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Chemo-mechanical couplings in compacted argillite submitted to high-pH environment

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Abstract: In the French concept of deep nuclear wastes repository, the galleries should be backfilled with excavated argillite after the site exploitation period. After several thousands of years, the degradation of the concrete lining of the galleries will generate alkaline fluid (pH > 12) that will diffuse through the backfill. The objective of the paper is to describe the influence of such solute diffusion on the microstructure and the mechanical behavior of compacted argillite. Saturated-portlandite water was circulated through compacted samples for 3, 6 and 12 months at 20 °C or 60 °C, respectively. The microstructures before and after fluid circulation were determined with mercury intrusion porosimetry. Since it was planned to introduce additives (bentonite or lime) in the remoulded argillite to backfill the deep galleries, such mixtures were also studied. The results show that the influence of the alkaline fluid on the properties of the argillite is a function of the nature of the additive. The pure argillite undergoes slight modifications that can be related to a limited dissolution of its clayey particles. Conversely, intense alteration of the bentonite-argillite mixture was observed. Lime addition improves the mechanical characteristics of the argillite through the precipitation of cementitious compounds.

Key words: chemo-mechanical couplings; alkaline plume; argillite; microstructure; shear strength

1   Introduction

Under extremely alkaline conditions, i.e. pH > 12, most of the usual soil minerals undergo physico-chemical transformations [1, 2]. Very high-pH water causes the dissolution of the soil primary minerals accompanied by the formation of secondary minerals like calcium silicate hydrates (CSHs) and calcium aluminate hydrates (CAHs) (pozzolanic reactions). Available studies have been realized on both pure minerals [3, 4] and natural materials [5–8]. Many geochemical modelling studies have also been performed [9]. Recent works on these topics conclude that these physico-chemical reactions should alter the physical properties of the backfill like porosity changes that are associated with the permeability variations [10, 11].

Such high-pH conditions are expected to occur in the galleries of deep repositories for nuclear waste. In the French concept of nuclear waste storage, the stability of the galleries will be ensured with a concrete lining. The repository will be backfilled after use. Among other functions, this backfill will limit the convergence of the galleries after the concrete lining breaks (i.e. after thousands of years); it will also constrain the bentonite sealings during their hydration. One key point is the degradation of the concrete lining of the galleries that will generate alkali-rich and high-pH solutes [12] that will then diffuse into the backfill. This will give rise to a phenomenon called the hyperalkaline plume. Only very few studies have been carried out on these processes at the scale of compacted clay samples. Pusch et al. [6] studied the interaction between the Friedland Ton clay and the low-pH cement water, and a slight drop in the clay hydraulic conductivity was shown. Robinet [10] showed that the permeability of MX-80 bentonite was not sensitive to alkaline fluid circulation but to the temperature of experiment. Karnland [13] submitted MX-80 samples to several alkaline water types (NaOH and Ca(OH)$_2$ solutions). Their results showed that the

swelling pressure in the bentonite was strongly reduced due to exposure to NaOH solution while little effect on swelling pressure was found in the samples exposed to $Ca(OH)_2$ solution.

In this context, a comprehensive study of the influence of an alkaline fluid circulation on compacted argillite was undertaken. Compacted argillite samples were submitted to a circulation of an alkaline fluid (pH > 12) up to 12 months. Investigations at the microscopic level were carried out with mercury intrusion porosimetry (MIP). The mechanical behaviors of different materials were determined based on triaxial tests. A more comprehensive and detailed inter-pretation of the MIP test results was available in Ref.[14]. The objective of this paper is to examine the possible alteration of the mechanical behavior of compacted argillite submitted to an alkaline fluid circulation.

