chlorite (3.23 wt. \%), feldspar (0.55 wt. \%) and pyrite (0.45 wt. \%). In Fig. 3 the increase of calcite with depth is highlighted.

The amount of I/S mixed layer clays and illite/muscovite do not exhibit a strong tendency with depth. The maximum amount of I/S mixed layer clays and illite/muscovite in the dataset with 23.69 wt. \% and 19.53 wt. \% respectively is observed in the 200 m cutting-sample. The amount of kaolinite/chlorite indicates only a slight tendency with depth, exhibiting the lowest amount in the deepest cutting-sample. The analyses of the oriented cutting-samples (Fig. 4) have demonstrated that quartz is ubiquitously present in the $<2 \mu\text{m}$ fraction. This amount of quartz was called “microquartz”. The differentiation of chlorite vs. kaolinite was determined in oriented cutting-samples after heating to 550°C . Chlorite content increases with depth in the sample set. Chlorite content could not

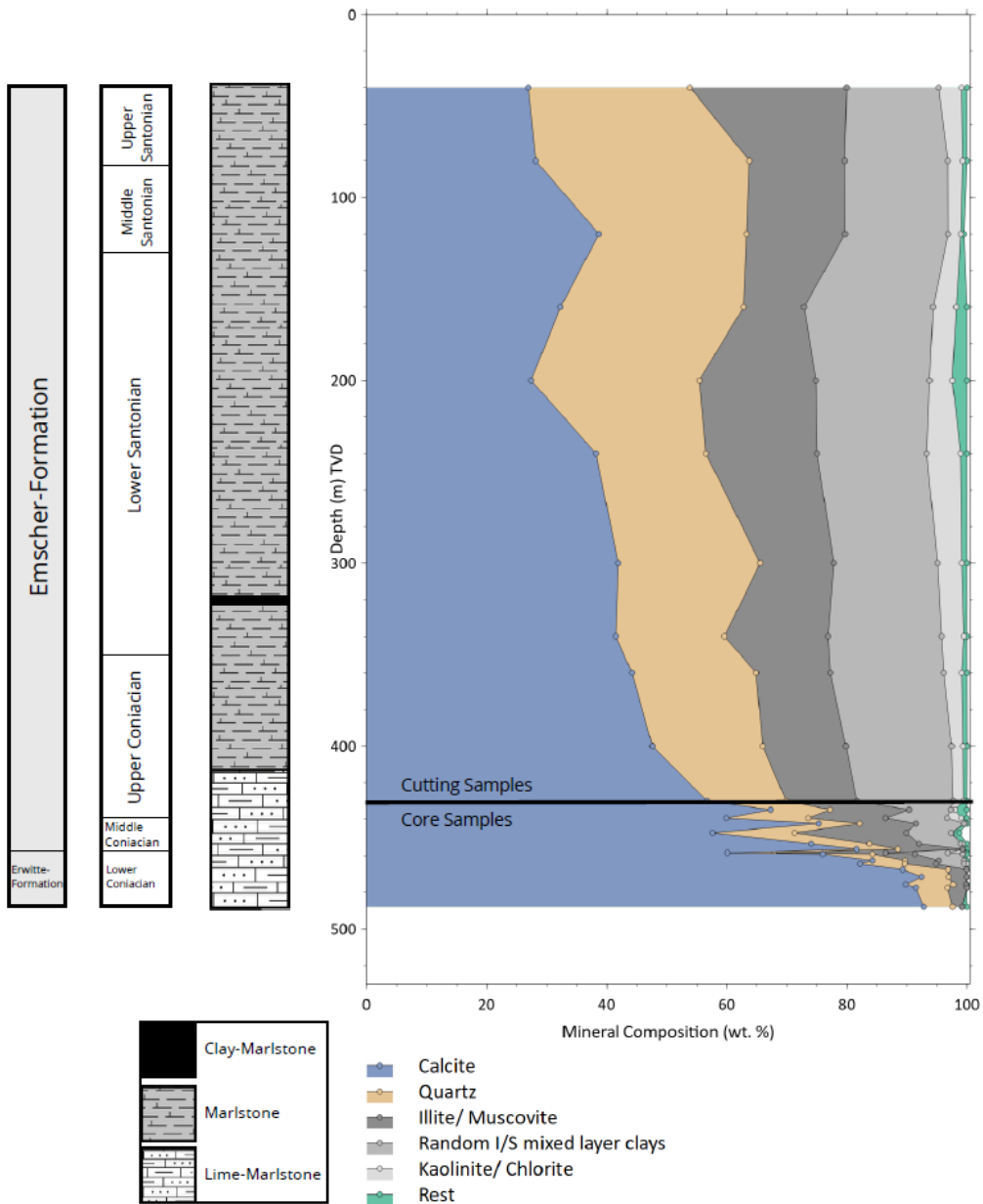


Figure 3 Mineral composition of the random powder samples vs. depth, including lithostratigraphy

be quantified in the random powder cutting-samples. The ordering type of I/S mixed layer clays was determined to be random. The amount of illite within the I/S mixed layer clays was measured to be in between 10 – 25 wt. % in all oriented cutting-samples.

