Impact of salinity and alkalinity on the microstructure of partially saturated Opalinus Clay from the lower sandy facies (LSF) of Mont Terri site

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Abstract. In the context of deep waste disposals, the geological barrier *(i.e.*, the host rock) will be exposed to saline plumes from bituminous waste and alkaline plumes from concrete degradation. These chemical disturbances will affect the hydraulic and mechanical properties of the clay rock by modifying its microstructure. As a result, the self-sealing of the fractures created during excavation could be affected, further affecting the long-term safety of the repositories. To this end, the effect of salinity and alkalinity on the microstructure of a partially saturated Opalinus Clay from the lower sandy facies of Mont Terri was investigated. It was found that at $w = 4.1\%$, salinity decreases the density and the peak of the mesopores compared to the synthetic water. This is due to the water transfer from the meso to the macro pores and to the decrease of the thickness of the diffuse double layer. For the same water content, alkalinity generates meso and macro pores. The dissolutions of clay and non-clay minerals are the main mechanisms involved.

1 Introduction

In Switzerland, the Opalinus Clay is considered as potential host rock for deep nuclear waste repositories due to its low hydraulic conductivity and self-sealing properties [1]. When excavating underground facilities, an Excavation Damaged Zone (EDZ) is created in the host rock. While self-sealing of the EDZ is expected, thanks to the re-saturation by underground water seepage, the initial hydraulic and mechanical properties of the claystone might be recovered over time [2]. However, during the operational phase of the repository, saline plumes may seep from the saline wastes, increasing the salinity of the underground water [3]. Also, due to the degradation of concrete resulting in the release of alkaline plumes, the pH of the under-ground water, initially at 7.5 [4] is expected to rise up to 13.5 [5]. These chemical disturbances will affect the hydro-mechanical properties of the host rock by modifying its microstructure further affecting the self-sealing process. Thereby, the aim of this work is to study the effect of salinity and alkalinity on the microstructure of the Opalinus Clay and to identify the mechanisms involved. To this end, three series of tests were conducted on Opalinus Clay samples from the lower sandy facies (LSF) of Mont Terri site (1) with a hyper- alkaline solution at $pH = 13.5$ and an osmotic suction of $\pi = 1.16\ MPa$ (2) with a highly concentrated saline solution at $\pi = 34\ MPa$ and $pH = 7$ and (3) with a less concentrated saline solution at $\pi = 15\ MPa$ and $pH = 7$. As a reference, a fourth series was carried out with the synthetic water having the same salt concentration

($\pi = 1\ MPa$) and pH (7.5) as the natural neutral pore water.

2 Materials

2.1 Claystone studied

The material studied is the Opalinus Clay from the lower sandy facies of Mont Terri URL. It is composed of clay minerals (between 38% and 52%), carbonate (between 10% and 20%) and silts (mainly quartz, between 37% and 38%) [6,7]. Smectite is present in the form of interstratified illite/smectite type $R1$ (i.e., 80% illite and 20% smectite).

2.2 Hydration solutions

In this study, four solutions were used.
(1) A synthetic water similar in chemical composition to the pore water of the lower sandy facies ($NaCl - 0.138\ mol.L^{-1}, KCl - 0.0404\ mol.L^{-1}, CaCl_2 - 0.013\ mol.L^{-1}, MgCl_2 - 0.013\ mol.L^{-1}, NaHCO_3 - 0.00194\ mol.L^{-1}, Na_2S_2O_3 - 0.00884\ mol.L^{-1}$) [4,8]. It presents a neutral pH of 7.5 and an osmotic suction of 1 MPa.
(2) A hyper alkaline solution having the same chemical components and pH (13.5) as the concrete pore water from field conditions ($NaOH - 0.05\ mol.L^{-1}, KOH - 0.27\ mol.L^{-1}, Ca(OH)_2 - 6 \times 10^{-4}\ mol.L^{-1}$) [9].

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(3) A highly concentrated $NaNO_3$ solution at $\pi = 34\ MPa$.

(4) A less concentrated $NaNO_3$ solution at $\pi = 15\ MPa$.

The two saline solutions were prepared following the relationship proposed by [10] between the osmotic suction and the sodium nitrate concentration. The pHs of the saline solutions, measured with a conventional pH meter are neutral. Thereby, no contribution of pH should be considered in this case. The osmotic suction of the hyper-alkaline solution measured via a Dew-point PotentiaMeter is $\pi = 1.16\ MPa$. Therefore, no contribution of the osmotic suction should be considered in this case.

3 Methods

3.1 Test procedure

In the five series of tests, the initially dried samples ($w = 1.1\%$, $S_r = 25\%$) were exposed to the dedicated solution at $w = 4.1\%$ using a vaporizer. For series 1 and 4, the samples were left in cups sealed with parafilm paper for 22 days. For series 2 and 3, the samples were left for 18 days. After that, microstructural investigation were carried out.

In parallel, to meticulously investigate the effect of alkalinity on the mineralogy of the LSF Opalinus clay, especially in terms of non-clay minerals, two LSF Opalinus Clay samples were immersed for 6 and 12 months in the hyper-alkaline solution. The pHs were monitored for both tests. They kept a constant value.