2   Materials properties

An outcrop of the Callovo-Oxfordian argillite provides the material used in this study. The sampling was performed in the upper part of the Callovo-Oxfordian argillite. The Manois argillite (MA) was carefully homogenized and crushed into very fine grain powder. Chemical and XRD analyses indicate that the MA contains 26%–32% calcite, 22%–27% quartz, and 41%–49% clays (fraction less than 2 μm). The clays are mainly illite, kaolinite and interstratified illite-smectite. The specific surface determined with BET is (40.4 ± 1) m^2/g. The geotechnical parameters of the MA are given in Table 1.

Table 1 Compaction characteristics of different mixtures.

Mixture	Optimum water content (%)	Maximum dry unit weight (kN/m^3)
MA	23.0	1.61
80% MA + 20% MX-80	25.5	1.54
96% MA + 4% lime	25.5	1.50

The Meuse-Haute Marne (MHM) site in the eastern Paris Basin, France, is an underground laboratory built to study the feasibility of creating a deep repository for nuclear waste in a clay-rich formation of Callovo-Oxfordian argillite. The stability of the galleries will be ensured with concrete lining. This repository will be backfilled after use. Among other functions, this backfill will limit the convergence of the galleries after

the concrete lining breaks (i.e. after thousands of years); it will also constrain the bentonite sealings during their hydration. One possible backfill material is the excavated argillite, which will be stored on surface during exploitation and reversibility periods (i.e. over one hundred years). However, if submitted to atmospheric conditions, the excavated Callovo-Oxfordian argillite exhibits reduced mechanical properties and is unsuitable for direct backfill. Hence, it is necessary to improve the argillite characteristics with an additive.

For the study of the backfill of deep galleries, two different additives intending to improve the properties of the argillite were considered. The first was MX-80 bentonite, which was selected to enhance the sealing properties of the backfill through improved swelling [15]. This clay contains more than 80% mont-morillonite with sodium and calcium as exchangeable cations, and 86.1% of the particles are smaller than 2 μm. The mixture used 20% MX-80 and 80% MA on a dry-weight basis.

The second additive used was quicklime, which could improve both the cohesion and the friction angle of clayey materials [16, 17]. When added to the soil, the hydration reaction of the lime increases the concentrations of Ca^{2+} and OH^-. It induces cation exchange of Ca^{2+} from the exchangeable cations existing in clay lattices. This causes the flocculation of the particles, further affecting soil plasticity [18]. Moreover, the release of hydroxy anions increases the pH value of the soil up to 12.4, leading to the dissolution of silica and alumina from soil minerals that react with calcium, permitting the formation of CSH and CAH compounds that cement soil particles and increase the mechanical characteristics [19, 20]. The quicklime used in those studies is composed of more than 97% pure CaO. A lime content of 4% with the remainder MA on a dry-weight basis was selected for the experimental program.

3   Samples preparation

The MA and the MX-80 were dried at 50 °C and then the selected materials were thoroughly mixed together at the corresponding proportions. Tap water was added to reach the target water content during mixing. The mixture was stored in an airtight container for at least two days to reach moisture equilibrium.

To prepare the lime-MA mixtures, the MA was wetted first and left in an airtight container for two

days to reach moisture equilibrium. The MA and the lime were then thoroughly mixed, and after a mellow period of 24 hours, the mixture was ready for compaction. After compaction, lime-treated samples were sealed and cured for 90 days at 20 °C before a given circulation test.

The samples were prepared by static compaction in seven layers. To define the compaction pressure, the standard Proctor curve of the MA was first determined, using the maximum dry density of 1.61 Mg/m^3 and the optimum water content of 23.0%. The static compaction pressure was adjusted to reach the same dry density as a standard Proctor for the water content of 23.0%. The static compaction pressure was about 470 kPa. This pressure was used to prepare all tested samples. All mixtures in the study were prepared at their respective optimum water content determined from the standard Proctor test. The optimum water contents for each mixture statically compacted under the pressure of 470 kPa are given in Table 1 together with the initial dry density of each mixture when the static compaction is used.

