Effect of mineralogical composition and pore structure on the swelling of COx claystone

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ABSTRACT: In this study, we use experimental methods to investigate the relationship between the mineralogical composition and pore structure of re-sealed Callovo-Oxfordian (COx) claystone. The apparent swelling pressure (P_{app}) is measured in the absence of confining pressure, to simulate the industrial case (close to excavated and damaged tunnel walls). Quantitative XRD (QXRD) demonstrates that the amount of smectite, which is a swelling clay, present in COx claystone, is weakly correlated with P_{app}. Meanwhile, the R1-type interstratified illite/smectite (R1-I/S) is highly correlated to P_{app}. Nitrogen isotherms data imply that the Gurvich total pore volume ($V_{Gurvich}$) and the specific surface area (*SSA*) are linearly related to R1-I/S. Based on these results, it can be concluded that nitrogen adsorption tests provide an easier and more effective technique than QXRD for assessing COx swelling capacity, as both $V_{Gurvich}$ and *SSA* have been proven as effective indicators.

Keywords: claystone, quantitative XRD, Nitrogen adsorption test, apparent swelling pressure

I. INTRODUCTION

In France, the Callovo-Oxfordian (COx) claystone is the main candidate to be the host rock for the geological long-term disposal of long-lived and high level (LL-HL) nuclear waste, thanks to several favorable attributes, such as a stable geological structure, extremely low water permeability, and excellent self-sealing potential of cracks (Davy et al., 2007; Zhang and Rothfuchs, 2004). When building the nuclear waste repository, the host rock will be subjected to damage and de-saturation due to the unavoidable excavation and ventilation processes. As a consequence, a so-called Excavation Damaged Zone (EDZ) is formed around artificial structures (tunnels, galleries, etc.) and embraces numerous tensile and shear cracks with heterogeneous orientation, see FIGURE 1. Progressively, during the repository operation, the EDZ will re-saturate and self-sealing will occur with time. A number of researchers have been using experimental and simulation methods to study self-sealing. They have reported that the two main reasons for the occurrence of self-healing are the swelling of clay minerals and the effect of *in situ* stress (Bernier et al., 2007; Giot et al., 2019; Zhang, 2011). Therefore, an interesting question arises: in the absence of stress, such as confining pressure, what are the impact factors that affect the swelling capacity of the EDZ?

In order to help answering this question, we carried out a series of experiments on the COx claystone, including quantitative XRD, nitrogen adsorption tests, and a swelling test without stress, i.e. without applying a confining pressure to the claystone.

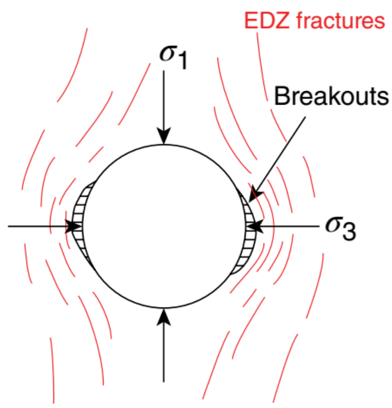

FIGURE 1. Diagram of the Excavation Damaged Zone (EDZ) around a tunnel, from (Bossart et al., 2019)

II. SAMPLE PREPARATION

The COx claystone used in this study is extracted at different depths in the COx formation, from the Meuse/Haute-Marne URL, as provided by ANDRA (French National Agency for Nuclear Waste Management). Samples are received sealed in especially designed so-called T1 cores. The dimension of the original T1 core is of 300 mm height and 75 mm in diameter. For quantitative XRD and nitrogen sorption tests, powdered claystone is used. For the swelling tests, six cylindrical samples are taken from four cores; each sample is re-cored to a diameter of 37 mm and a length of 40 mm. To mimic the EDZ, five of six samples are macro-cracked using a Brazilian splitting test, see FIGURE 2. The crack width was around tens of microns. In terms of geological sequence (defined by ANDRA) and damage state, the six sample are named: UT-C, UA1-C, UA2-C, UA3-C1, UA3-C2, UA3-I, where UT refers to transition unit and UA refers to the clay-rich unit. C means that the sample is macro-cracked and I is for the intact (as received) state. After coring, and while waiting for the swelling test, all the re-cored samples are wrapped in a plastic film, sealed in vacuum bags and then submerged in oil, in order to retain their initial water content.

