Chemical Engineering Journal 155 (2009) 19–25

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Review

Retention and swelling properties of a calcareous soil during leaching by zinc solutions

Hanène Souli[a,*], Jean-Marie Fleureau[b,1], Malika Trabelsi-Ayadi[c,2]

[a] *Laboratoire de Tribologie et Dynamique des Systèmes, Ecole Nationale d'Ingénieurs de Saint Etienne (ECL/ENISE/ENSMSE) (CNRS UMR 5513), 58 rue Jean Parot, 42023 Cedex 02, Saint Etienne, France*
[b] *Laboratoire de Mécanique des sols, structures & matériaux, CNRS UMR8579, Ecole Centrale Paris, Grande voie des vignes, 92295 Châtenay-Malabry, France*
[c] *Laboratoire de Physico Chimie Minérale, Faculté des Sciences de Bizerte, Bizerte, Jarzouna 7021, Tunisie*

ARTICLE INFO

Article history:
Received 5 March 2008
Received in revised form 11 July 2009
Accepted 14 July 2009

Keywords:
Compacted clayey soil
Zinc
Swelling
Selective sequential extraction

ABSTRACT

The paper presents the results of leaching tests carried out on compacted calcareous clay samples using water and zinc solutions as permeants. Sequential selective extraction was used to evaluate the contribution of the different soil constituents to zinc retention. The retention and swelling properties of the soil under the different conditions were related to its porosity by means of mercury intrusion tests. During the leaching tests, the swelling of the samples varies from 27% in the case of water to 16% and 21% in the case of zinc solutions with concentrations of 2.97 and 297 g/l, respectively. The quantity of zinc retained by the soil is derived from two methods: selective sequential extraction (SSE) and acid digestion. The results from SSE show that the total quantities of absorbed zinc are equal to 76.7 and 27.2 mg/g of soil for the samples saturated with zinc at the concentrations of 2.97 and 297 g/l, respectively. This method shows that carbonate plays a significant role in the retention process through two main mechanisms: (i) the formation of precipitates of zinc carbonates, oxides and hydroxides at the lowest zinc concentration and (ii) calcite dissolution at the highest zinc concentration. Acid digestion confirms the value of the total quantity of absorbed zinc, with a relative difference of 8% with SSE. Mercury intrusion porosimetry (MIP) shows that wetting the sample with water or zinc solutions results in different pore distributions. Compared to the initial state, the pore volume of the samples increases during hydration with water or with zinc solutions. In the initial state, the sample is characterised by pores located at 10 and 0.7 μm. When the sample is saturated with water, the inter-aggregate pores increase to 30 μm and the interparticular pores, to 1 μm. When the sample is hydrated with the 2.97 g/l zinc solution, the increase of the pore size (to 20 μm) only concerns the inter-aggregate pores but is slightly lower than in the case of water. When the sample is hydrated with the 297 g/l zinc solution, the interparticular pores disappear and only an inter-aggregate pore at 20 μm is observed.

The combination of the mercury intrusion and selective sequential extraction (SSE) results suggests that, for the sample saturated with the 2.97 g/l solution, the formation of precipitates leads to the obstruction of the pores, the reduction of the accessible porosity and a decrease in the swelling properties. On the other hand, carbonate dissolution leads to a widening of the pores and an increase in the accessible pore volume which is responsible for the increase in the swelling properties.

1. Introduction

In industrial waste repositories, compacted clays are often used as confining barriers, either alone or in combination with geomembranes (GCLs), because of their swelling capacity and ability to retain the pollutants contained in the leachates, such as heavy metals. Typical design of waste landfills includes compacted clay layers at the bottom of the landfill to prevent infiltration of leachates into the groundwater when the permeability of the natural clay is too high or its thickness too small. In the case of dangerous wastes, French regulations require the clay layer to be at least 5 m thick and its permeability to be lower than 10^{-9} ms^{-1}. Therefore, it is important to assess the properties of these clay layers in the presence of pollutants. In this paper, the attention will be focused on two main properties: swelling and retention of metallic ions.