4 Experimental procedures and testing program

4.1 Ageing procedure

The main objective is to study the influence of an alkaline fluid circulation on the behavior of compacted argillite. Special cells were designed to circulate the fluid through compacted soil samples over a long period of time. A schematic diagram of those cells is given in Fig.1. The sample diameter is 90 mm and its height is 80 mm. Soil samples were directly compacted inside the PVC mould to avoid preferential path formation. The cells were designed to prevent any
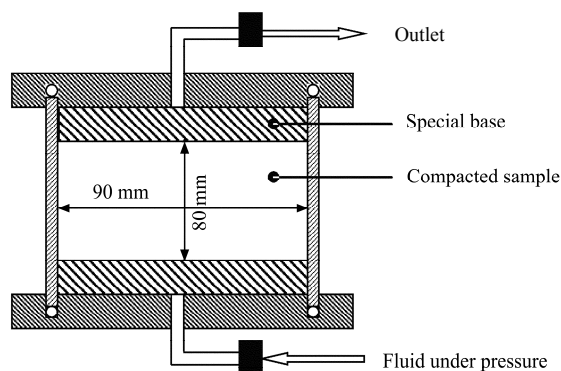

Fig.1 Schematic diagram of the circulation cells.

macroscopic swelling of the tested samples upon hydration. The fluid was injected through the base of the cells and circulation was maintained up to 12 months. A portlandite-saturated water with a pH value of about 12.4 was used to simulate the cement-pore water. That composition was selected for ease of preparation and to insure the chemical stability of the cement water.

As the objective of the study is to depict the influence of the circulation of an alkaline fluid after several years, it is necessary to speed up the kinetics of the chemical reactions by performing experiments at an elevated temperature. The dissolution kinetics of clay particles in high-pH media and pozzolanic reactions increase sharply at high temperatures. The selected temperature for the experiments was 60 °C.

After the compaction of samples, the circulation cell was closed and transferred to the oven set to be 60 °C. The circulation began immediately, with an injection pressure of 40 kPa. If the sample pore volume was used as the volume unit, about 18 pore volumes flowed through a sample of compacted MA each month. During the experiment, the fluid pH value was periodically measured at the outlet of the cells. A few days after the fluid circulation began, it was observed that the pH value stabilized between 12 and 13. That pH value remained nearly constant throughout the experiment.

4.2 Sample preparation for MIP

After the circulation period, small specimens with a volume between 1 and 2 cm^3 were taken from the sample. Due to technical requirements, both MIP tests must be conducted on totally dry samples. Freeze-drying was selected in this study as an alternative to oven drying to prevent the effects of shrinkage of the sample microstructure. Soil pieces were quickly frozen with liquid nitrogen (temperature of –196 °C) and then placed in a freeze-drier for 72 hours for the sublimation of the water.

4.3 Mechanical testing procedure

At the end of the circulation period, each cell was carefully dismantled. Triaxial core samples were then trimmed to the desired dimensions (3.5 cm in diameter and 7 cm in height) and used to perform triaxial consolidation undrained tests with measurement of internal pore water pressure. The effective consolidation pressure was between 140 and 590 kPa. All the mechanical tests were performed at room temperature (about 20 °C).

5   Experimental results

5.1 Behaviors of pure argillite

The results of the MIP tests performed on the MA are given in Fig.2(a). The initial microstructure of the MA is common for compacted clayey soils. There is a macropore class from 10 up to 100 μm and a class of micropores between 0.01 and 1 μm. The soil is composed of aggregates, the pores inside the aggregates are the micropores and the spaces between the aggregates and the macropores. The mechanical behavior of the compacted pure MA was also determined. The stress paths in the s'-t plane with $s' = (\sigma_1' + \sigma_3')/2$ and $t = (\sigma_1' - \sigma_3')/2$, are given in Fig.2(b). The maximum deviatoric stress was used as the failure criterion for that case. This gives an effective cohesion c' of 25.6 kPa and an effective friction angle φ' of 18.6° for the pure MA after its compaction. It is representative of the behavior of a compacted soil that is slightly overconsolidated.