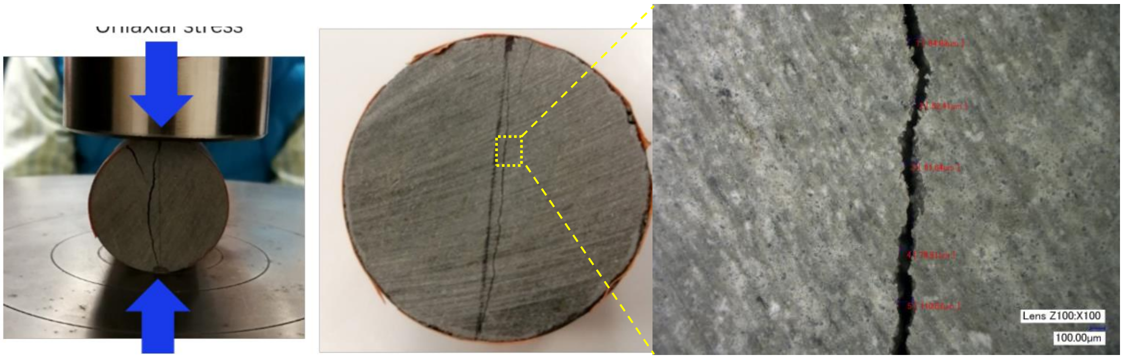

FIGURE 2. **Creation of a diametral macro-crack in a cylindrical COx claystone sample by using a Brazilian splitting test**

III. EXPERIMENTAL METHODS

The quantitative XRD and nitrogen adsorption tests are carried out on two samples for each core. A detailed description of the principle of these experiments, and the procedure followed, are presented in (Song et al., 2017).

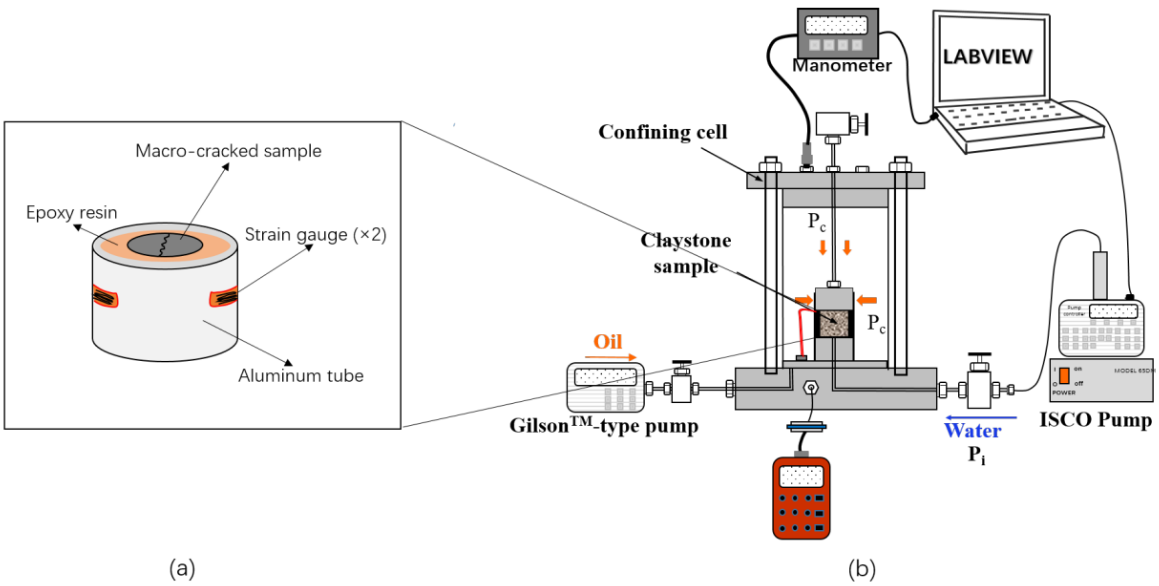

FIGURE 3. **Sketch of the experimental set-up: (a) a mock-up formed by the sample surrounded by an aluminum-epoxy tube avoids that external stress are applied to the sample; (b) the hydrostatic triaxial cell used for the swelling and self-sealing experiments.**