Research about this subject has been mainly devoted to the study of the mechanisms of adsorption of heavy metals on clays. For instance, results have shown that the adsorption of heavy metals on clays is influenced by clay mineralogy, metal concentration

---

[*] Corresponding author. Tel.: +334 77 43 75 24; fax: +334 77 43 75 39.
E-mail addresses: hanene.souli@enise.fr (H. Souli), jean-marie.fleureau@ecp.fr (J.-M. Fleureau), malikatrabelsi_ayadi@yahoo.fr (M. Trabelsi-Ayadi).
[1] Tel.: +331 41 13 1320; fax: +331 41 13 1442.
[2] Tel.: +216 71 770 285; fax: +216 71 772 255.

1385-8947/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2009.07.030

[1], [2] and pH value [3]. Other researchers studied the influence of the other constituents of the soil like carbonates on the retention of heavy metals. Griffin et al. [4], Yong and Phadungchewit [5], Maskall and Thornton [6] and Yong et al. [7] showed that heavy metals precipitate in carbonates and that amorphous oxides and hydroxides play a primary role when the pH of the soil increases. More recently, Lafuente et al. [8] showed that sorption of different heavy metals in carbonated soils is important and that the mobility of heavy metals is low in this type of soil. The authors also carried out tests on acidic and calcareous soils: they showed that, in spite of the differences in the physico-chemical properties of the soils, the retention of the metals remained nearly the same. The influence of heavy metal adsorption on some hydromechanical properties of heterogeneous soils has been investigated in a few papers. Concerning the swelling capacity, Shackelford et al. [9], Ouhadi et al. [10], Jullien et al. [11] showed that the swelling capacity of clays dramatically decreases when the heavy metal concentration increases. The interpretation of the phenomenon generally refers to the double layer theory. The latter authors showed that the total porosity decreased at low copper concentrations whereas it increased at high copper concentrations. The porosity decrease was interpreted as a reduction of the swelling capacity due the cationic exchange, and the porosity increase was linked to carbonate dissolution.

In this work, the behaviour of a compacted calcareous clay in the presence of zinc solutions is studied. The interest is focused on two aspects which are strongly related. The first one is the retention capacity of the clay during leaching by water and two zinc solutions. The second one is to compare the swelling of the specimens under these conditions. To understand and analyse the results, three sets of tests were carried out after the leaching tests: (i) selective sequential extractive analysis (SSE) to determine the quantity of metal adsorbed on calcite, hydroxides or present in the interlayer space; (ii) acid digestion, (iii) mercury intrusion porosimetry to evaluate the changes in total pore volume and size of pores. Two zinc concentrations (2.97 and 297 g/l) were chosen to perform the leaching tests to simulate two levels of pollution and study the phenomena under two very different pH conditions.

2. Experimental methods

2.1. Physicochemical and geotechnical methods

The soil studied comes from a large deposit in the region of Gafsa in the southwest of Tunisia. The blocks of natural soil were dried, crushed and finally ground in an agate mortar, then the powder was passed through a 80 μm sieve. Mineralogical identification was carried out by X-ray diffraction, using a Siemens D5000 diffractometer equipped with a X-ray generator, under a tension of 40 kV and an intensity of 20 mA, with Ni-filtered Cu-K$_\alpha$ ($\lambda = 0.15418$ nm); the X-ray diffractograms were recorded for angles ranging from 2.8° to 70°, by steps of 0.02°. The Si, Al, Fe, Mg, K, Na, Mn, Ca and Ti contents were obtained by means of a Jobin-Yvon JY emission spectrophotometer. For this analysis, the soil samples were prepared according to the procedure of the NF X 31-147 standard [12]. The content in zinc after the leaching test was determined by means of an ICP-MS spectrophotometer. The values of the cation exchange capacity (CEC) and specific surface area (SSa) were determined using the copper ethylene diamine [13] and ethylene glycol methods [14], respectively.

