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Effects of *pH* and exposure time to alkaline solutions on the mineralogy of the Opalinus Clay from the lower sandy facies of Mont Terri site

Yara Barakat[a, b], Yu-Jun Cui[a, *], Nadia Mokni[b], Pierre Delage[a], Frédéric Bernier[c]

[a] *Ecole des Ponts ParisTech, Laboratoire Navier/CERMES, Marne La Vallée, France*
[b] *Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSE-ENV/SEDRE/LETIS, Fontenay-aux-Roses 92260, France*
[c] *Agence Fédérale de Contrôle Nucléaire (AFCN), Belgium*

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ABSTRACT

The Opalinus Clay is a claystone considered as potential host rock for deep geological disposal of radioactive wastes in Switzerland and Gemany. During the operational phase of the repository, an increase in underground water *pH*, from 7.5 to a value as high as 13.5 is expected, due to the release of alkaline plumes from concrete degradation, resulting in possible changes in the mineralogy of the host rock. While clay mineral dissolution is known to occur and affect the hydro-mechanical properties of the host rock, the dissolution of other minerals present in claystone, *i.e.,* quartz and calcite, can also take place. This study focuses on identification of such dissolutions by considering $NaOH$, $Ca(OH)_2$ and KOH alkaline solutions at different *pHs* (8.5, 11.5 and 13.5). A low $pH = 8.5$ was investigated to consider the gradual increase in *pH* of the underground water resulting from the progressive infiltration of alkaline plumes. Series of Opalinus Clay samples from the lower sandy facies of Mont Terri site were immersed in these solutions for six months and for one year. It was found that quartz dissolution occurred significantly at *pHs* higher than 11.5, but also at *pHs* as low as 8.5. The longer the exposure time, the more significant the quartz dissolution. Calcite dissolution was observed after six months at *pH* higher than 11.5, and after one year at *pH* higher than 8.5. Thus, the quartz dissolution seemed to be governed by the exposure time, while the calcite dissolution seemed to depend on both exposure time and *pH* value, due to carbonation phenomenon. While generally attention has been paid to the effect of alkalinity on clay minerals, this paper meticulously studies the dissolution of quartz and calcite initially present in significant proportions in the Opalinus Clay from the lower sandy facies of Mont Terri site by investigating a wide range of *pHs*. The dissolution of such minerals will undoubtedly affect the hydraulic and mechanical properties of the claystone. Thereby, it is of paramount importance to study this phenomenon in order to ensure the long-term safety of the nuclear waste disposal. Furthermore, by investigating a wide range of *pHs*, attention is paid to both the early stage of site water *pH* increase (low *pHs*) and the late stage (high *pHs*).

1. Introduction

It is well known that changes in *pH* strongly affect the mineralogy of claystones used as host rock in deep geological repositories for radioactive wastes (Adler et al., 1999; Chermak, 1992; Chermak, 1993; Claret et al., 2002; Fernández et al., 2013; Gaucher and Blanc, 2006; Melkior et al., 2004; Pusch et al., 2003). Indeed, during the operational phase of the repository, alkaline plumes resulting from the degradation of concrete structures, necessary for stability, can contaminate the underground water (Fernández et al., 2009; Fernández et al., 2010; Ye et al., 2014), further affecting the chemo-hydro-mechanical behavior of claystone through modifying its mineralogy. The dissolution of clay minerals as well as other main minerals, *i. e.*, quartz and calcite (Kneuker and Furche, 2021; Lauper et al., 2018), will occur. Hence, it is of paramount importance to investigate the impact of alkaline solutions on the mineralogy of claystones, especially in terms of calcite and quartz dissolutions. Furthermore, *pH* of the underground water, initially around 7.5 (Gaucher and Blanc, 2006; Pearson et al., 2003), will increase gradually with the infiltration of the alkaline plumes until reaching 13.5 (Taylor and Harry, 1987; Ye et al., 2014). Hence, it is of interest to consider a large *pH* range, from 7.5 to 13.5, in order to study both the early stages of site water *pH* increase (low *pHs*) and the late stages (high *pHs*), in contrast to previous studies that only focused on high *pH* values (Adler et al., 1999; Chermak, 1992; Chermak, 1993; Claret et al., 2002).

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* Corresponding author at: Ecole des Ponts ParisTech, 6-8 av. Blaise Pascal, Cité Descartes, Champs-sur-Marne, 77455 Marne-la-Vallée cedex 2, France.
E-mail address: yu-jun.cui@enpc.fr (Y.-J. Cui).

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Clay minerals, especially kaolinite and montmorillonite, can be dissolved in an alkaline environment (Bauer et al., 1998; Bauer and Velde, 1999; Di Pietro et al., 2020; Heller-Kallai and Lapides, 2007; Lalan, 2016; Sivapullaiah and Manju, 2005; Wahid et al., 2011a; Wahid et al., 2011b; Ye et al., 2014). Indeed, for Kaolinite, the density of negatively charged $-SiO^-$ groups in the tetrahedral sheet increases when increasing the pH from 7 to 10. Once the pH becomes higher than 10, the density of negatively charged $-AlO^-$ groups in the octahedral sheet increases (Walther, 1996). The increase in the negatively charged groups (respectively$-SiO^-$ and $-AlO^-$ groups) with pH increase (respectively $7 < pH < 10$ and $pH > 10$) results in weak bonds between silicon (or aluminum) and oxygen; thus, silicon (or aluminum) can be unleashed from the tetrahedral (or octahedral) sheet and higher silicon (or aluminum) detachment rate is generated (Wahid et al., 2011a; Wahid et al., 2011b). Based on the primary dissolution mechanism, kaolinite seems to be more easily dissolved than montmorillonite since the octahedral sheet is trapped between two tetrahedral sheets in smectite minerals and thus less accessible to hydroxide ions (Bauer et al., 1998). Smectite dissolution could be followed by illite precipitation in alkaline solutions containing potassium hydroxide (Adler et al., 1999).

Given that mineral dissolution is well known to depend on both pH and temperature (Adler et al., 1999; Chermak, 1992; Chermak, 1993; Claret et al., 2002), natural clay rocks have been exposed to hyper alkaline solutions at different temperatures in many previous studies. Claret et al. (2002) exposed the Callovo-Oxfordian claystone to an alkaline solution (KOH, $NaOH$ and $Ca(OH)_2$) with a pH of 13.2 for 1 year at 60°C. A low reactivity of the clay phase was observed, due to the presence of organic matter. Smectite dissolution and the formation of interstratified I/S was also detected, together with quartz dissolution and precipitation of $C-S-H$ (hydrated calcium silicate). Chermak (1992, 1993) exposed Opalinus Clay to $NaOH/KOH$ solutions with pHs higher than 11.5 at 150°C, 175°C and 200°C for 40 and 50 days, respectively. As a result from the dissolution of kaolinite, quartz and chlorite, they observed the precipitation of analcime ($NaAlSi_2O_6.2H_2O$) with the $NaOH$ solution and of phillipsite ($(Ca, Na_2, K_2)_3Al_6Si_{10}O_{32}.\ 12H_2O$) with the KOH solution. Smectite precipitation was also found in both cases. An acceleration of the dissolution of quartz (Knauss and Wolery, 1988) and clay minerals (Bauer and Berger, 1998; Köhler et al., 2003) was observed with the increase of temperature. Also, the higher the temperature, the more the precipitation of better crystallized phases. Adler et al. (1999) exposed, in diffusion cells, Opalinus Clay to KOH, $NaOH$ and $Ca(OH)_2$ solution with a pH of 13.2 at 30°C for 4, 6, 12 and 18 *months*. They found that zeolites (for example $Na_2Al_2Si_3O_{10}.\ 2H_2O$) and $Ca-Al-Si-$hydrate phases ($C-AS-H$) precipitated first, followed by clay mineral-calcite precipitation. Calcite precipitation finally occurred, due to the dissolution of dolomite ($CaMg(CO_3)_2$) and ankerite ($Ca(Fe, Mg, Mn)(CO_3)_2$). Only high pHs were investigated. However, because of the progressive infiltration of alkaline plumes, the pH of underground water will gradually increase from 7.5 to 13.5, hence the interest of investing lower pHs.