The swelling tests without external stress are carried out on an original experimental set-up, see FIGURE 3. The circular cylindrical sample is placed in an aluminum-epoxy composite tube. The latter has a sufficient elasticity (flexibility), aimed at preventing that any external stress applies on the sample. Two strain gauges are glued symmetrically on the tube outer surface, in order to record the evolution of tube strain with time. The tube strain is converted to an apparent swelling pressure of the claystone sample, owing to a preliminary calibration procedure (by applying a known gas pressure inside the tube, before the claystone sample is placed inside it). During the swelling test, the mock-up (formed by the sample + surrounding tube) is installed into a hydrostatic triaxial cell and subjected to a 4 MPa confining pressure. An ISCO pump is used to inject water into the sample from one end surface to re-saturate it and allow swelling. At the beginning of each test, water flows out from the cell downstream (i.e. the upper valve of the cell) in a short time, which indicates that the Brazilian splitting test creates cracks across the whole sample. The water pressure is chosen at a lower value than the confining pressure, to avoid any leakage around the sample.

IV. RESULTS AND ANALYSIS

FIGURE 4 shows two examples (UT-1 and UA1-1) of XRD spectrum of the bulk powder and oriented clay fractions. TABLE 1 exhibits the quantitative XRD results of the claystone, limited to the clay minerals (the content in other minerals is not shown). The total clay content is slightly lower for the UT core (with values ranging between 30.4 and 39.3%) than for the UA cores (values in the range 40.1 t 50.0%). Moreover, the results demonstrate that among all clay minerals, the illite/smectite mixed layers R1 and R0 constitute the vast majority. Indeed, the illite/smectite mixed layers are divided into two types: the R1-I/S, which includes 70% illite and 30% smectite, and the R0-I/S, which consists of 22% illite and 78% smectite. In R1-I/S, smectite is arranged in regular alternance with illite. Among these, smectite is the only one reputed to be a swelling clay.

TABLE 1. Quantitative XRD analysis of clay minerals for different cores (mass percentage)

Core name	UT-1	UT-2	UA1-1	UA1-2	UA2-1	UA2-2	UA3-1	UA3-2
kaolinite	-	-	2.2	2.7	3.3	3.4	2.9	3.0
Chlorite	0.9	1.2	1.1	1.4	1.5	1.7	1.7	1.7
Illite & muscovite	2.5	9.0	4.7	12.9	13.1	14.3	18.8	20.2
Illite/smectite R1 (70/30)	14.2	13.3	23.5	20.6	22.6	23.2	24.2	23.4
Illite/smectite R0 (22/78)	12.9	15.8	8.5	6.1	8.5	7.4	6.2	6.0
Total smectite	14.3	16.3	13.0	10.9	13.4	12.7	12.1	11.7
Total clay content	**30.4**	**39.3**	**40.1**	**43.7**	**49.0**	**50.0**	**46.8**	**46.7**