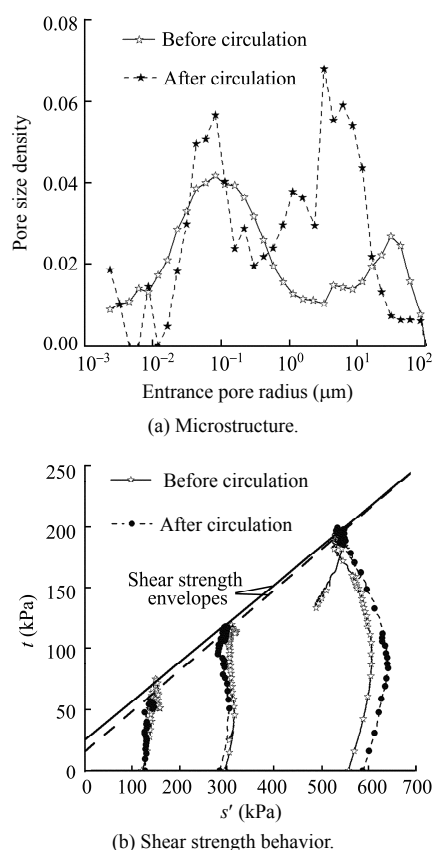(a) Microstructure.

(b) Shear strength behavior.

Fig.2 Influence of the cement water circulation on the MA microstructure and its shear strength behavior.

The impact of the alkaline fluid circulation at 60 °C for 12 months was then examined. The MIP results demonstrate that the fluid circulation leads to an increase in the amount of pores with a radius between 0.5 and 30 μm (Fig.2(a)). From a mechanical point of view, the alkaline fluid circulation for 12 months leads to a slight modification of the shear strength behaviors (Fig.2(b)).

5.2 Behaviors of argillite with 20% MX-80 bentonite mixture

The pore size density (PSD) function of the as-compacted MX-80 mixture features three pore classes, two of which are macropore classes (> 0.2 μm), as shown in Fig.3(a). There is one macropore class of the same order of magnitude as the class identified in the compacted MA and an additional class with a pore radius of about 2 μm. From a mechanical point of view, it can be seen that the addition of 20% bentonite tends to lower the cohesion of the MA. The effect of the MX-80 addition on the friction is not significant, and the mixture behaves as a normally consolidated clayey material (Fig.3(b)).
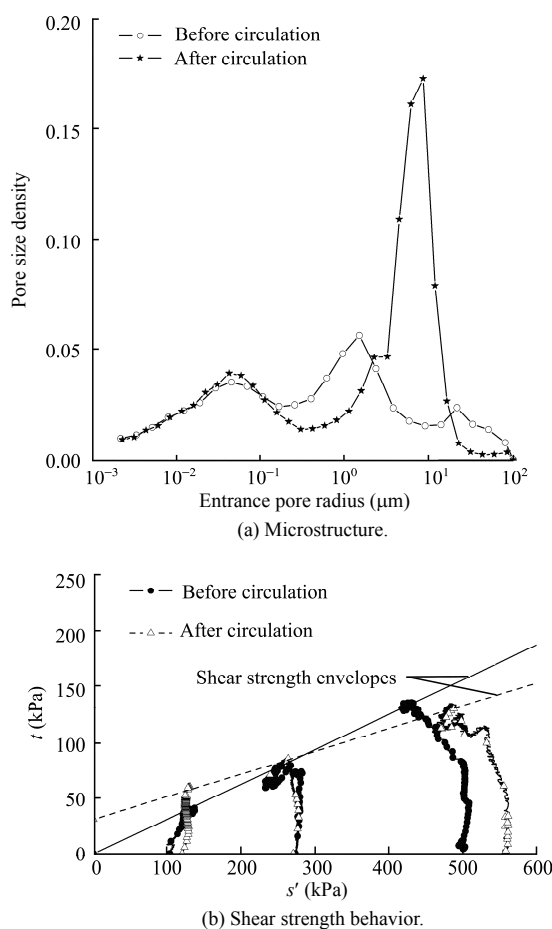

(a) Microstructure.