Besides natural clay rocks, clayey soils as well as clay minerals have also been investigated in previous studies. Sivapullaiah and Manju (2005) studied kaolinite-alkali interaction by exposing red earth and a kaolinite soil to $1M\ NaOH$ and $4M\ NaOH$ solutions for 3 days. Kaolinite dissolution was observed, with the formation of sodium aluminum silicate hydroxide hydrate ($NASH$) $Na_8(AlSiO_4)_6(OH)_2.\ 4H_2O$. Heller-Kallai and Lapides (2006) also studied the interaction of kaolinite with sodium hydroxide solution. Hydrosodalite was identified as a primary product resulting from the basic attack. On the other hand, the interaction of kaolinite with a high molar potassium hydroxide solution was investigated by Bauer et al. (1998). The basic attack produced several metastable minerals as illite, KI-zeolite and phillipsite, respectively. The final and stable product was K-feldspar.

Previous studies investigated the dissolution of pure quartz in alkaline solutions. Bérubé et al. (1990) observed the precipitation of $C-S-H$ after exposing quartz to a pH of 12.5 for 265 days at 23°C. Savage et al. (1992) and Bateman et al. (1999) exposed quartz to a pH of 13 and 12.5, respectively for 70 days. The main product of quartz dissolution was C$-S-H$. Also, the impact of pH variation on the dissolution rate of quartz was widely investigated (Bennett et al., 1988a; Brady and Walther, 1990; Henderson et al., 1970; Kline and Fogler, 1981; Knauss and Wolery, 1988; Schwartzenruber et al., 1987; Wollast and Chou, 1986). Brady and Walther (1990) studied the kinetics of quartz dissolution at different pHs at 25°C and 60°C. They found that the rate of quartz dissolution was function of pH and ionic strength. In basic solutions, it was proportional to the negative silica surface charge, that increases with pH increase due to the increase in basic attack. In acid solutions, the rate of quartz dissolution decreased when the pH decreased from 7 to 3. However, when the pH became lower than 3, an increase in quartz dissolution rate was observed due to the increase in the positively charged surface species, $SiOH^{2+}$. Wollast and Chou (1986) also observed a minimum dissolution rate of quartz for $pH = 3$. Schwartzenruber et al. (1987), Knauss and Wolery (1988) and Bennett et al. (1988a) observed an increase in the dissolution rate of quartz with pH increase even for pHs near the neutral one (Bennett et al., 1988a). An acceleration of the dissolution of quartz was observed with the increase of temperature (Knauss and Wolery, 1988).

Calcite dissolution was also widely investigated (Dolgaleva et al., 2005; Fredd and Fogler, 1998a; Fredd and Fogler, 1998b; Plummer et al., 1978; Plummer et al., 1979; Sjöberg and Rickard, 1984a; Sjöberg and Rickard, 1984b). Dolgaleva et al. (2005) experimentally studied the impact of the pH variation on the dissolution rate of calcite. They observed that increasing the pH from 2 to 5 strongly decreased the calcite dissolution rate. On the contrary, varying the pH from 5 to 10 did not affect the dissolution rate of calcite. However, a further pH increase lead to further decrease in dissolution rate. Fredd and Fogler (1998) and Plummer et al. (1978, 1979) observed a significant decrease in calcite dissolution rate with a pH increase from 1 *to* 6.

Further examination of the studies mentioned above shows that the effect of alkaline solutions on the mineralogy of natural clay rocks as well as clay minerals, was addressed only for $pHs > 11.5$. No attention has been paid to lower pHs. Furthermore, attention has been paid to the product of the dissolution of clay minerals, but not to the dissolution process of various minerals that make up the argillaceous rock. In this study, the impact of alkaline solutions on the mineralogy of a natural Opalinus Clay was investigated with pHs ranging from 8.5 to 13.5. Emphasis was put on quartz and calcite dissolutions at different exposure times.

2. Materials and methods

2.1. Material

The rock studied is the Opalinus Clay from the lower sandy facies of Mont Terri site in Switzerland. The samples were taken from $BFI-2$ borehole that was drilled in November 2018 in the direction perpendicular to the bedding plane. Upon reception, the cores were already desaturated. The mineralogical composition (wt%) found in previous works is shown in *Table* 1. It can be seen that quartz is the dominant mineral (Silty fraction $38-37$%). It is as abundant as clay minerals according to Lerouge (2014). The carbonate fraction varies between 10 *and* 20%.

2.2. Alkaline solutions

Three alkaline solutions were used in this study, with pHs of 8.5, 11.5 and 13.5, respectively. First, the solution with the highest pH (13.5) was prepared following the recipe proposed by Lalan (2016). It has the same chemical components and pH as the concrete pore water (Table 2). The solution at a pH of 11.5 was prepared by diluting the solution of 13.5 with a dilution factor equal to 100. The solution with a *pH* of 8.5 was prepared by diluting the solution of 11.5 with a dilution factor equal to 1000. The *pHs* of the three solutions were monitored for three days before the beginning of the tests. The *pHs* were measured using a *pH* meter of the brand *WTW* model Multi 3420. The probe is of the brand *Si* Analytics GmbH model $D-55122$ Mainz with a measuring range from 1 to 14. Before each use, the *pH*meter was calibrated using 4 standard solutions: 4, 6.8, 9.1 and 12, respectively.

2.3. Test procedure

32 dry Opalinus Clay subsamples from sample 6 (*Table* 3) were immersed in small containers filled with the dedicated alkaline solution (*i. e.* , 8 subsamples per solution)(*Table* 4). The soil/solution ratio was approximately $1:25$, $2:25$ and $1:50$ for the alkaline solution of $pH = 13.5$, 8.5 and 11.5, respectively. The experiments were conducted at room temperature (20 ± 1°C). The *pHs* of the solutions were monitored throughout the tests. It was found that the solution of $pH = 13.5$ kept a constant *pH* over time (Fig. 1). However, this was not the case for the solution of $pH = 11.5$, for which the *pH* decreased to a value of 8.7 approximately (Fig. 2). To maintain a constant basic attack, another series of Opalinus Clay samples were soaked in the solution of $pH = 11.5$. For this series of tests, the *pH* was monitored over time. Once a *pH* decrease was observed, the solution was renewed. As Fig. 3 shows, the basic solution at $pH = 11.5$ was renewed 8 times (after 23, 53, 65, 100, 142, 181, 219 and 266 *days*, see Fig. 3). For the series of tests with $pH = 8.5$ and $pH = 13.5$, a constant *pH* was observed over time (Fig. 4).

