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Ageing effect on the mineral and chemical composition of Opalinus Clays (Mont Terri, Switzerland) after excavation and surface storage

Isabelle Techer [a,*], Norbert Clauer [b], Nicole Liewig [c]

[a] CEREGE, Laboratoire GIS, Universités de Nîmes et d'Aix-Marseille, CNRS-UMR 6635, Parc Scientifique et Technique Georges Besse, 150 rue Georges Besse, 30035 Nîmes, France
[b] Laboratoire d'Hydrologie et de Géochimie de Strasbourg (CNRS-UdS), 1 rue Blessig, 67084 Strasbourg, France
[c] Institut Pluridisciplinaire Hubert Curien, UMR 7178, 23 rue Becquerel, 67087 Strasbourg, France

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ABSTRACT

Samples of Opalinus Clays from Mont Terri Underground Research Laboratory in the Swiss Jura were analyzed repetitively relative to the duration of their exposure to atmosphere. The objective was the evaluation of such a progressive exposure on the chemical composition of whole-rock samples, and on the chemical and Sr isotopic compositions of leachates obtained by leaching the rock powders with dilute acetic acid. This chemical study was complemented by scanning electron microscope observations to identify the related mineral alterations. The chemical data for the rock powders remained quite constant whatever the duration of the storage, whereas significant changes were observed for the leachates. Similar changes were observed in the leachates of samples collected progressively closer to the walls of a previously excavated niche. When storage time or distance to gallery wall increases, the main variations are: (1) a progressive decrease of the element contents and of the $^{87}Sr/^{86}Sr$ ratio in the leachates, (2) an alteration of pyrite followed by precipitation of Ca-sulfate in the rocks, both observed by SEM, and (3) a probable precipitation of new mineral phases in the rocks, such as Fe-oxyhydroxides and/or jarosite that could not be visualized by electron microscopic observation because of their very limited amount and very small grain size. The modifications call for an oxidation of pyrite that probably induced also an oxidation of the organic matter. It could also be shown that the reactions were enhanced by temperature increase, and that they were less pronounced in the samples behind the gallery wall than in the cores stored in laboratory conditions.

Of importance for the waste-disposal assessment is the fact that the chemical characteristics, and therefore the mineral assemblages, of the studied argillaceous rocks are reactive to changing oxidation/reduction conditions monitored by dehydration. The resulting mineral reorganization seems to contribute to a sealing of the rocks, as the amounts of elements released into the leachates decrease progressively with storage time. This tendency is detectable after several months for the core samples stored under vacuum in Al-foil at room temperature but with periodic exposure to atmosphere, and after several years for the *in situ* samples collected behind an excavation wall.

1. Introduction

The petrophysical and geochemical study of deep-seated geological sedimentary sequences requires, either core drilling and storage of the recovered samples for laboratory measurements and observations, or shaft excavation for *in situ* investigations. In the case of studies on the potential reliability of nuclear-waste storage in deep repositories, such data should be as representative as possible of the intrinsic characteristics of the target rocks before human interference. Determination of their physical and chemical properties represents the ultimate reference of the confining performance of the potential repository and, therefore, of the safety studies. In this respect, the challenge is to describe as closely as possible the original reference material, that is to say before drilling or excavating, on the basis of expected alteration processes that modify the rocks during core drilling and afterwards during storage, or *in situ* behind gallery walls after excavation. It is agreed that such changes are very limited and therefore difficult to identify, especially by routine analyses. Alternately, it is essential to ensure that the rock properties determined on drilled cores, or from gallery and niche walls, are most representative of the original *in situ* rock sequences in order to evaluate the respective impact of drilling, excavation and storage on the physical and chemical properties of the study rocks.

Drilled or excavated rocks are expected to exchange rapidly with their new atmospheric environment, which includes the loss of constitutive fluids by dehydration, making very challenging a

* Corresponding author. Fax: +33 (0)4 66 70 99 89.
E-mail address: isabelle.techer@unimes.fr (I. Techer).

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precise characterization of the initial stage for adequate evaluation of the storage effects. To minimize any potential exchange reaction, various storage conditions of the extracted rocks, such as in plastic or in Al-sealed bags, under vacuum or not, and with or without addition of a neutral gas, were tested. Different types of drillings were also applied, but it transpires that, despite all the care taken for drilling and conditioning, stored samples undergo various chemical exchange and reactions that might be more or less pronounced (De Craen et al., 2004). In fact, most of the interactions are initiated by contact with the atmosphere that favors oxidation due to the almost instantaneous supply of O_2, CO_2, and water in some cases, to rocks that were confined in reduced conditions with limited amounts of fluids and gases for millions of years. Additional perturbations may also occur due to instantaneous dehydration during coring, sample recovery and conditioning under vacuum, and possibly to further re-hydration depending on the handling of the recovered samples. As contact with air induces changes in both the mineral composition of the rocks and the chemical composition of the pore waters (Descostes et al., 2002; De Craen et al., 2004), the challenge to identify as precisely as possible the initial stage from results generated by laboratory studies consists, therefore, of: (1) avoiding as much as possible any chemical perturbation from sampling to laboratory analyses and observations, which depends, as mentioned, on the conservation technique used or (2) identifying and quantifying the changes relative to storage time allowing a theoretical back-evaluation of the composition to the time of drilling or excavation.

