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Resolving Cl and SO₄ profiles in a clay-rich rock sequence

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Abstract

The chloride and sulfate concentration profiles in a 260 m thick clay-rich Mesozoic sediment sequence have been analyzed by various methods. Chloride data generally indicate a good consistency between different methods if anion exclusion is accounted for in leaching tests. For sulfate, however, there is an apparent inconsistency between leaching data and those obtained from the other methods, which points to the dissolution of a sulfur-bearing mineral. Traces of diagenetic gypsum seem to be a likely source, but other sulfur minerals cannot be ruled out.

Keywords: clay-rich rocks, chloride, sulfate.

1. Introduction

The likely predominance of solute transport by diffusion in low permeability clay-rich rocks can be tested by studying porewater profiles of water tracers and anions which show no or only weak interactions with the rock matrix [1]. For anions, ion exclusion needs to be accounted for in such rock formations, given the considerable amount of illite and smectite minerals carrying a negative structural charge. Considering anion exclusion in the back-calculation of aqueous leaching data, consistent profiles for chloride could be obtained in claystones by applying aqueous leaching, squeezing and water sampling in boreholes [e.g. 2, 3]. For sulfate, the existing data are sparser. In the Opalinus Clay at the Mont Terri Rock Laboratory, Switzerland higher SO₄/Cl ratios derived from leachates as compared to squeezing and borehole data were assigned to sulfide oxidation during the drilling process and sample treatment and the

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possible dissolution of celestite traces [2]. High \( \text{SO}_4 \) concentrations observed in leachates of core samples of the Callovo-Oxfordian (COx) formation in Bure (France) were explained by dissolution of celestite traces in the rock [4]. A multi-method approach, based on our previous experience [2, 3] was adopted to characterize the mineralogical and geochemical properties of a \( \sim 260 \) m thick, predominantly clay-rich rock sequence. The analyzed cores stem from Mesozoic sediments located at a depth of 730 – 990 m below surface. Here, the depth profiles for chloride and sulfate are presented and discussed.

2. Geologic setting

The borehole close to the village of Schlattingen (northern Switzerland) is located in the border area of the Eastern Molasse basin, about 10 km NE of the well-studied borehole at Benken [5]. Below the Quaternary and Tertiary overburden, Jurassic and Triassic sediment rocks dip gently to the SE. These are underlain by heterogeneous Permian sediment rocks and Variscan gneisses. The studied rock sequence can be roughly divided into four units: The top unit (\( \sim 25 \) m thick) corresponds to the lower part of the Effingen Member (Malm) and is made up of silty to sandy calcareous marls. The underlying unit (\( \sim 77 \) m thick), termed “Brauner Dogger”, exhibits rather variable lithology. It consists predominantly of clayrocks and marls with variable contents of calcite and quartz. The third unit is the \( \sim 120 \) m thick Opalinus Clay which is characterized by fairly homogeneous silty to fine sandy claystones. The lowest unit (Liassic, \( \sim 53 \) m thick) is also rather rich in clay content and made up of a variable sequence of marls and claystones.

Based on the analogous setting in the Benken borehole, it can be expected that the underlying aquifer in the Stubensandstein formation (Keuper) and the overlying one in the Upper Malm influence solute transport in the studied rock sequence.

3. Experimental procedures

Representative rock core samples were taken approximately every 5 m, packed on-site according to a standardized protocol to protect them from air and water loss, stored cool and sent to the laboratory for subsequent analyses. These were conducted according to the procedures outlined in [2,3].

Mineralogical compositions, water contents and density measurements were obtained for 30 samples. From water contents and grain density, water-loss porosity was derived [3]. Aqueous leachates were prepared for 30 samples at a solid/liquid (S/L) ratio of 1 for a period of 48 h. All procedures, except for milling (see below), were carried out under \( \text{N}_2 \) in a glovebox. Squeezing tests were conducted on 12 selected clay-rich samples at CRIEPI (Japan). Porewaters were extracted at 200 to 500 MPa, but only data from lowest squeezing pressure of 200 MPa are reported here. Porewater was also extracted with the advective displacement technique from a core sample at 799 m depth. In addition, one groundwater sample could be collected by pumping from the depth interval of 799-833 m during hydraulic testing of the borehole. From analysis of tracers it turned out that the groundwater was contaminated by the drilling fluid by a fraction of \( \sim 33-50\% \). Nevertheless, from the analyses and the groundwater/ drilling fluid mixing ratio, chloride and – to a lesser degree – sulfate concentrations could be roughly estimated.

4. Results and discussion

4.1. Clay content, porosities and chloride profile

Water-loss porosities exhibit an increasing trend with depth, down to about 800 m. This trend is related to the clay content, which also increases with depth (Fig. 1a). One sample at 759 m depth, with a porosity
of 17% and a high clay content, which was extracted from an iron oxide-rich oolitic horizon, falls off this trend. In the sequence below, where the clay content is generally rather high (≥ 30 wt.%), porosities remain fairly constant.