For the mineralogy analysis, the first samples were collected after 6 months and the second ones after 12 months for the four series of tests. In total, 7 subsamples were collected (2 subsamples from $pH = 13.5$, 2 subsamples from $pH = 11.5 -$ *non renewing*, 1 subsample from $pH = 11.5 -$ *renewing*, 2 subsamples from $pH = 8.5$). The other subsamples were left in the alkaline solutions for future analyses (Table 4).

2.4. X-ray diffraction studies

Once collected at the time planned, after 6 or 12 months, the samples were dried in an oven at 105°*C* for 24 *h* prior to being crushed into powder using a marble mortar and pestle. X-ray diffraction (*XRD*) measurements were performed on 1 *g* disoriented powder by means of a PANalytical X'Pert Pro with *Cu Kα* ($\lambda = 1.54060\ \mathring{A}$) radiation operating at 40 *kV*, 30 *mA* and 600 *W*. The angular interval varied from 2° to 64° by steps of 0.02°/s. The divergence was set at ¼ and a 20 *mm* mask was used to control the irradiated width on the sample. A nickel filter was placed at the rear to remove unwanted radiation such as $K\beta -$ *line* and continuous radiation from the X-ray beam. The low knife mode was adopted, allowing a start angle less than 5°.

2.5. Scanning electron microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDS)

SEM and *EDS* were performed in order to carry out a semi-quantitative chemical characterization of Opalinus Clay samples at their initial intact state and after exposure to a hyper alkaline solution of $pH = 13.5$ for 35 days in an oedometric cell (diameter 35 cm). This experimental set-up was used to prevent the sample from crumbling due to the basic attack. Before *SEM* and *EDS*, the specimens were cut and immersed into an epoxy resin and polished with abrasive papers with decreasing grain size from grade 120 to 4000 in order to obtain a smooth surface. After that, the samples were sputtered under vacuum with gold and palladium. Finally, observations were conducted in conventional *SEM* under a high vacuum condition to allow a precise focusing of the incident electrons on the sample and to prevent the emitted electrons from interacting with the atmosphere. An acceleration voltage of 10 *kV*, a magnification of 80 and a focal distance of 17 *mm* were adopted for image acquisition.

3. Results

3.1. Intact samples

Before launching the batch experiments, X-ray diffraction profiles of six dried Opalinus Clay samples from three different cores from $BFI-2$ borehole at their intact initial state were determined (Figs. 5 and 6). Fig. 5 shows the sketch of the borehole drilled in the lower sandy facies of Mont Terri site as well as the location of the three cores. The borehole was drilled at 420 *m* beneath the ground level and had a total length of 9.9 *m*. *Table* 3 indicates the depth within the borehole of the six different samples.

The X-ray diffraction profiles of the six intact Opalinus Clay samples are presented in Fig. 6. It can be seen that the six samples contain the same minerals (Calcite, Illite, Kaolinite, Quartz and Chlorite). However, the intensities of the peaks at 20.850 2θ/26.652 2θ and 29.406 2θ, cor-

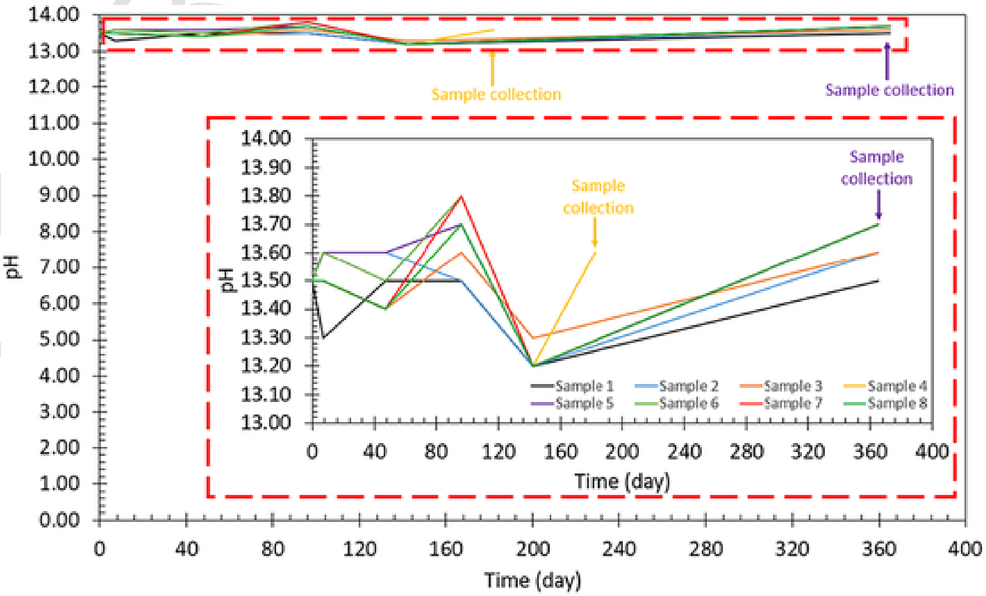

Fig. 1. *pH* monitoring over time for the solutions with an initial *pH* of 13.5.

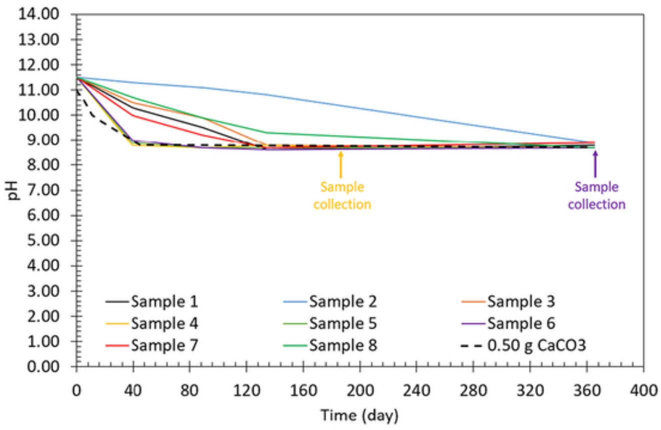

Fig. 2. *pH* monitoring over time for the solutions with an initial *pH* of 11.5.