(b) Shear strength behavior.

Fig.3 Influence of the cement water circulation on microstructure and shear strength behavior of the MA + 20% MX-80 mixture.

The dry density of that mixture was determined after 12 months of alkaline fluid circulation at 60 °C. It

decreases from 1.54 to 1.34 Mg/m^3. This decrease is not related to swelling since the circulation is performed at a constant volume. The PSD obtained after fluid circulation demonstrates that the dry density variation is related to the increase in the macropore volume of the mixture, while the micropores are unchanged (Fig.3(a)). This point is confirmed by the MIP tests that evidence a remarkable stability of the microstructure of the mixture after the alkaline fluid circulation.

After the alkaline fluid circulation, it can be seen in Fig.3(b) that the effective friction angle decreases to 13.5°, while the effective cohesion increases to about 30 kPa. These modifications are related to the alteration process that has taken place at the microstructural level. The decrease in the friction angle can be related to the strong decrease in the sample dry density. It is likely that the increase in the effective cohesion is related to the formation of some secondary products that cement the remaining particles.

5.3 Behaviors of argillite with 4% quicklime mixture

The microstructure of the lime-treated MA at the end of the initial curing phase of 90 days at 20 °C is illustrated in Fig.4(a). There are two classes of pores different from those identified in the pure MA. The main effect of lime addition is the creation of a micropore class with a mean radius much lower than that of the MA alone. Such effect of lime has also been evidenced by Le Runigo et al. [21] on lime-treated silt. This behavior has been attributed to the flocculating effect of lime [22].

The shear strength behavior of the 4% lime-treated material was tested after 90 days of curing at a constant water content at 20 °C. Figure 4(b) compares the behaviors of the pure argillite and the 4% lime-
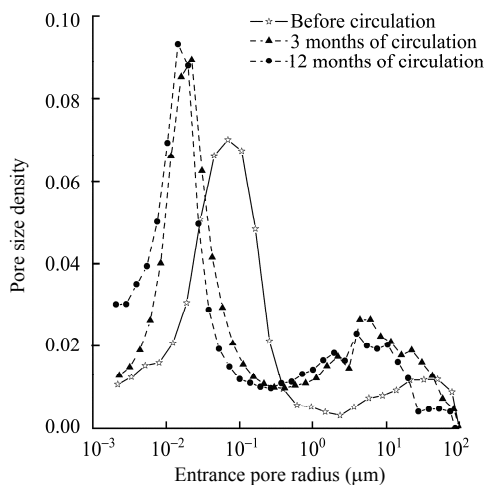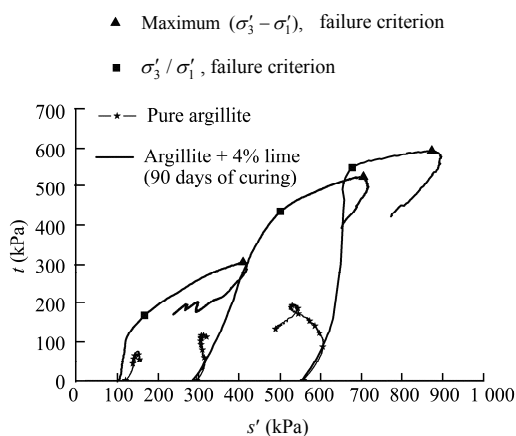
(b) Shear strength behavior.