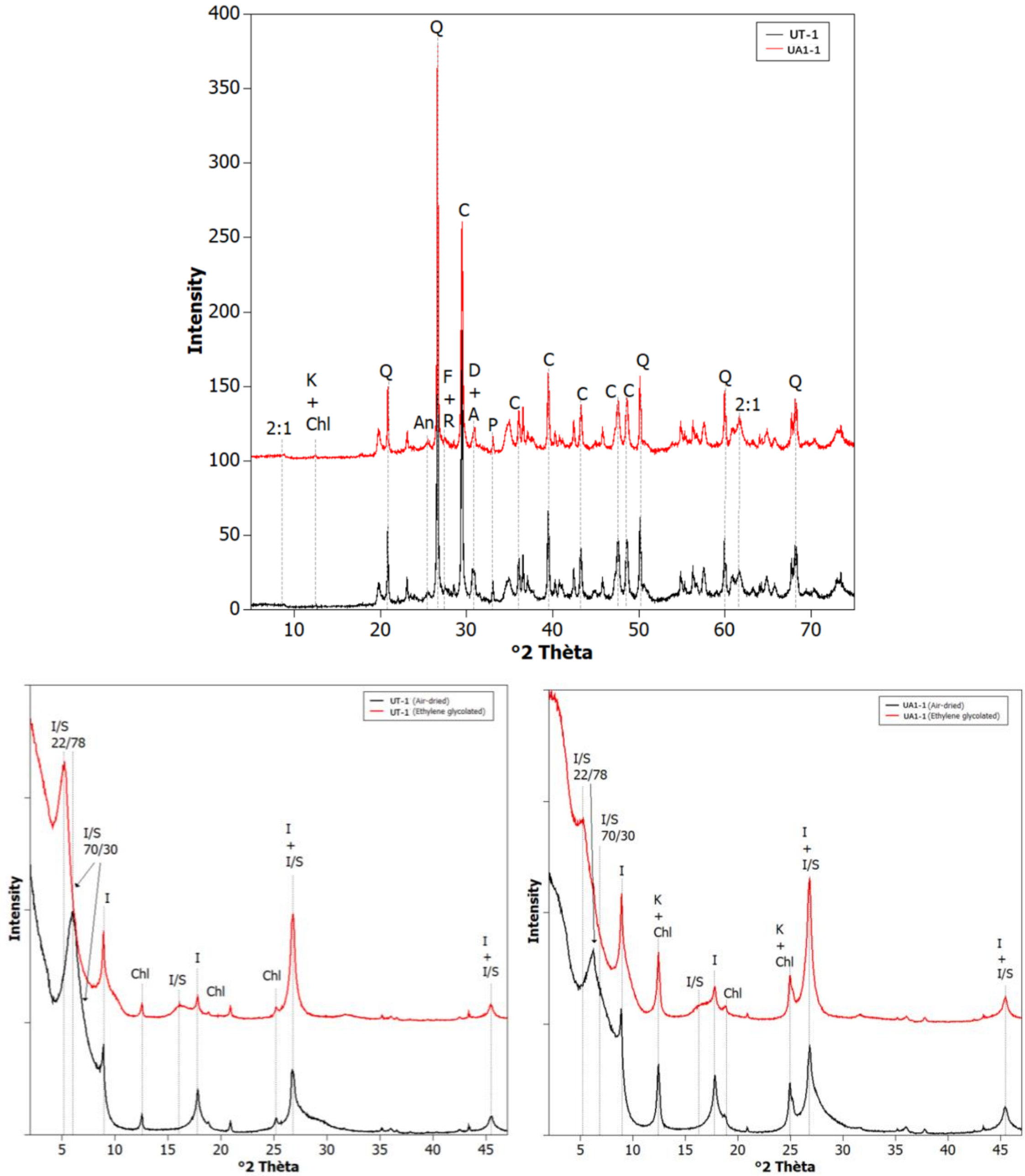

FIGURE 4. XRD spectrum examples of the bulk powder and oriented clay fractions (UT-1 and UA1-1)

TABLE 2 shows the apparent swelling pressure (P_{app}) of the samples at the end of the experiment, i.e. at stabilization of the strain gauge values. It is observe that, in the absence of external stress, the P_{app} of the macro-cracked UT sample (1.00 MPa) is much smaller than that of macro-cracked UA samples, which range from 4.55 to 5.10 MPa. For comparison purposes, the P_{app} of an intact sample UA3-I is also measured at a value of 5.88 MPa, i.e. at a slightly greater value than all the initially macro-cracked samples. This is attributed to the fact that the macro-crack, located at the core of the sample, also induces inward swelling, which is not measured by the outer strain gauges.

TABLE 2. **Apparent swelling pressure (P_{app}) of each tested sample**

Sample name	UT-C	UA1-C	UA2-C	UA3-C1	UA3-C2	UA3-I
Apparent swelling pressure (MPa)	1.00	5.10	4.55	5.00	4.69	5.88

By combining the quantitative XRD results, we analyzed whether there is a specific mineral that affects the swelling capacity of the COx claystone. To this purpose, the mass content of each clay mineral is related linearly (in the least squares sense) to the apparent swelling pressure P_{app} (FIGURE 5). The total interstratified I/S content is correlated to swelling pressure P_{app} with a Pearson coefficient R^2 of 44%. It is observed that the clay mineral which is most correlated to swelling pressure P_{app} is R1-I/S, with a R^2 of 83%. On the opposite, the Pearson coefficient between smectite content and P_{app} is of only 10%. The lowest correlation (R^2=6%) is obtained for R0-I/S, although it contains 78%mass smectite. These results demonstrate that the total smectite amount and the content in mixed I/S clay are not the driving factors of the magnitude of P_{app} at the laboratory scale. The structure that makes it easier for water molecules to enter the clay layers seems to be a more significant factor.