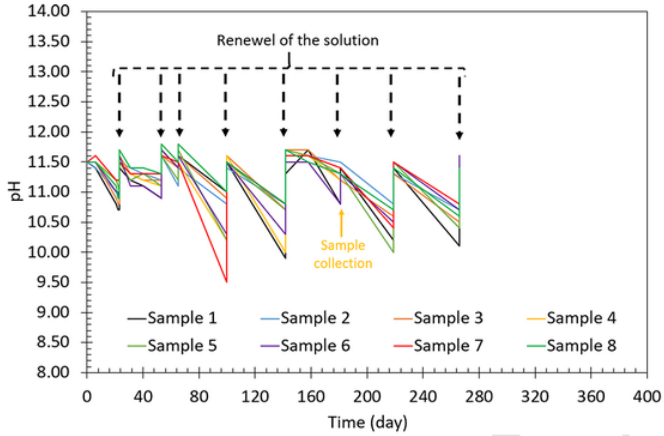

Fig. 3. *pH* monitoring over time for the solutions with an initial *pH* of 11.5 and solution renewing.

responding to quartz and calcite respectively, vary among the six samples. Indeed, *sample* 2 and *sample* 5 do not contain as much calcite as the other four samples. The quartz content also varies, but in a less pronounced way (Fig. 6). These observations underline the significant heterogeneity of the sandy facies of the Opalinus Clay in terms of mineralogy, in agreement with the observations by Lerouge (2014) and Ould Bouya (2014). Indeed, the lower sandy facies of the Mont Terri site is highly heterogeneous and can be divided into three subfacies according to Lauper et al. (2018) and Kneuker and Furche (2021).

For the batch experiments, to minimize the artefacts caused by the heterogeneity in the mineralogy of the three studied cores, all the samples immersed in the alkaline solutions were taken at the same depth as sample 6, *i.e.*, at 426 *m* beneath the ground level (Table 4).

3.2. Impact of alkalinity

X-ray diffraction profiles of one intact and four Opalinus Clay samples immersed for six months in four alkaline solutions with different *pHs* are presented in Fig. 7. It can be observed that calcite is dissolved only for *pHs* higher than 11.5, with no calcite dissolution identified after 6 months of exposure for lower *pHs*. This result indicates that the dissolution rate of calcite increased for *pHs* higher than 11.5 contrary to the result observed by Dolgaleva et al. (2005). Conversely, quartz dissolution occurs at lower *pH*. Increasing the *pH* from 7.5 to 8.5 triggered the quartz dissolution, but further *pH* increase did not lead to more quartz dissolution (Fig. 7).

The first decrease in *pH* of the solution initially at $pH = 11.5$ happened after 23 days of sample immersion (Fig. 3). Since no calcite dissolution was observed after 6 months in the sample immersed in the non-renewed alkaline solution of $pH = 11.5$ (Fig. 10), it can be inferred that the time needed to trigger calcite dissolution at $pH = 11.5$ is >23 days.

Fig. 8 shows the X-ray diffraction profiles of one intact Opalinus Clay sample and three Opalinus Clay samples immersed in three alkaline solutions at different *pHs* for 12 months. Compared to the results in Fig. 7, the decrease in peak intensity of quartz appears more pronounced. Moreover, calcite dissolution did not occur previously at low *pHs* after six months of exposure (Fig. 7), but did take place for *pHs* as low as 8.5 after 12 months of exposure. Thus, it can be inferred that an exposure time longer than 6 months is needed for calcite dissolution at

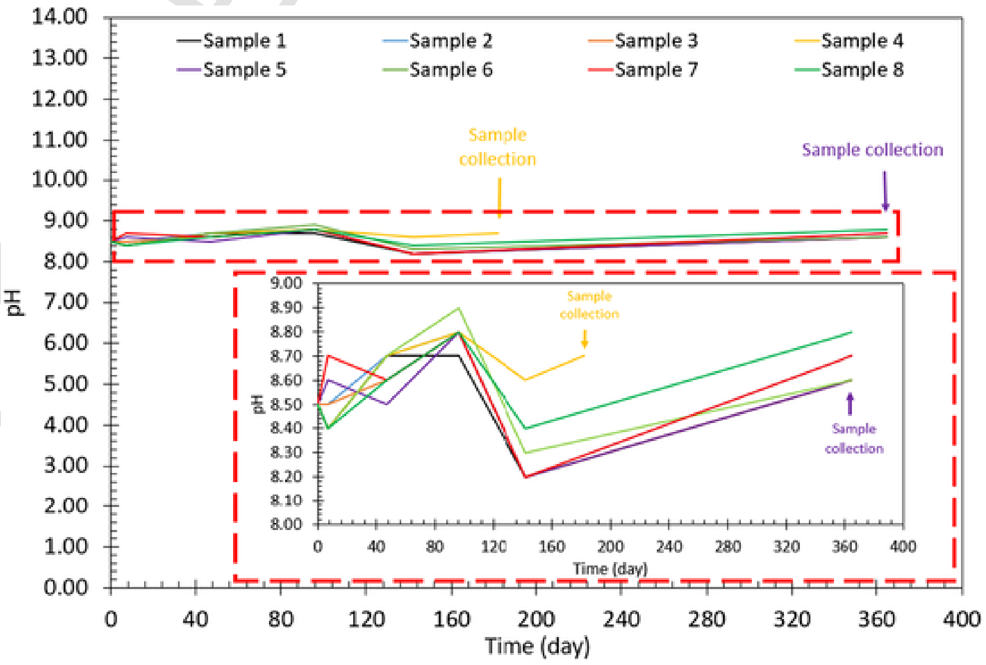

Fig. 4. *pH* monitoring over time for the solutions with an initial *pH* of 8.5.

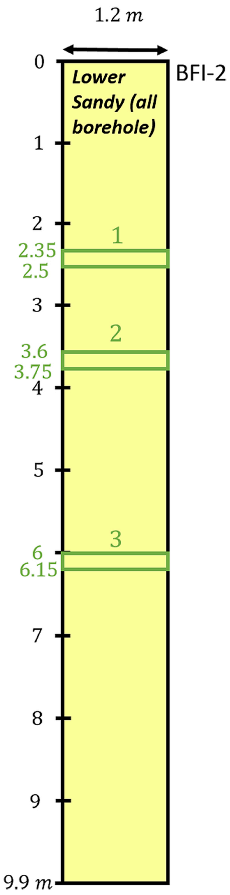

Fig. 5. Sketch of BFI-2 borehole and the location of the three cores.

low *pHs* (Fig. 8), suggesting that calcite dissolution depends on both *pH* and exposure time. The higher peak of calcite, detected at 29.406 2θ for $pH = 11.5$ – *non renewing*, comparing to $pH = 8.5$,is probably due to the carbonation phenomenon that will be discussed later in section 5.1 (Fig. 8).

Fig. 9 shows the X-ray diffraction profiles of one intact Opalinus Clay sample and two Opalinus Clay samples immersed in the alkaline solution with $pH = 13.5$ for 6 and 12 months respectively. It can be seen that 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. 9).

Fig. 10 shows the X-ray diffraction profiles of one intact Opalinus Clay sample and two Opalinus Clay samples immersed for 6 and 12 months respectively in the alkaline solution at an initial *pH* of 11.5. Note that the *pH* of this solution decreased over time until reaching a *pH* of 8.7 (Fig. 2). Thus, the basic attack was not constant during the test. Calcite dissolution, that did not occur after 6 months of exposure, occurred after 12 months of exposure (Fig. 10). As for the quartz dissolution, it increased with the exposure time. These observations are similar for the two Opalinus Clay samples immersed for 6 and 12 months, respectively, in the alkaline solution with $pH = 8.5$ (Fig. 11). In fact, the solution initially at $pH = 11.5$ presented a decrease in *pH* after 23 days of exposure down to a final *pH* of 8.7. These two series of tests show that calcite dissolution at $pH = 11.5$ took place after 23 days. For lower *pHs*, *i.e.*, 8.5 and 8.7, calcite dissolution happened after an exposure time >6 months.