Fig.4 Influence of the cement water circulation on microstructure and shear strength behavior of the MA + 4% lime mixture.

treated argillite. If the maximum shear stress failure criterion is used, the effective cohesion is 50.3 kPa and the effective friction angle is 39.5°. Previous investigators have related similar increases in the cohesion after lime addition to the formation of cementitious compounds between soil particles [23–25]. The flocculating effect of lime on the MA clay particles must be taken into account to understand the effect of lime on the friction angle. It is known that lime tends to aggregate the clay particles of a soil, causing them to become cemented. As shown by Lambe [26], these larger aggregates are highly interlocked, resulting in an increase in the cohesion and the effective friction angle. This hypothesis has been confirmed by Lade and Overton [27].

The impacts of different fluid circulation periods (3, 6 and 12 months) were assessed. The MIP test results are plotted in Fig.4(a). It is shown that most changes induced by the alkaline fluid circulation occur during the first three months: there is a reduction in the mean micropore radius and creations of some macropores. It is interesting to note that for MIP, there is no major modification at the macropore level between 3 and 12 months of the alkaline fluid circulation.

The shear strength behavior of the lime-treated material was determined after 3, 6 and 12 months of cement water circulation. It is shown that the alkaline fluid circulation modifies the shear strength behavior of the lime-treated MA. The major effect is the increase in the peak shear strength. The shear strength envelope of the circulated material is determined and plotted in Fig.5, where the maximum shear stress is used as the failure criterion. It can be assumed that all
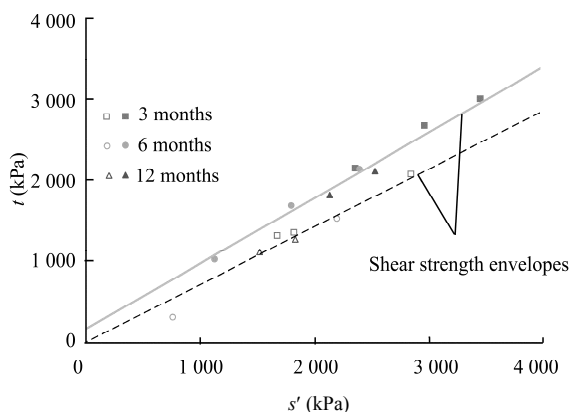

(a) Microstructure.

Fig.5 Shear strength of the lime-treated argillite circulated 3, 6 and 12 months with cement water: peak strengths (solid symbols), residual strengths (open symbols).

the failure points fall on the same shear strength envelope and this does not depend on circulation duration. Most modifications of the shear strength behavior of the lime-treated MA occur during the first three months of water circulation. Longer circulation periods slightly lower the peak shear strength of the lime-treated MA. That may be explained by the fact that the samples are submitted to a temperature of 60 °C. After submitting the samples to fluid circulation, a few days are required before a constant flow of water is obtained at the exit of the cells. Before that, the lime-treated samples are cured at conditions very favourable for the pozzolanic reactions, enhancing the formation of cementitious compounds before exposure to water. The modifications of the shear strength behavior observed after three months of the alkaline water circulation may be a consequence of this phenomenon and is directly related to the presence of lime inside the samples. Thus, it can be concluded that the alkaline water circulation does not produce a significant modification of the shear strength behavior of the lime-treated MA.

6   Discussions

This work shows that the circulation of an alkaline fluid can induce drastic modifications to the microstructure and the mechanical behavior of the MA. Experimental and modelling studies of the stability of clays and clay minerals both have shown that a high-pH environment will lead to dramatic modifications of the materials porosity [28]. Nevertheless, this work demonstrates that a key parameter for the modification of the porosity of a compacted clayey soil submitted to an alkaline plume is the nature of the additive. For the

MA, an increase in the pore volume linked to the dissolution of the clay particles is observed. The pore volume increase is higher when the MX-80 clay is added to the MA. This is related to the fact that the MX-80 particles are less stable in high-pH environments than the MA particles. Conversely, the addition of calcareous sand seems to protect the MA from dissolution. This behavior is likely related to the nature of the added sand fraction that is composed of calcite grains. Calcite may buffer the pH value of the mixture to a value close to its equilibrium pH value near 8.3, where MA particles are not sensitive to dissolution. The lime-mixture behaves in a different manner. The formation of cementitious compounds during the 90-day curing period alters the MA microstructure before the start of the fluid circulation. Such secondary products are common [29, 30]. It is also shown that the subsequent 3–12 months of fluid circulation does not lead to a significant alteration in the microstructure of the mixture. A stationary regime with some precipitation/dissolution phenomena seems to be established after three months of alkaline fluid circulation.