3.2 Microstructural investigation

To explore the effect of pH and salinity increase at microstructural scale, MIP and nitrogen adsorption/desorption tests were carried out on the exposed LSF Opalinus Clay samples. MIP tests were performed on an AutoPore IV 9500 (Micromeritics Instrument Corp.) porosimeter at a controlled ambient temperature of $20 \pm 1°C$. The applied pressure ranged between $3\ kPa$ to $227\ MPa$, allowing identification of entrance pores between $343\ \mu m$ and $5\ nm$ [11]. To avoid excessive shrinkage, instantaneous freezing was carried out by plunging cubic-shaped small samples in slush nitrogen ($-210°C$) previously submitted to vacuum [12]. The specimens were then placed into the freeze dryer for $24\ h$. To extend the investigation to small pore sizes, nitrogen-adsorption/desorption tests were carried out on a Micromeritics- 3D flex equipment. The relative pressure of the nitrogen ranged between 0.1 and 0.39, allowing the identification of entrance pores between $57\ nm$ to $3.2\ nm$ based on the BJH approach.

3.3 X-ray diffraction studies (XRD)

XRD measurements were performed on 1 g disoriented powder by means of a PANalytical X'Pert Pro with $CuK\alpha$ ($\lambda = 1.54060$ Å) radiation operating at $40\ kV$, $30\ mA$ and $600\ W$.

4 Results

4.1 Effect of salinity and alkalinity on the microstructure of the (LSF) Opalinus Clay

Fig. 1 shows the pore size density functions of LSF Opalinus clay samples exposed at $w = 4.1\%$ to synthetic water, saline solutions at $\pi = 34\ MPa$ or $\pi = 15\ MPa$ or to the hyper-alkaline solution at $pH = 13.5$. From Fig. 1a, it appears that the cumulative intruded void ratio decreases with salinity and increases with alkalinity compared to the synthetic water. However, for the two saline solutions, similar cumulative void ratios were recorded.
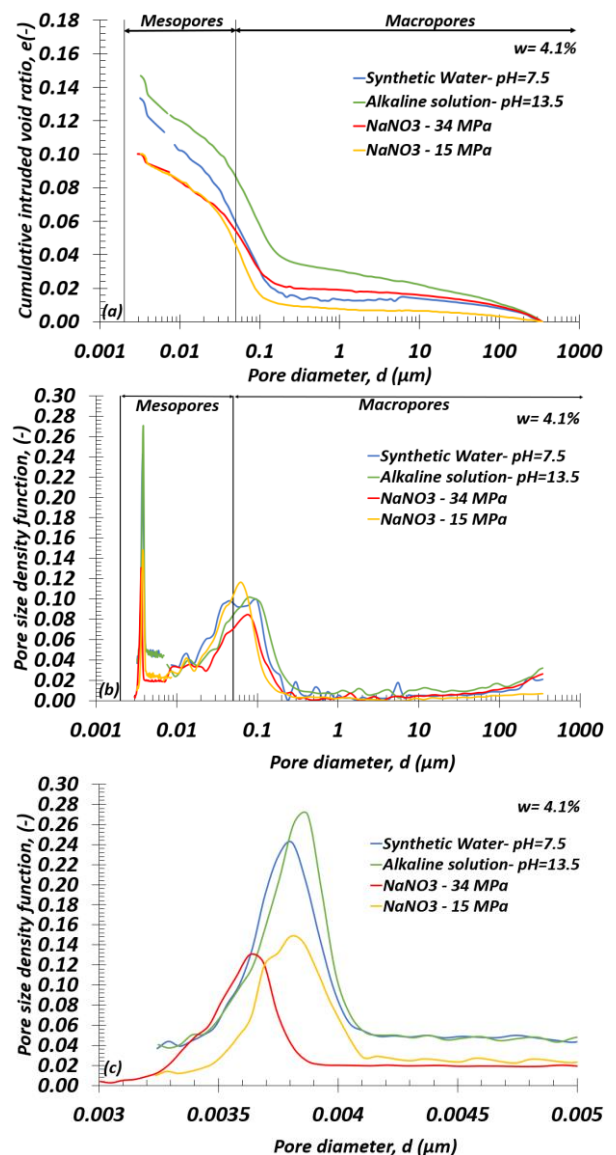

Fig. 1. Pore size distribution curves of LSF Opalinus Clay samples exposed to the sodium nitrate solution at $\pi = 34\ MPa$ or $\pi = 15\ MPa$, to the hyper-alkaline solution at $pH = 13.5$ or to the synthetic water. All the curves are at w= 4.1% (a) cumulative curves (b) density functions (c) density functions obtained via BJH approach

Also, it appears that the macropore proportion increases with alkalinity and for the highly concentrated saline solution.