Fig. 12a and b show a *SEM* image and an *EDS* result of an intact Opalinus Clay sample, respectively. The quartz mainly composed of *Si* is a dominant mineral as identified previously by Lerouge (2014) and Ould Bouya (2014) (Table 1). The calcite identified through *Ca* is also present. Fig. 12c and d respectively show the *SEM* image and *EDS* result of an Opalinus Clay sample exposed to the hyper alkaline solution ($pH = 13.5$) for 35 days in an oedometric cell. The *EDS* result shows a significant decrease in the quartz content. Calcite content also decreases to a lesser extent. These results are in agreement with the observed decrease in quartz and calcite peaks visible in the *XRD* profiles (Figs. 7 and 8) and indicate that quartz is dissolved more easily in an alkaline environment than calcite. Although the *EDS* mapping of the Opalinus Clay sample exposed to the alkaline solution remains semi-quantitative, it shows 67.58% of *Al, Si* (clay minerals), 5.2% of *Al, Si, Ca* (contact points between calcite and clay minerals), 2.98% of *Ca* (calcite), 2.26% of *Ca, Si* (contact points between calcite and quartz) and 20.72% of *Si* (quartz). *Na* and *K*, that probably dissolved the calcite and quartz are present in insignificant quantities.

4. Discussions

4.1. Carbonation

The three alkaline solutions used in this study have the same chemical components as the concrete pore water. Therefore, the well-known phenomenon of carbonation of concrete (Gaucher and Blanc, 2006), corresponding to the dissolution of CO_2 from the air in the concrete

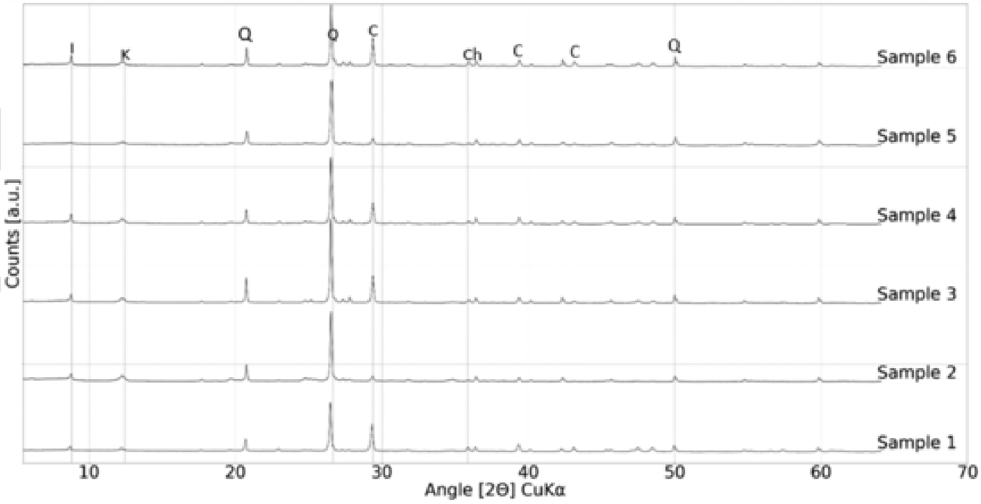

Fig. 6. X-ray diffraction profiles of six intact Opalinus Clay samples from the lower sandy facies of Mont Terri site- I: Illite, K: Kaolinite, Ch: Chlorite, Q: Quartz, C: Calcite.

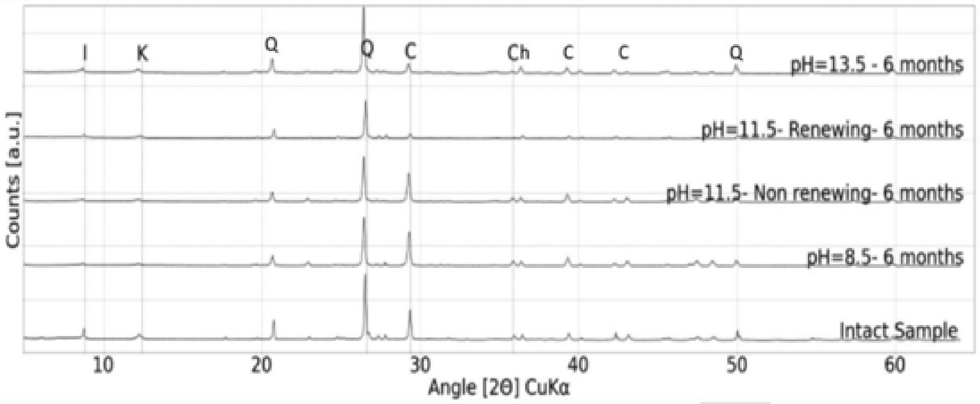

Fig. 7. X-ray diffraction profiles of four Opalinus Clay samples derivate from sample 6 from the lower sandy facies of Mont Terri site immersed in four alkaline solutions for 6 months- I: Illite, K: Kaolinite, Ch: Chlorite, Q: Quartz, C: Calcite.

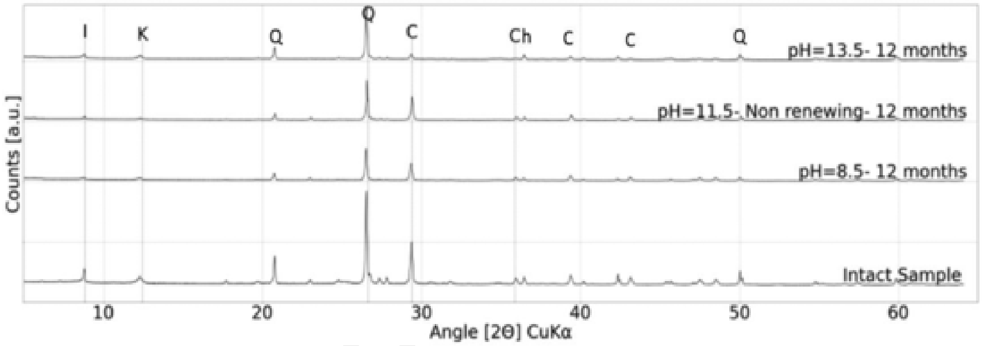

Fig. 8. X-ray diffraction profiles of three Opalinus Clay samples derivate from sample 6 from the lower sandy facies of Mont Terri site immersed in three alkaline solutions for 12 months- I: Illite, K: Kaolinite, Ch: Chlorite, Q: Quartz, C: Calcite.