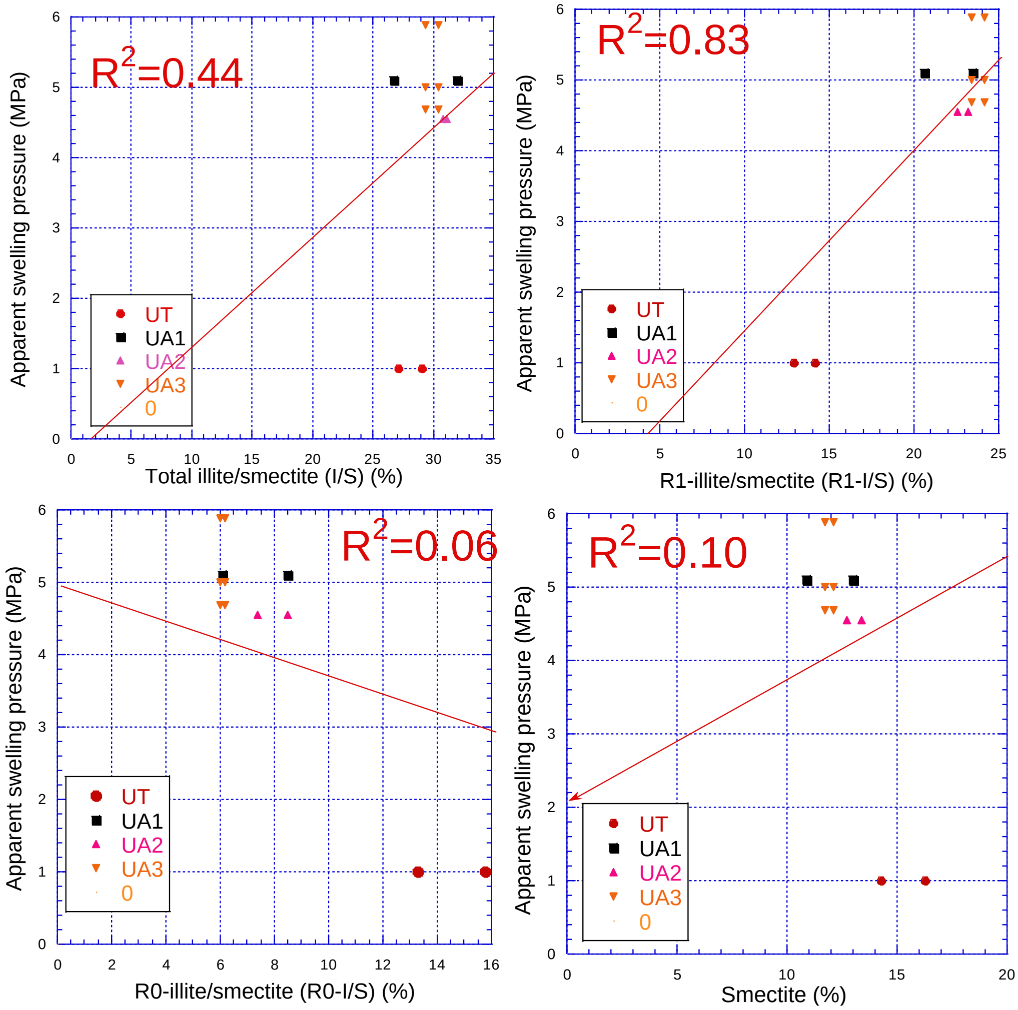

FIGURE 5. Apparent swelling pressure P_{app} **as a function of specific clay mineral content**

To verify this argument, we conducted nitrogen adsorption tests and two important parameters are obtained, namely the Gurvich pore volume ($V_{Gurvich}$) and the specific surface area (SSA). $V_{Gurvich}$ and SSA reflect the ability of water molecules to come into contact with minerals (particularly with smectite). The $V_{Gurvich}$ pore volume corresponds to the total amount of water molecules that can fill the interlayer pores. The specific surface area SSA represents the surface area of water molecules that can be adsorbed on clay minerals.