The amount of calcite in the measured bulk core samples continues to increase until a max. of 92.8 wt. %. The amount of all other

mineral decreases with kaolinite not being able to quantify in most core-samples (Fig. 3). The average amount of minerals within the entire random powder core sample set in decreasing wt. % order are: calcite (78.26 wt. %), illite/muscovite (8.18 wt. %), quartz (7.96 wt. %), I/S mixed layer clays (4.46 wt. %), kaolinite/ chlorite (0.44 wt. %), pyrite (0.35 wt. %) and feldspar (0.26 wt. %). Because

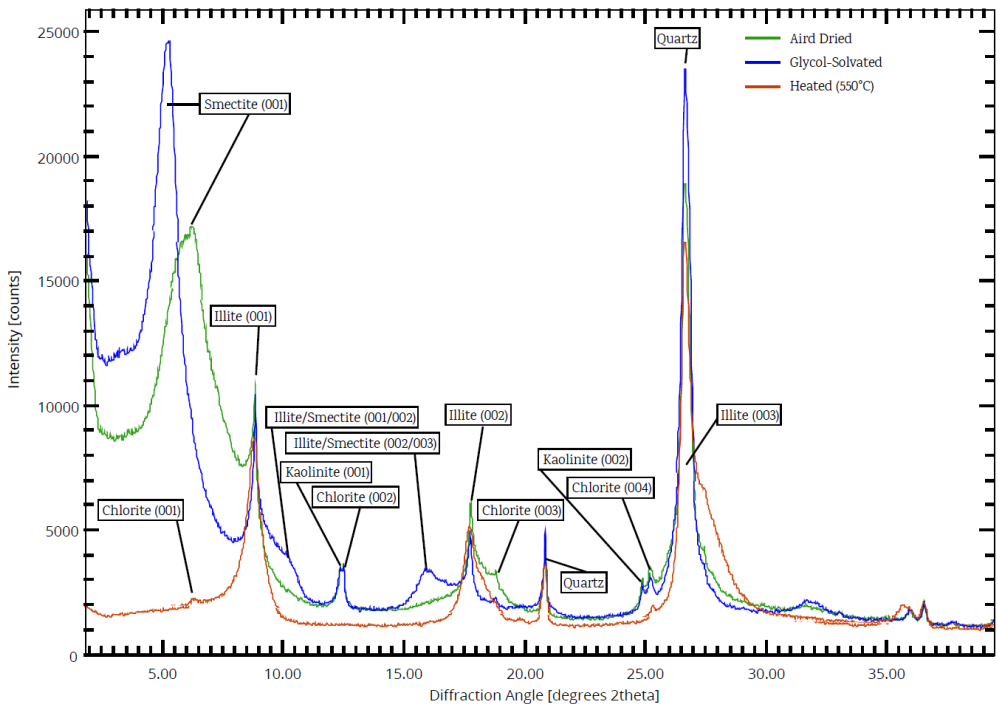


Figure 4 Diffractograms of de-carbonated, oriented texture samples, core depth 430m; pre-treatment: air dried (green); glycol solvated (blue) and 550°C heated (red); (hkl) lattice planes notation.

CaCO₃ was measured thermally for both sample sets (cutting and core), the amount of calcite quantified via Rietveld vs. CaCO₃ thermal method could be compared. The deviation of the two procedures has a mean value of 7 wt. %.

Conclusions

The plasticity of smectite in I/S mixed layer clays is an important parameter when it comes to permeability of formations and the behaviour of the rock with respect to its “self-healing potential” of brittle deformation features, i.e. crack/joint/fracture propagation. High smectite content in I/S mixed layer clays, indicate high potential for impermeable behaviour – even in tectonically exposed regions. The observed ordering type in I/S mixed layer clays as geothermometer indicates low diagenesis potential with moderate temperatures up to 60°C. As a second diagenetic indicator, chlorite formation was examined. Its amount increases with depth in the formation as a potential indication for its diagenetic nature (Moore & Reynolds, 1997).

Consistently, Gasse, (1987) who previously analysed the geochemistry of the Emscher-Formation using XRD, observed a similar trend of chlorite content in the lower part of the formation. The increasing amount of calcite with depth indicates a trend to the more hemipelagic carbonate dominated Cenomanian-Turonian “Plänerkalkstein” within the basin history in contrast to more detrital dominated formations during later stages of the basin fill. The higher detrital sediment supply stems either from inversion related uplift in the northern part of the basin, or from reworked older sediments or a combination of both. The observed high abundance of microquartz (quartz in the <2 µm fraction) might influence the permeability of the rock. The rock might behave more brittle if more microquartz is present and could act as a fracture dominated fluid conduit compared to a tight formation.

Due to the high amounts of quartz, possible >60° 2Theta clay mineral peaks, could not be identified. The quartz phase has a set of intensive peaks in that range which

makes it impossible to identify other peaks. The huge variants of thermal vs. Rietveld measured CaCO_3 might be caused by small sample sizes and poor grinding caused by the ball mill.

Outlook

For further research of the clay fraction, which probably contains high amounts of microquartz, SEM analyses are planned. Analysis of samples from the wells "Pferdekamp 1" and "Ost 5" are planned. For more reliable X-ray diffractograms, the samples need to be more homogeneous in terms of sample mass and grain size. This is being achieved with a greater sample mass, which is easier to take on core-samples. A more homogeneous grain size distribution achieved using an XRD dedicated mill. To make the Rietveld analyses and quantifications more precise, an internal standard (Corundum) is being used in the Bulk and decarbonated powder samples. To identify the different clay minerals better, the texture samples will be prepared with $<1 \mu\text{m}$ sample material, so that quartz phases aren't interfering with the clay phases. Also $<1 \mu\text{m}$ powder samples will be prepared, to identify the $>60^\circ 2\theta$ clay mineral peaks, without the interference of quartz phases. For a better lithological classification, the grain size distribution will be determined for all samples. For a better verification of the calculated elementary composition, X-ray fluorescence analyses of core-samples will be investigated.

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