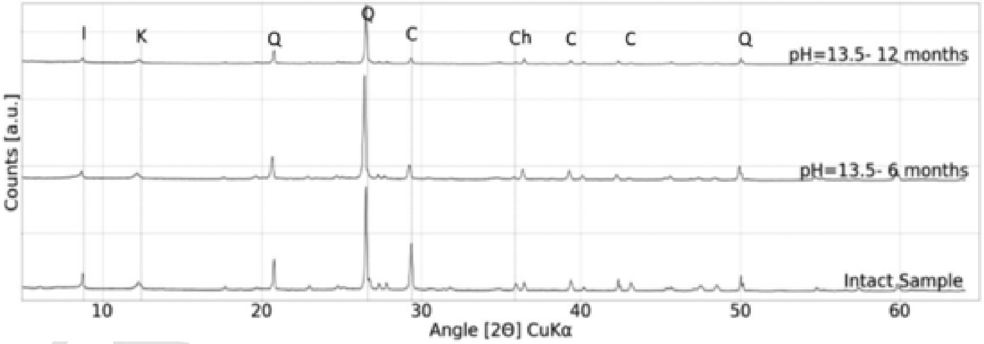

Fig. 9. X-ray diffraction profiles of three Opalinus Clay samples derivate from sample 6 from the lower sandy facies of Mont Terri site immersed in an alkaline solution with a $pH = 13.5$ for 6 months and 12 months respectively- I: Illite, K: Kaolinite, Ch: Chlorite, Q: Quartz, C: Calcite.

pore water (Eq. (1)) should be considered, when interpreting the results. This phenomenon leads to an acidification, *i.e.*, a reduction of the *pH* to nearly 9.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

Consequently, carbonation can explain the decrease in *pH* observed in the solutions of $pH = 11.5$. A constant *pH* was measured in the solutions of $pH = 13.5$ because the concentration of hydroxide ions was 100 times higher than that in the solutions of $pH = 11.5$, then masking the carbonation phenomenon.

The dissolution of the calcite initially present in the Opalinus Clay samples might accelerate the phenomenon of carbonation. To verify that, amounts of 0.25 *g*, 0.5 *g* and 2 *g* of solid $CaCO_3$ were soaked in 140 *mL* of solution at $pH = 11.5$, while the *pH* of the solutions were monitored over time (Fig. 13). It can be seen that the *pH* decreased over time until reaching a value of 8.6. Moreover, the greater the calcite mass, the faster the *pH* decrease. The final value of 8.6 was obtained after 41, 45 *and* 57 *days* for 0.25 *g*, 0.5 *g and* 2 *g* of calcite, respectively.

Calcite is the main product of carbonation (Eq. (1)). This suggests that carbonation will probably limit calcite dissolution (Dolgaleva et al., 2005). Thereby, calcite dissolution might accelerate the carbonation while carbonation limits calcite dissolution. In future studies, the composition of alkaline solutions (especially Ca^{2+}) will be monitored in order to make a more comprehensive analysis on the carbonation phenomenon.

4.2. *Variability of the sandy facies of Mont Terri site*

As shown in Fig. 6, the Opalinus Clay from the lower sandy facies of Mont Terri site exhibits a strong heterogeneity regarding its mineralogi-

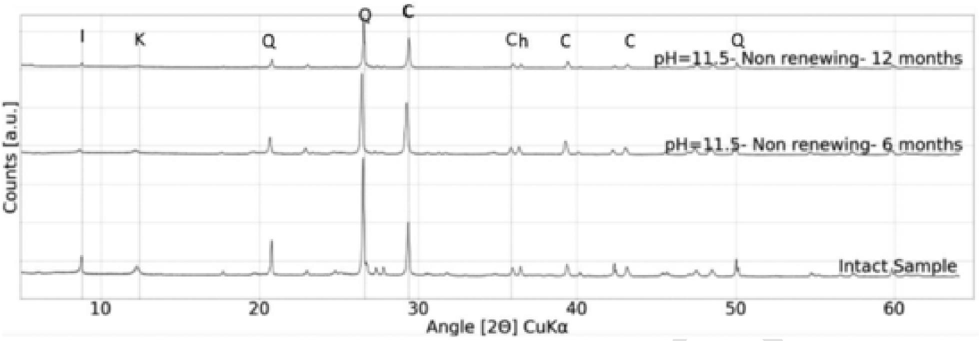

Fig. 10. X-ray diffraction profiles of three Opalinus Clay samples derivate from sample 6 from the lower sandy facies of Mont Terri site immersed in an alkaline solution initially presenting a $pH = 11.5$ for 6 months and 12 months respectively- I: Illite, K: Kaolinite, Ch: Chlorite, Q: Quartz, C: Calcite.

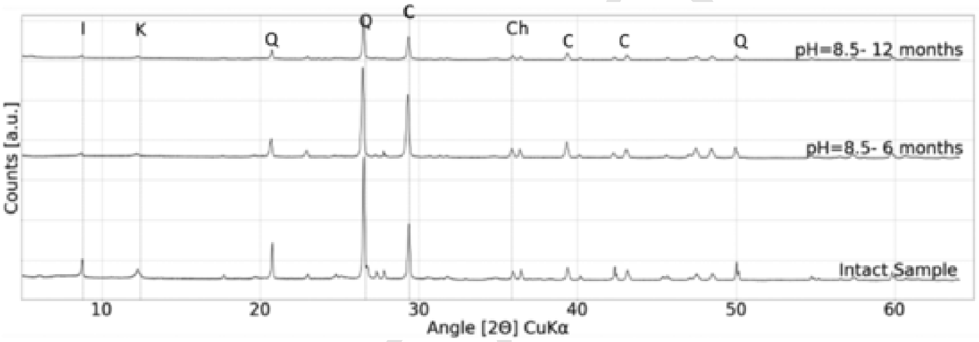

Fig. 11. X-ray diffraction profiles of three Opalinus Clay samples derivate from sample 6 from the lower sandy facies of Mont Terri site immersed in an alkaline solution with a $pH = 8.5$ for 6 months and 12 months respectively- I: Illite, K: Kaolinite, Ch: Chlorite, Q: Quartz, C: Calcite.

cal composition. The quartz and calcite fractions vary with depth within the same borehole and same facies. Lauper et al. (2018) and Kneuker and Furche (2021) identified three subfacies in the lower sandy facies: an argillaceous-silicious subfacies, a silicious-argillaceous subfacies and a siliciеous-calcareous subfacies. In the present study, the variability in the mineralogical composition of the lower sandy facies of Mont Terri site is excluded since the 32 investigated subsamples derivate from the same sample (Sample 6) (Table 4) collected at 426 *m* beneath the ground level (Table 3).

4.3. Quartz and calcite dissolution

At $pH = 8.5$,quartz dissolution took place after 6 months of exposure, whereas 12 months of exposure were needed to trigger calcite dissolution, showing that quartz dissolves more easily in an alkaline environment than calcite. Indeed, quartz is composed of silica (silicon dioxide) linked into a continuous framework of SiO_4 silicon-oxygen tetrahedron, with each oxygen shared between two tetrahedrons. SiO^- groups are easily formed as a result of the basic attack. $Si - O$ bonds weaken, leading to Si detachment. Kouassi (2011) also found experimentally that silica goes into solution very quickly in a basic environment which explains the decrease in quartz peaks as soon as the pH increases from 7.5 to 8.5.