When a deeply buried sedimentary sequence is excavated for shaft and gallery openings, the disturbances in the rock walls are mainly initiated and expectedly amplified by the excavation technique and working conditions that produce the so-called "excavated damaged zone" (EDZ) and "excavated disturbed zone" (EdZ) in the target rocks (Anon, 2001; Bossart et al., 2002; Meier et al., 2002; Alheid, 2003; Charpentier et al., 2003; Matray et al., 2007; Mayor et al., 2007). The petrophysical and geochemical properties of the rocks from these zones are apparently more or less modified due to physical constraints that initiate cracks and reopen previous discontinuities. The EDZ is generally considered to correspond to an altered zone in which plastic deformation is expected as a result to stress redistribution during and after excavation. A fracture network consisting of unloaded fractures and desaturation cracks develops in the rocks of this zone, increasing their porosity and water content. Horseman (2001) proposed that this temporal evolution in the stress path leads to a reduction in the permeability. Processes like hydration/dehydration and desaturation due to air conditioning and renewing in galleries of Underground Research Laboratories (URL) during and after excavation, also contribute to petrophysical and thermo-hydro-mechanical modification, mainly in rocks of the thicker EdZ. It may also be mentioned that the magnitude and degree of the geochemical processes in the two zones have not yet been precisely evaluated in all presently accessible galleries dedicated to experiments for deep repositories, neither in space nor in time, even though understanding them is important because of their potential impact on repository design and performance.

In order to provide further information about these limited modifications in drilled cores stored on laboratory shelves whatever their conditioning and in larger rock samples exposed to air after shaft opening, and to discuss the evolution of the geochemical records in such rocks, the authors have completed a geochemical study on Opalinus Clays collected in the Mont-Terri URL, Switzerland. The underlying question of the study was to evaluate how such geochemical modifications resulting from exposure to air can contribute to a self-sealing (self-healing is another term used) of the excavated and/or cored sedimentary formation, as such a process can be broadly subdivided into: (a) mechanical and hydro-mechanical processes that relate to the changes in the stress field, the movements of the pore waters, and to the physical properties of the rocks, such as swelling, softening, plastic deformation and creeping and (b) geochemical processes linked to chemical alterations, element transport in aqueous solution and new mineral precipitation. The EDZ may, therefore, not be a long-term safety issue, if its sealing capacity can be proven (Wieczorek et al., 2001). More specifically, the study was designed to detail the evolution of the geochemical properties of the rocks by determining the chemical composition of the solid rocks and of their soluble mineral phases. These soluble phases were gently extracted by reacting rock powders with dilute acid, soon after recovery and after various storage periods in the laboratory. Leaching of the rock samples was specifically applied as it allows removing the soluble minerals as well as the chemical elements and complexes dissolved in the fluids of the rock pore-space. Such leaching experiments are also expected to oxidize the organic matter that might be present in the rocks. This organic matter is known to contain elements such as Sr, which $^{87}Sr/^{86}Sr$ ratio might be significantly different from that of the Sr incorporated in mineral phases (e.g., Clauer et al., 2006). These components are known to be most sensitive to changing oxidation–reduction conditions induced by core drilling on the elements and complexes dissolved in the pore fluids, as air and some moisture are able to penetrate the pore system during lasting interactions on laboratory shelves and at gallery walls.

The study of the mineralogical and chemical disturbances induced by gallery excavation was not an initial objective of this work. The studied core samples were purposely collected behind the EDZ and EdZ of a niche excavated several years earlier in the research-dedicated gallery of the URL. However, it was of interest to report on changing results observed in the sample collected closest to the niche wall, as it appeared to provide interesting complementary information by comparing modifications due to rock excavation relative to rock drilling. It may also be mentioned that the chemical modifications in the wall rocks became obvious only after the experiment had already been in progress for several months, which prevented any additional sampling of more rock samples taken closer to the gallery wall in the EDZ or EdZ, at least during this experiment.

2. Description of the samples and the experimental procedure

The study area is located in the Mont-Terri URL built next to the reconnaissance gallery of the motorway tunnel excavated between the Swiss plateau (Bern) and the French Jura (Belfort). This laboratory is mainly dedicated to multidisciplinary research programs that were first completed in the reconnaissance gallery itself and in eight niches. Later, starting in 1997–1998, the laboratory was extended into the so-called 'new gallery', where additional niches were excavated to host further research projects (Thury and Bossart, 1999a,b; Fig. 1).

The URL was built in the Opalinus Clays (stratigraphic age: Aalenian or Early Dogger) that consist of a clay formation of low permeability, mechanically quite stable and containing 'swelling' clay minerals. The overall amount of the clay material varies from 40% to 80% depending on the rock lithology. Other components include quartz, calcite, siderite, pyrite, feldspar and organic C (Thury and Bossart, 1999a,b; Thury et al., 2000). Three different facies were described: (1) a predominant shaly facies in the lower section of the sequence, (2) a sandy-limy facies in the middle of the sequence, and (3) an interbedding of sandy and shaly units in the upper section. The rock strata dip at an angle of approximately 45° towards the SE. The study samples belong to the upper shaly facies of the sequence. Beyond the mineralogical description of