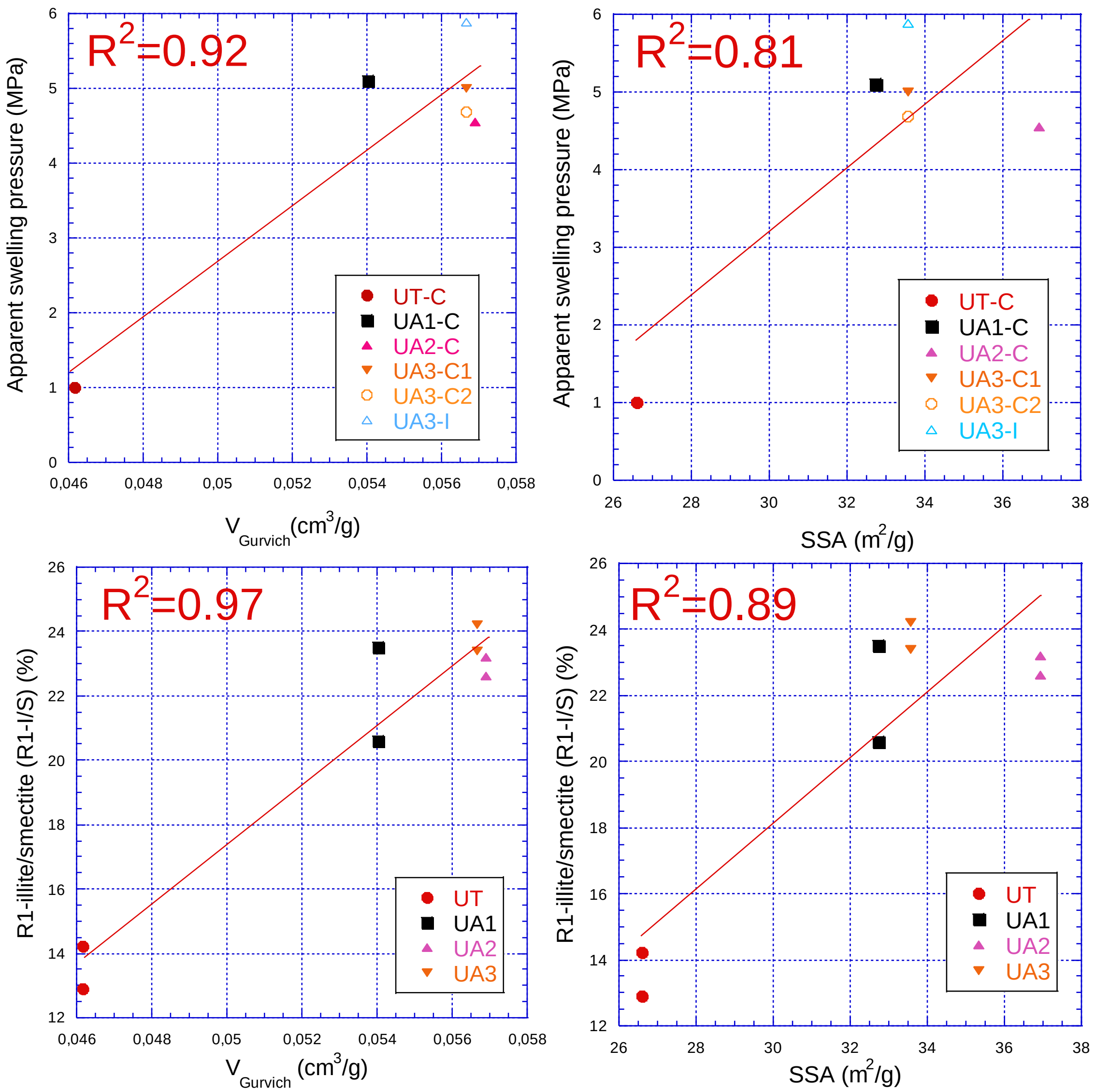

FIGURE 6. Correlation of nitrogen adsorption data with apparent swelling pressure P_{app}: (a) P_{app} vs. $V_{Gurvich}$ (b) P_{app} vs. SSA (a) R1-I/S vs. $V_{Gurvich}$ (b) R1-I/S vs. SSA