Comparing Figs. 7 and 8 shows that quartz dissolution appears more significant after 12 months of exposure. This indicates the important role of exposure time in the dissolution process of quartz: the longer the exposure time, the more significant the quartz dissolution. However, for the same exposure time, increasing the pH did not increase quartz dissolution. These observations confirm that quartz dissolution mainly depends on the exposure time and that the mechanism behind quartz dissolution is the formation of SiO^-groups which exhibit weakened covalent bonds leading to Si detachment. This mechanism is also behind the primary dissolution of clay minerals (Wahid et al., 2011a; Wahid et al., 2011b; Walther, 1996).

Calcite dissolution depends on both pH value and exposure time. After 6 months, calcite dissolution was observed for pHs equal to 11.5 and 13.5. The longer the exposure time, the more significant the calcite dissolution. However, for $pH = 8.5$, no calcite dissolution was observed after 6 months. In this case, a longer exposure time (12 months) was needed to trigger calcite dissolution to a lesser extent.

According to Dolgaleva et al. (2005), the presence of $CaCO_3$ ions can limit calcite dissolution. $CaCO_3$ ions are the main product of carbonation (Eq (1)) which is a dominant mechanism for $pHs < 11.5$. Apparently, this mechanism becomes less strong once a threshold time is exceeded. The production of $CaCO_3$ ions is then weaker, allowing for calcite dissolution. Thereby, calcite dissolution was forbidden for the first 6 months in pHs lower than 11.5 due to carbonation. Once this phenomenon become less dominant, *i. e.*, after 12 months, calcite dissolution took place. The main phenomenon behind the dependence of calcite dissolution on both pH value and exposure time appears to be the carbonation. Also, carbonation explains the higher peak of calcite detected at 29.406 2θ for $pH = 11.5 -$ *non renewing*, comparing to $pH = 8.5$, after 12 months of exposure (Fig. 8). Carbonation, that is more significant in the solution of $pH = 11.5$ than in the solution of $pH = 8.5$, probably results in a smaller dissolution rate of calcite in the former case.

4.4. Implications and transferability of the results

According to Lauper et al. (2018) and Kneuker and Furche (2021), quartz and calcite, in addition to clay minerals, are the main components of Opalinus Clay from the lower sandy facies of Mont Terri site. The interaction of quartz and calcite with an alkaline environment can greatly affect the mechanical and hydraulic properties of the clay rock, compromising the long-term safety of the nuclear waste repository. As shown in this study, the interaction of these minerals with an alkaline environment led to their dissolution. Some microstructure changes as macropore generation might occur, resulting in porosity increase. Consequently, the permeability of the Opalinus Clay might increase. Also,

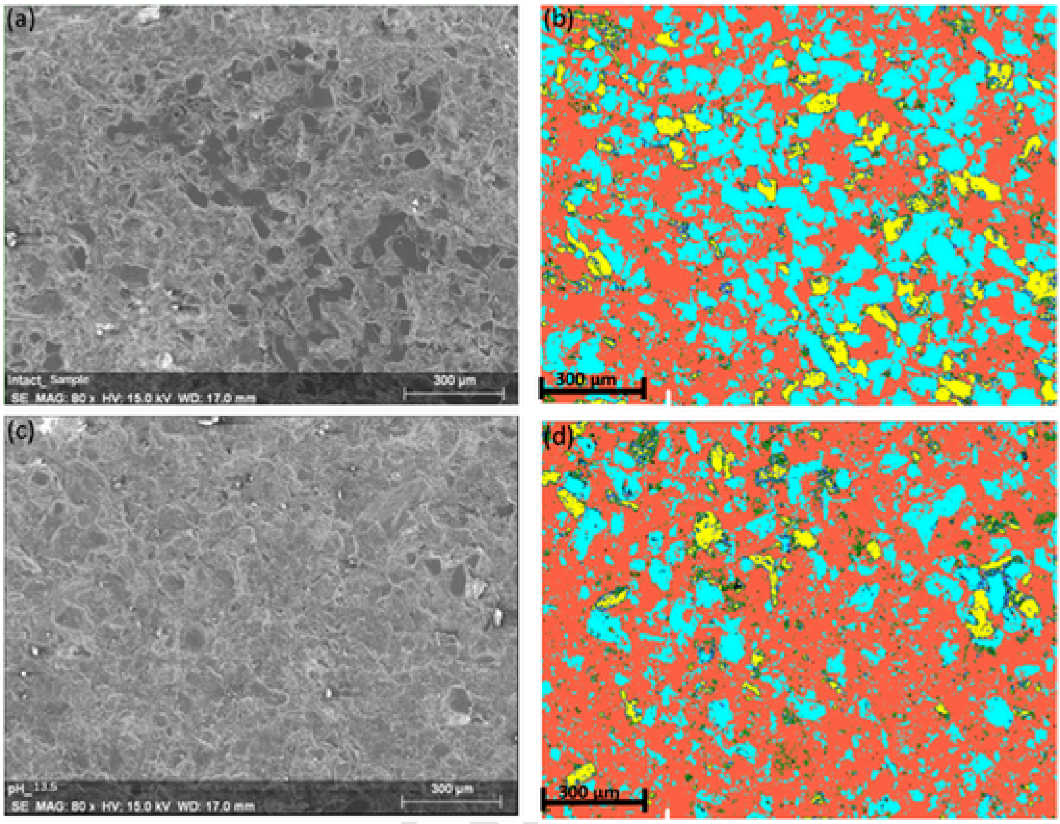

Fig. 12. (a) SEM picture oriented perpendicular to bedding of an intact Opalinus Clay sample (b) EDS result of an intact Opalinus Clay sample (c) SEM picture of an Opalinus Clay sample exposed to an alkaline solution of $pH = 13.5$ (d) EDS result of an Opalinus Clay sample exposed to an alkaline solution of $pH = 13.5$ (Red: Al, Si; Green: Al, Ca, Si; Blue: Si, Yellow: Ca).

Table 1
Averaged mineralogical composition (wt%) of the Opalinus Clay from the lower sandy facies of Mont Terri site-Switzerland.

Mineral	Lerouge (2014)	Ould Bouya (2014)
Clay fraction	**38%**	**52%**
Illite	14%	35%
Chlorite	1%	7%
Kaolinite	9%	9%
I/R (Type *R*1)	14%	–
Carbonate fraction	**20%**	**10%**
Calcite	8%	7%
Dolomite	12%	3%
Silty fraction	**38%**	**37%**
Feldspars	6%	3%
Quartz	32%	34%
Pyrite	**4%**	**1%**
Total	**100%**	**100%**

Table 2
Chemical composition of concrete pore water presenting a *pH* of 13.5 (Lalan, 2016).

Compound	Concentration ($mol \times L^{-1}$)
$NaOH$	5×10^{-2}
KOH	2.7×10^{-1}
$Ca(OH)_2$	6×10^{-4}

these microstructural changes, *i.e.* macropore generation, are expected to decrease the matric potential, further affecting the liquid retention properties of the Opalinus Clay.