The amount of carbonate was determined using the NF P 94-048 standard [15]. Mercury intrusion tests were performed on samples of 1 g, with a Micromeritics Auto IV pore 9500 porosimeter, in a range of pressures varying from 0.0035 to 200 MPa corresponding, for cylindrical pores, to diameters between 350 and 0.0063 μm. The samples were freeze-dried following the protocol described by Tessier and Berrier [16] to avoid disturbance in the soil fabric during drying. The void ratio of the specimens was derived from the external volume measured at the end of the tests, by weighing the specimen in air and in a non-wetting liquid (kerdane). Furthermore, considering the importance of pH conditions on the adsorption properties of clay, on the formation of precipitates and on the dissolution of calcite, pH measurements were performed in the presence of water and solutions of zinc at concentrations of 2.97 and 297 g/l. The pH values of the soils polluted by zinc were also measured using the NF ISO 10390 standard procedure [17] by means of a Knick 646 digital pH-meter with a glass electrode. The geotechnical properties of the soil were determined according to the AFNOR and ISO standards: NF P 94-051 [18] for the measurement of the Atterberg limits, NF P 94-057 [19] for the sedimentation tests, NF P 94-048 [20] for calcite determination and ISO 17313 [21] for permeability measurement in a flexible wall permeameter.

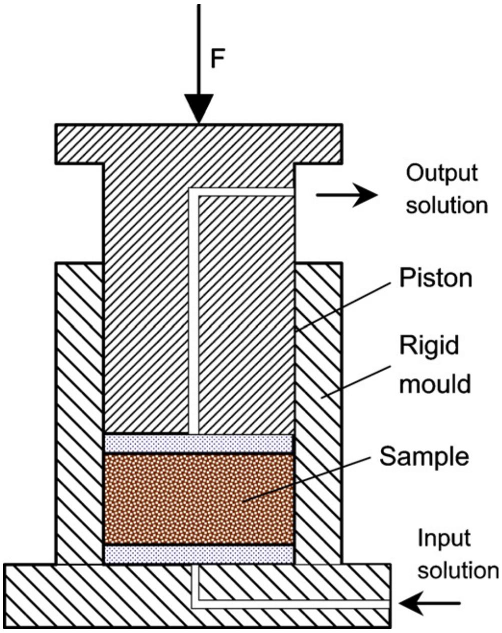

Fig. 1. Schematic representation of the experimental device.

2.2. Leaching tests

The tests were performed on raw soil samples prepared in two steps:

First step: The samples were compacted to the standard Proctor optimum water content and maximum density. For this material, the optimum moisture content and maximum density, determined according to the ASTM D698-91 standard [22], are 28.5% and 1.54 g/cm^3, respectively; they correspond to an initial void ratio of 0.82 and a degree of saturation of 89%. Due to the difficulty of obtaining homogenous specimens using the standard dynamic procedure, compaction was carried out in an oedometer (Fig. 1) under quasi-static conditions by means of a loading frame at the rate of 1 mm/min. After compaction, the dimensions of the specimen were 40 mm in diameter and 20 mm in height. The initial weight of the sample is 50 g.

Second step: The samples were hydrated in the compaction cell under the piston weight (10 kPa) following the AFNOR Standard XP P 94-091 [23]. Three solutions were used to saturate the specimens: (i) distilled water, (ii) a solution containing Zn^{2+} ions at 2.97 g/l (0.01 M) concentration, (iii) a solution containing Zn^{2+} ions at 297 g/l (1 M) concentration. The solutions were obtained by dissolving the $Zn(NO_3)_2$, $6H_2O$ (98%) salt (from Fluka®) in deionised water. The vertical deformation of the samples was recorded versus time and the samples were considered as saturated when the displacement of the piston became constant (less than 0.01 mm in 24 h).

Once the vertical strain was stabilized, the specimen was extracted from the mould; it was weighed and its volume was measured by immersion in a non-wetting liquid (kerdane), thus avoiding volume changes during the measurement. The sample was finally dried in an oven at 105 °C and weighted again to derive its void ratio (e).

The total swelling strain of the sample is calculated using this formula:

$$\varepsilon_v(\%) = \frac{e - e_0}{1 + e_0} 100$$

where e is the void ratio of the sample after the leaching test and e_0, the void ratio after compaction.