7   Conclusions

The influence of the alkaline fluid circulation on the shear strength behavior of compacted pure argillite or that with an additive (sand, bentonite or quicklime) was studied. These materials are options for the backfill of galleries of deep nuclear waste repositories. Special circulation cells were designed to simulate a long-term alteration process. Circulations were performed with portlandite-saturated water between 3 and 12 months at 60 °C.

The results show that the MA particles are sensitive to the alkaline fluid circulation at the microstructural level. Such fluid circulation leads to the increase in the macropore void ratio and the dissolution of the particles, mainly the clayey particles. The increase in the macropore void ratio is related to the nature of the clayey particles. Some of the dissolved compounds allow the formation of cementitious compounds that probably increase the shear strength, hence compensating for the decrease in density that will lower the shear strength. However, it seems that the formation of cementitious compounds is complicated because of the permanent flow of the alkaline water. The dissolved components leaking out of the material are dependent on the hydraulic properties of each

mixture. Hence, even with such severe experimental conditions, there is no evidence of dramatic loss of shear strength of the studied materials in alkaline environment. The MA is the most stable mixture, while the MX-80 mixture and lime-treated MA are highly reactive mixtures.

References

[1]   Boardman D I, Glendinning S, Rogers C D F. Development of stabilisation and solidification in lime-clay mixes. Geotechnique, 2001, 51 (6): 533–543.

[2]   Huertas F, Farias J, Griffault L, et al. Effects of cement on clay barrier performance—ECOCLAY project. [S. l.]: [s. n.], 2000.

[3]   Bauer A, Berger G. Kaolinite and smectite dissolution rate in high molar KOH solutions at 35 ºC and 80 ºC. Applied Geochemistry, 1998, 13 (7): 905–916.

[4]   Bauer A, Velde B. Smectite transformation in high molar KOH solutions. Clay Minerals, 1999, 34 (2): 259–273.

[5]   Chermak J A. Low temperature experimental investigation of the effect of high pH KOH solutions on the Opalinus shale, Switzerland. Clays and Clay Minerals, 1993, 41 (3): 365–372.

[6]   Pusch R, Zwahr H, Gerber R, et al. Interaction of cement and smectitic clay—theory and practice. Applied Clay Science, 2003, 23 (1–4): 203–210.

[7]   Claret F, Bauer A, Schäfer T, et al. Experimental investigation of the interaction of clays with high-pH solutions: a case study from the Callovo-Oxfordian formation, Meuse-Haute Marne underground laboratory (France). Clays and Clay Minerals, 2002, 50 (5): 633–646.

[8]   Ramírez S, Cuevas J, Vigil R, et al. Hydrothermal alteration of "La Serrata" bentonite (Almería, Spain) by alkaline solutions. Applied Clay Science, 2002, 21 (5/6): 257–269.

[9]   Gaucher E C, Blanc P, Matray J M, et al. Modeling diffusion of an alkaline plume in a clay barrier. Applied Geochemistry, 2004, 19 (10): 1 505–1 515.

[10] Robinet J C. Effects of an alkaline plume on the hydraulic and hydromechanical properties of the bentonite MX-80. In: ECOCLAY II—Effects of Cement on Clay Barrier Performance (Final Report). [S. l.]: European Commission, 2005: 88–104.

[11] Rodwell W, Baker A, Schwyn B, et al. Work package 6: summary and performance assessment. In: ECOCLAY II—Effects of Cement on Clay Barrier Performance (Final Report). [S. l.]: European Commission, 2005: 300–313.