Based on the initial mineralogical composition, a transferability of the mechanisms identified for the Opalinus Clay from the lower sandy facies of Mont Terri site can be made to the shaly facies. Compared to the lower sandy facies, the shaly facies is less heterogeneous and more argillaceous (Kneuker and Furche, 2021; Lauper et al., 2018). Indeed, according to Lauper et al. (2018) and Kneuker and Furche (2021), the shaly facies is composed of one subfacies in contrast to the lower sandy facies composed of three subfacies. While clay minerals are dominant in the former facies type ($>50\%$), the proportions of quartz and calcite are $<10\%$ and 5%, respectively (Lauper et al., 2018). When exposing the shaly Opalinus Clay to an alkaline environment, the dissolution of quartz and calcite will probably occur. However, the impact of this dissolution on the hydraulic and mechanical properties is expected to be less significant compared to the sandy facies since the quartz and calcite are present in smaller proportions. On the contrary, the mechanisms of dissolution of the clay minerals will be more dominant, leading to precipitation of more new compounds. This may also significantly affect the hydro-mechanical properties of the Opalinus Clay.

Table 3
Depth within BFI-2 borehole for the six investigated Opalinus Clay samples.

Borehole	Core	Sample	Depth within the borehole (m)
$BFI-2$	1	1	2.35
		2	2.50
	2	3	3.6
		4	3.75
	3	5	6
		6	6.15

5. Conclusions

The degradation of concrete structures in deep geological repositories for high-level and intermediate level long lived radioactive wastes

Table 4
Samples immersed in the alkaline solutions.

Borehole	Core / Sample	Subsample	Depth within the borehole (m)	*pH*	Renewing / Non-renewing	Months of immersion
BFI – 2	3/ 6	1	6.15	13.5	–	Present
		2	6.15	13.5	–	Present
		3	6.15	13.5	–	Present
		4	6.15	13.5	–	6
		5	6.15	13.5	–	12
		6	6.15	13.5	–	Present
		7	6.15	13.5	–	Present
		8	6.15	13.5	–	Present
BFI – 2	3/ 6	1	6.15	11.5	Renewing	Present
		2	6.15	11.5	Renewing	Present
		3	6.15	11.5	Renewing	Present
		4	6.15	11.5	Renewing	6
		5	6.15	11.5	Renewing	Present
		6	6.15	11.5	Renewing	Present
		7	6.15	11.5	Renewing	Present
		8	6.15	11.5	Renewing	Present
BFI – 2	3/ 6	1	6.15	11.5	Non-Renewing	Present
		2	6.15	11.5	Non-Renewing	Present
		3	6.15	11.5	Non-Renewing	Present
		4	6.15	11.5	Non-Renewing	6
		5	6.15	11.5	Non-Renewing	12
		6	6.15	11.5	Non-Renewing	Present
		7	6.15	11.5	Non-Renewing	Present
		8	6.15	11.5	Non-Renewing	Present
BFI – 2	3/ 6	1	6.15	8.5	–	Present
		2	6.15	8.5	–	Present
		3	6.15	8.5	–	Present
		4	6.15	8.5	–	6
		5	6.15	8.5	–	12
		6	6.15	8.5	–	Present
		7	6.15	8.5	–	Present
		8	6.15	8.5	–	Present

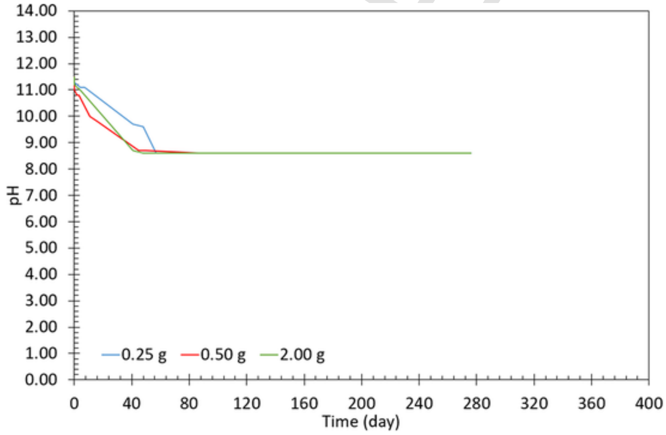

Fig. 13. *pH* monitoring over time for the solutions with an initial *pH* = 11.5 and 0.25 g (bleu curve), 0.5 g (red curve) and 2 g (green curve) of $CaCO_3$.

results in an increase of underground pore water *pH* from an initial value of 7.5 (Gaucher and Blanc, 2006; Pearson et al., 2003) up to 13.5 (Taylor and Harry, 1987; Ye et al., 2014). This increase is gradual and can affect the mineralogy of the claystone by dissolving clay minerals and other minerals, *i.e.*, quartz and calcite. Subsequently, the chemo-hydro-mechanical behavior of the claystone is affected. While previous study investigated clay minerals dissolution in natural claystones exposed to only high *pHs*, this study focuses on the dissolution of quartz and calcite by considering a larger range of *pHs* to cover *in situ* conditions. Indeed, those minerals are dominant in the case of the Opalinus Clay and their interaction with an alkaline environment should be assessed.

In this study, dissolution of quartz and calcite in solutions of different *pHs* was investigated in Opalinus Clay samples extracted from the lower sandy facies of Mont Terri site in Switzerland, using X-ray diffractometry. Three *pH* values (8.5, 11.5 and 13.5) and two exposure times (6 and 12 months) were considered. Based on the obtained results, the main conclusions can be drawn as below:

1) The initial fraction of calcite and quartz minerals exhibit significant heterogeneity in the studied lower sandy facies, in agreement with the observations by Lerouge (2014), Ould Bouya (2014), Lauper et al. (2018) and Kneuker and Furche (2021).
2) The exposure time is a key factor in quartz dissolution. Indeed, quartz dissolution happens at a *pH* as low as 8.5 after 6 months of exposure unlike calcite dissolution. For the same exposure time, increasing *pH* does not increase quartz dissolution. However, with the same *pH*, the longer the exposure time, the more significant the impact of quartz dissolution.
3) The main mechanism behind the dependence of quartz dissolution on the exposure time appeared to be the basic attack, that results in the formation of SiO^- groups, with weak $Si - O$ bonds analogue to the mechanism described in Walther (1996) and Wahid et al. (2011a, 2011b).

4) Both the *pH* value and exposure time are key factors in calcite dissolution. Indeed, after 6 months of exposure, calcite dissolution occurs only at *pHs* higher than 11.5. However, after 12 months of exposure, calcite dissolution occurs at *pHs* as low as 8.5.

4) With the same *pH*, the longer the exposure time, the greater the calcite dissolution.

For $pH = 8.5$, carbonation, that produces $CaCO_3$, probably forbids calcite dissolution for the first 6 months.

These laboratory data, at ambient laboratory temperature, provide some first indications about the fate of some typical constitutive minerals of the Opalinus Clay, with respect to changes in *pH* and in the exposure time. To better understand the real phenomena that will occur in deep repositories, further investigations are necessary to assess the fate of these minerals under elevated temperature and along a much longer period.

CRediT authorship contribution statement

Yara Barakat: Validation, Investigation, Writing – original draft. **Yu-Jun Cui:** Conceptualization, Methodology, Writing – review & editing. **Nadia Mokni:** Investigation, Resources. **Pierre Delage:** Investigation. **Frédéric Bernier:** Investigation.

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