2.3. *Selective sequential extraction procedure*

Selective extraction of the metals was carried out to know the sites on which the metals were fixed. The extraction method was described by Yong and Phadungchewit [5], Yanful et al. [24], Tessier et al. [25] and Gupta and Chen [26]. The aim is to release the metals from the soil using the appropriate reagents permitting the selective destruction of the bonds between the metals and each constituent of the soil. For the selective sequential extraction tests, 1 g of soil is taken from the specimens after the permeability tests. The procedure is as follows:

Step 1: To release the metals fixed as exchangeable cations, 8 ml of 1 M potassium nitrate (KNO_3) are added to the soil specimen; the pH is adjusted to 7 using nitric acid, for this pH value, the KNO_3 is not expected to cause the dissolution of the soil. The samples are continuously shaken for 1 h at 20 °C.
Step 2: To release the metals fixed on calcite, 8 ml of 1 M sodium acetate (NaOAc) are added to the residue of the first step; the pH is adjusted to 5 using acetic acid (HOAc) and the suspensions are shaken for 5 h.
Step 3: To release the metals fixed on oxides and hydroxides, 20 ml of 0.04 M hydroxylamine hydrochloride (NH_2OH HCl) in 25% (v/v) acetic acid are added to the residue from the second step. This solution is capable of breaking the bonds between the metals and the amorphous and poorly crystallized Fe oxides without attacking either silicate minerals or the links between heavy metals and the organic matter. The samples are agitated for 6 h at 96 °C.
Step 4: To release the metal from the residual fraction: The residual fraction is composed of metal species strongly adsorbed on the soil mineral lattice. This fraction can be extracted by digestion. The residue of the previous step is digested with 5 ml of hydrofluoric acid (HF), 5 ml of aqua regia, which is a mixture of 60 ml of 5 M nitric acid (HNO_3) solution and 180 ml of hydrochloric acid (5 M HCl), and finally with 5 ml of hydrochloric acid (5 M, HCl).

Between the different steps, the suspension was passed through a 0.45 µm filter to assure the separation between the solid and liquid fractions. The remaining soil sample was washed twice with water whereas the supernatant was collected and analysed using a ICP-MS PerkinElmer 5000 spectrometer. The concentrations in metal of the solutions derived from ICP, expressed in mg/l, were then converted in mg per g of soil to highlight the retention capacity of the material. Each test was carried out on three identical specimens; the dispersion of the measurements is mentioned in the results.

Table 1
Comparison of the Tunisian soil properties with the Belgian guidelines for the building of anti pollution barriers [31].

	Guidelines for the building of anti-pollution barriers	Tunisian clay
Grain size distribution	2 µm >15% 60 µm > 30%	50% 30%
Percentage of swelling clay in the clay fraction	>10%	90%
CEC (meq/100 g of clay)	>30	60 (±5%)
Liquid limit (w_L) (%)	<80%	60% (±2%)
Plasticity index (I_p) (%)	$10\% < I_P < 40\%$	30% (± 3%)
Permeability (ms^{-1})	$<10^{-9}$	3.1×10^{-11} (± 12%)

3. Experimental results

3.1. *Geotechnical and physico-chemical characterization of the soil*

The percentage of grains smaller than 2 µm, derived from sedimentometry, is equal to 50%. The liquid and plastic limits are equal to 60% and 30%, respectively, which classify the material as a plastic clay with a large swelling potential according to Seed et al. [27], Dakshanamurphy and Raman [28], Williams and Donaldson [29] and Chen [30]. The permeability of the sample is 3.1×10^{-11} ms^{-1}. Marcoen et al. [31] has proposed a classification of clays presenting suitable properties to be used in a landfill barrier, based on plasticity index and liquid limit. According to these criteria, this soil appears to be suitable for a landfill barrier, as shown in Table 1.

The X-ray diffractogram of the clay sample shows a (0 0 1) reflection at 1.4 nm, corresponding to either Ca or Mg smectite [32]. The intense and fine peaks at 0.303, 0.289, 0.208 and 0.186 nm are characteristic of the carbonate; those at 0.340, 0.227, 0.191 and 0.159 nm are related to the quartz (Fig. 2). It results from the X-ray and chemical analyses that the soil is composed of 46% of smectite, with a beidellitic character, 22% of carbonate and 22% of quartz. The soil chemical composition shown in Table 2 indicates that the sample has a strong content in calcium, probably due to