[12] Anderson K, Allard B, Bengtsson M, et al. Chemical composition of cement pore solutions. Cement and Concrete Research, 1989, 19 (3): 327–332.

[13] Karnland O. Laboratory experiments concerning compacted bentonite contacted to high pH solutions. In: ECOCLAY II—Effects of Cement on Clay Barrier Performance (Final Report). [S. l.]: European Commission, 2005: 143–162.

[14] Cuisinier O, Masrouri F, Pelletier M, et al. Microstructure of a compacted soil submitted to an alkaline plume. Applied Clay Science, 2008, 40 (1–4): 159–170.

[15] Dixon D A, Gray M N, Thomas A W. A study of the compaction properties of potential clay-sand buffer mixtures for use in nuclear waste disposal. Engineering Geology, 1985, 21 (3/4): 247–255.

[16] Brandl H. Alteration of soil parameters by stabilization with lime. In: The 10th Int. Conf. on Soil Mechanics and Foundation Engineering. Stockholm, Sweden: [s. n.], 1981: 587–594.

[17] Fossberg P E. Some fundamentals engineering properties of a lime-stabilized clay. In: The 6th Int. Conf. on Soil Mechanics and Foundation Engineering. Montréal, Canada: [s. n.], 1965: 221–225.

[18] Locat J, Bérubé M A, Choquette M. Laboratory investigations on the lime stabilisation of sensitive clays: shear strength development. Canadian Geotechnical Journal, 1990, 27 (3): 294–304.

[19] Bell F G. Lime stabilization of clay minerals and soils. Engineering Geology, 1996, 42 (4): 223–237.

[20] Little D N. Stabilization of pavement subgrades and base courses with lime. Arlington: National Lime Association, 1995.

[21] Le Runigo B, Cuisinier O, Cui Y J, et al. Impact of the initial state on fabric and permeability of a lime treated silt under long term leaching. Canadian Geotechnical Journal, 2009, 46 (11): 1 243–1 257.

[22] Shi B, Liu Z B, Cai Y, et al. Micropore structure of aggregates in treated soils. Journal of Materials in Civil Engineering, 2007, 19 (1): 99–104.

[23] Balasubramaniam A S, Buessucesco B, Oh Y N E, et al. Strength degradation and critical state seeking behaviour of lime-treated soft clay. In: Deep Mixing'05, Proceedings of the International Conference on Deep Mixing—Best Practice and Recent Advances. Stockholm, Sweden: [s. n.], 2005: 35–40.

[24] Rallings R A. The effect of pre-treatment moisture content on the properties of cement and lime stabilized clay soils. Australian Road Research, 1971, 4 (6): 10–31.

[25] Wissa A E Z, Ladd C C, Lambe T W, et al. Effective stress strength parameters of stabilized soils. In: Int. Conf. on Soil Mechanics and Foundation Engineering. Montréal: [s. n.], 1965: 412–416.

[26] Lambe T W. A mechanistic picture of shear strength in clays. In: Conference on Shear Strength of Cohesive Soils. Boulder, USA: ASCE, 1960: 555–580.

[27] Lade P V, Overton D D. Cementation effects in frictional materials. Journal of Geotechnical Engineering, 1989, 115 (10): 1 373–1 387.

[28] Fernandez R, Cuevas J, Sanchez L, et al. Reactivity of the cement-bentonite interface with alkaline solution using transport cells. Applied Geochemistry, 2006, 21 (6): 977–992.

[29] Choquette M, Berube M A, Locat J. Mineralogical and microtextural changes associated with lime stabilization of marine clays from eastern Canada. Applied Clay Science, 1987, 2 (3): 215–232.

[30] Rossi P L, Ildefonse P, De Nobrega M T, et al. Study of structural and mineralogical transformations caused by compaction with or without lime addition to lateritic clays from Brazil. Bull. of the Int. Ass. of Eng. Geol., 1983, 28: 153–159.