Fig. 1b shows a decrease in the density of mesopores between 0.01 and $0.05\,\mu m$. The higher the osmotic suction, the more significant the decrease. Comparing the macropores at $\pi = 15\,MPa$ and $\pi = 34\,MPa$, it appears that the higher the osmotic suction, the higher the density of macropores between 0.1 and 0.2 µm and the bigger the dominant macropore.

As for the impact of alkalinity, a higher density of macropores was found between 0.06 and 0.3 µm compared to the synthetic water.

Focusing on the *BJH* data in Fig. 1c, it appears that alkalinity increases the density of the mesopores and the dominant *BJH* peak from 3.81 to 3.86 nm.

Salinity decreases the density of mesopores compared to the synthetic water. The higher the osmotic suction, the more significant the decrease. At $\pi = 34\,MPa$, the BJH peak also decreased to 3.63 nm.

4.2 Effect of alkalinity on the mineralogy of the LSF Opalinus Clay in terms of non-clay minerals

Fig. 2 shows the X-ray diffraction profiles of an intact *LSF* Opalinus Clay sample and of two *LSF* Opalinus Clay samples immersed in the hyper-alkaline solution at $pH = 13.5$ for 6 and 12 months. It can be clearly seen that quartz and calcite dissolutions occurred. The longer the exposure time, the more significant the quartz and calcite dissolutions. Furthermore, calcite dissolution seems to be more significant than quartz dissolution.
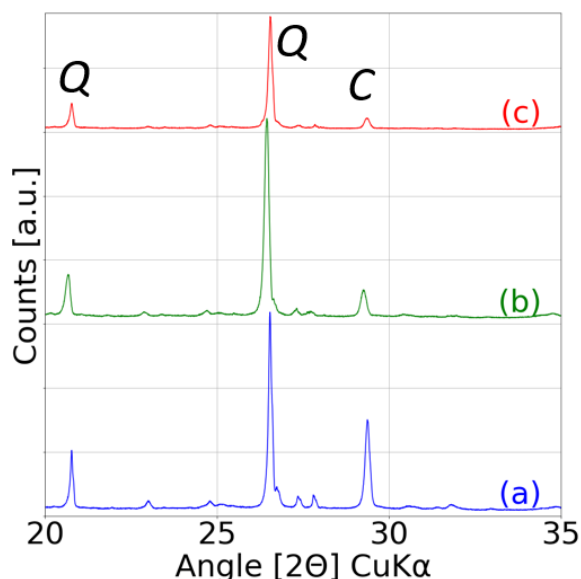

Fig. 2. X-ray diffraction profiles of three *LSF* Opalinus Clay samples from Mont Terri site (a) at initial state (b) immersed in an alkaline solution with a pH = 13.5 for 6 months and (c) immersed in an alkaline solution with a pH = 13.5 for 12 months respectively- Q: Quartz, C: Calcite.

5 Discussions

Given the initial dry state of the investigated *LSF* Opalinus Clay samples (w=1.1% and $S_r =$ 25%), increasing the water content to $w = 4.1\%$ leads to total porosity increase due to the dissipation of matric suction. Meso and Macro pores are created as a consequence of the wetting process.

At a constant water content, exposing the *LSF* Opalinus Clay to a saline solution ($\pi = 34\,MPa$) at high water content ($w = 4.1\%$) results in a decrease in the peak and density of mesopores compared to the synthetic water due to the water transfer from the meso to the macro pores under the chemical gradient [13] and to the decrease of the thickness of the diffuse double layer. The higher the osmotic suction of the hydration solution, the more significant the decrease. As a consequence, macropores might be generated.

However, exposing the *LSF* Opalinus Clay to a hyper-alkaline solution results in the creation of meso and macropores. This can be explained by three mechanisms:

(1) The dispersion of the structure [14], due to changes in the charge of the clay particles edges because of the acid-base attack [14] leading to an increase in the repulsive forces [15].

(2) Clay mineral primary dissolution that follows the first mechanism [15].

(3) Calcite and quartz dissolutions [16].

Even if calcite and quartz dissolutions were identified on longer exposure times, the dissolution of non-clay minerals did probably occur after 22 days but to a lesser extent.

While the first two mechanisms affect the mesoporosity, the third one increases the macroporosity.

6 Conclusions

Salinity and alkalinity affect the microstructure of the Opalinus Clay further affecting its hydraulic and mechanical properties. Since this claystone is considered as a potential host rock for deep geological disposal in Switzerland, it is of paramount significant to study the impact of chemical disturbances on its microstructure especially that the host rock will be exposed to saline and alkaline plumes during the operational phase of the repositories. To this end, this study focusses on the impact of osmotic suction and pH on the microstructure of a partially saturated *LSF* Opalinus Clay. It was found that salinity increases the macroporosity and decreases the mesoporosity. The higher the osmotic suction, the more significant the decrease. This is due to the water transfer from the meso to the macro pores under the chemical gradient and to the decrease of the thickness of the diffuse double layer. As for the impact of alkalinity, an increase in the meso and macro porosity was observed. This is due to the dispersion of the structure and to the dissolution of clay and non-clay minerals.

Macropore generation in both cases will probably affect the permeability of the host rock, which should be considered for safety assessment.

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