The chloride concentrations obtained from the different methods are depicted as a function of depth in Fig. 1b. Comparison of squeezing data with leaching data (extrapolated to in-situ densities) indicates a near-to-constant anion exclusion factor of ~0.5. Similar anion exclusion factors have been derived for clayrocks at other locations [1, 2, 4]. The leaching data are plotted in Fig. 1b, assuming a constant anion exclusion of 0.5 across the whole depth profile. The chloride concentration obtained from the groundwater sample agrees well with the corresponding squeezing data. On the other hand, the porewater sample analyzed by advective displacement exhibits somewhat lower concentrations than the corresponding squeezing data.

4.2. Sulfate

The profile for sulfate shown in Fig. 1c displays an entirely different behavior as that for Cl. Applying a constant anion exclusion factor of 0.5 to the leaching data and extrapolating these to in-situ densities, results in very high sulfate concentrations. Much lower concentrations and a different profile shape are obtained from squeezing, which are supported by advective displacement and groundwater data. Possible reasons for the “excess sulfate” observed in leaching data are: 1) oxidation of pyrite during the leaching procedure and 2) dissolution of sulfate-bearing phase(s). The amount of “excess sulfate” can be estimated by comparing squeezing with the corresponding leaching data:

\[
\Delta [SO_4^-] = \frac{C_{\text{leach}}}{r_{\text{saw}}} - f_a \frac{C_{\text{sq}}}{w_w}
\]

where \(\Delta [SO_4^-]\) is the “excess sulfate” concentration in mol/kg dry rock, \(C_{\text{leach}}, C_{\text{sq}}\) are the concentrations in the leachate and squeezed waters, respectively, \(r_{\text{saw}}\) is the S/L ratio of the leachate, \(f_a\) is the anion exclusion factor and \(w_w\) is the gravimetric water content. The calculated “excess sulfate” is in the range of 1-3 mmol per kg rock, corresponding to a very low proportion (< 2 wt%) of the total sulfur in the rock. Such a low mineral fraction would be difficult to detect analytically. It would correspond only to 0.06-0.2 g of pyrite or 0.14-0.4 g of CaSO_4 per kg of rock.

Pyrite oxidation hypothesis: Pyrite oxidation with molecular O_2 requires 3.75 moles of O_2 to produce 2 moles of SO_4. The only possibility of oxidation was during milling (see section 2). Pyrite oxidation rates in air are generally relatively fast, in the range of \(10^{-7} - 10^{-8}\) mol O_2/m^2/s [6]. Assuming spherical pyrite grains of 1µm (unpublished SEM images), the surface area can be estimated from geometric considerations [7], which yields a value of 1.2 m^2/g. From the pyrite content (not shown), a high rate of \(10^{-7}\) O_2 mol/m^2/s, and a milling time of 10 min., one obtains 0.07–1.6 mmol SO_4 per kg rock. This is about 5–70% of the “excess sulfate”, thus somewhat too low to explain leachate data.

Dissolution of sulfate-bearing mineral hypothesis: This has been tested with a simple equilibrium model with aid of PHREEQC, which includes cation exchange and calcite equilibria [2]. In a first step, the initial cation population on the exchanger was estimated from Na, Ca, Mg and K concentrations in squeezed samples, preliminary CEC data and published selectivity coefficients for Opalinus Clay [8]. In a second step, this exchanger composition was equilibrated with calcite with a fixed pCO_2 of 10^{-3.5} bar and a fixed amount of sulfate – as celestite phase – that was calculated according to eq. 1. The results indicate remarkable agreement between measured and calculated leachate compositions, notably also for alkalinity and pH, thus supporting this hypothesis. However, total Sr concentrations inferred from leaching and cation exchange data (not shown) are too low (by factor of 2-3) compared to “excess sulfate”. Another
possibility is CaSO₄ occurring as traces. From equilibrium modeling, the same results as for SrSO₄ are obtained, supporting the possibility of anhydrite or gypsum dissolution. Diagenetic gypsum has in fact been observed in one Opalinus Clay sample from the Mont Terri Rock Laboratory (H.R. Bläsi, pers. communication), but further evidence is lacking so far.

Fig. 1. Depth profiles for (a) water-loss porosity, clay content; (b) chloride; (c) sulfate. The leachate data in (b) and (c) were extrapolated to water-loss porosity and by assuming constant anion exclusion factor of 0.5. The oolitic sample (see text) is excluded from plots (b) and (c).

In summary, complete dissolution of CaSO₄ traces seems to be the most likely explanation for the apparent “excess sulfate” observed in leachates. However, it cannot be ruled out that traces of celestite and pyrite oxidation have contributed to the “excess sulfate” too. Further work is ongoing to confirm conclusions drawn here. Note that the rather flat profile of SO₄, in contrast to that of Cl, suggests that SO₄ is controlled by solubility, rather than behaving as conservative solute. This further supports the above conclusion.

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