The nitrogen adsorption results ($V_{Gurvich}$ and SSA) are correlated linearly with the apparent swelling pressure P_{app} (FIGURE 6). P_{app} is linearly correlated with $V_{Gurvich}$ and SSA, with R^2 of 0.92 and 0.81 respectively, see FIGURE 6 (a) and (b). If we relate the R1-I/S content (which is the most strongly correlated with P_{app}) with $V_{Gurvich}$ and SSA, a remarkably linear relationships is obtained with both nitrogen sorption parameters (R^2 = 97% and 87% respectively), see FIGURE 6 (c) and (d). As smectite is not present as single phase in the COx claystone (ANDRA, 2005), a plausible explanation is that the smectite present in R1-I/S is more favorable for water-smectite contact, because it brings to the claystone a greater pore volume and a larger specific surface area. Therefore, we can conclude that the spatial arrangement of smectite seems to be more important than its content, as regards the macroscopic swelling of COx claystone.

Whenever the swelling ability of the COx claystone needs to be quantified experimentally, the mineral composition of R1-I/S is very difficult to be determined directly (quantitative XRD requires specialized skills and long durations for data analysis). Instead, a nitrogen sorption test is more easily achievable, and it is an effective technique because both $V_{Gurvich}$ and SSA are highly correlated to the COx swelling capacity.

V. CONCLUSION

This study used three different experimental methods, namely quantitative XRD, nitrogen sorption, and an original swelling test without external stress, in order to investigate the relationship between the mineralogical composition, the pore structure and the swelling capacity of COx claystone. Results demonstrate that the R1-I/S content is the best correlation to the apparent swelling pressure P_{app}, rather than the total smectite content. Nitrogen sorption data show that R1-I/S is highly correlated to Gurvich pore volume ($V_{Gurvich}$) and specific surface area (SSA). Inbeed, in the COx claystone, the smectite distribution in R1-I/S induces greater pore volume and larger specific surface area, which are both favorable for water-swelling clay contact, leading to greater swelling amplitude. From a viewpoint of testing technology, as nitrogen sorption tests are more easily conducted than quantitative XRD, $V_{Gurvich}$ and SSA are simple and effective parameters to relate to the swelling capacity of the COx.

REFERENCES

ANDRA, 2005. Dossier 2005 Argile. Collection les Rapports.

Bernier, Li, Bastiaens, Ortiz, Van Geet, Wouters, L., Frieg, B., Blumling, P., Desrues, J., Viaggiani, G., Coll, C., Chanchole, S., De Greef, V., 2007. Fractures and Self-sealing within the Excavation DIsturbed Zone in Clays (SELFRAC).

Bossart, P., Nussbaum, C., Schuster, K., 2019. Generation and Self-Sealing of the Excavation-Damaged Zone (EDZ) Around a Subsurface Excavation in a Claystone, in: Dewers, T., Heath, J., Sánchez, M. (Eds.), Geophysical Monograph Series. Wiley, pp. 125–143. https://doi.org/10.1002/9781119066699.ch8

Davy, Skoczylas, Barnichon, Lebon, 2007. Permeability of macro-cracked claystone under confinement: Gas and water testing. Physics and Chemistry of the Earth, Parts A/B/C 32, 667–680.

Giot, R., Auvray, C., Talandier, J., 2019. Self-sealing of claystone under X-ray nanotomography. Geological Society, London, Special Publications 482, 213–223. https://doi.org/10.1144/SP482.4

Song, Davy, Bertier, Skoczylas, Talandier, 2017. On the porosity of COx claystone by gas injection. Microporous and Mesoporous Materials 239, 272–286.

Zhang, 2011. Experimental evidence for self-sealing of fractures in claystone. Physics and Chemistry of the Earth, Parts A/B/C 36, 1972–1980.

Zhang, Rothfuchs, 2004. Experimental study of the hydro-mechanical behaviour of the Callovo-Oxfordian claystone. Applied Clay Science 26, 325–336.