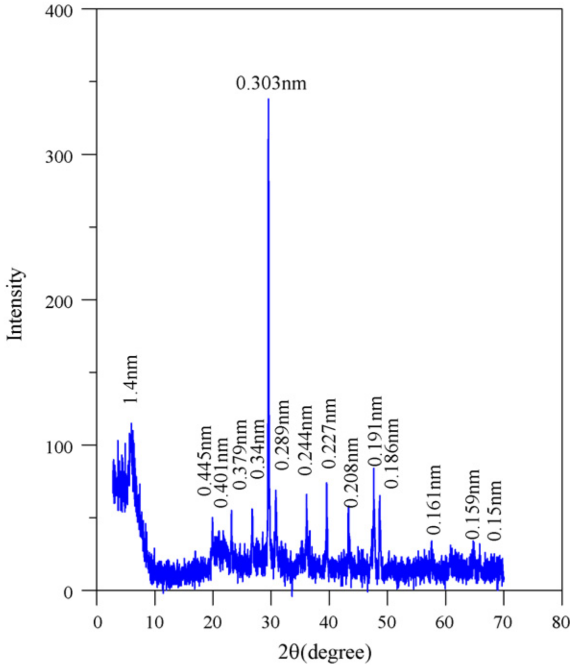

Fig. 2. X-ray diffractogram of the soil sample.

Table 2
Results of the chemical analysis of the Tunisian soil (the numbers between parentheses indicate the accuracy of the measurements).

Oxyde	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	Loss on ignition
Percentage	34.7 (<1%)	7.42 (<1%)	3.91 (<5%)	0.020 (<10%)	2.88 (<1%)	23.8 (<10%)	1.03 (<10%)	0.76 (<10%)	25.4 (<2%)

Table 3
Void ratios, cumulative pore volumes (in ml/g) and porosities (Φ%) of soil specimens measured by mercury intrusion tests after compaction and swelling.

		Void ratio	Inter-aggregate pore volume (pores > 1.5 μm)	Inter-particular pore volume (pores < 1.5 μm)
After compaction		0.82 (±0.02) (Φ = 45%)	0.038 (±0.02) (Φ = 42%)	0.052 (±0.02) (Φ = 58%)
After swelling	Water	1.31 (±0.02) (Φ = 57%)	0.147 (±0.02) (Φ = 41%)	0.216 (±0.02) (Φ = 58%)
	Zinc (2.97 g/l)	1.12 (±0.02) (Φ = 53%)	0.119 (±0.02) (Φ = 36%)	0.211 (±0.02) (Φ = 64%)
	Zinc (297 g/l)	1.20 (±0.02) (Φ = 55%)	0.089 (±0.02) (Φ = 69%)	0.038 (±0.02) (Φ = 31%)

the presence of calcite and calcium as exchangeable cations. The sample also presents a high iron content (about 5.2%).

The cation exchange capacity (CEC) is 60 meq/100 g (± 5%) of dried soil and the total surface specific area is equal to 270 m^2/g (± 5%). These small values, in comparison with those usually found for pure clays, are due to the presence of carbonate and quartz. In the presence of water, the pH of the soil is 7.5. At the zinc concentration of 2.97 g/l, the pH of soil is equal to 6.5. The increase in the metal concentration to 297 g/l reduces the pH to 4.

3.2. Swelling of the samples during the leaching test

In all the cases, saturation of the samples results in swelling, i.e. an increase in the void ratio of the samples (Table 3). During that phase, the void ratio of the sample wetted with water increases from 0.82 to 1.31, corresponding to an increase in porosity (Φ) from 45% to 57%. For the samples hydrated with the zinc solutions at the concentrations of 2.97 and 297 g/l, the void ratio increases from 0.82 (± 0.02) to 1.12 (± 0.02) (Φ = 53%) and 1.20 (± 0.02) (Φ = 55%), respectively. The sample hydrated with water presents a swelling strain of 27% whereas, when hydrated with the zinc solutions, the swelling strain decreases to 16% and 21%, for the concentrations of 2.97 and 297 g/l, respectively. It should be noticed that the largest reduction of the swelling strain is observed between water and the 2.97 g/l solution whereas swelling increases between 2.97 and 297 g/l. These results show that the swelling capacity of the soil depends on the presence of zinc and on its concentration.

The evolution of the swelling strain of the samples as a function of the square root of time is shown in Fig. 3. As usual, the curves present two domains: a first domain in which an important increase in the swelling strain occurs (primary swelling) and a second domain in which the swelling strain increases slowly and tends to stabilize (secondary swelling). pH and atomic absorption spectroscopy measurements carried out in the solution flowing out of the oedometer showed that the main changes in pH and zinc concentration occurred during primary swelling whereas these values remained nearly constant and equal to those of the input solutions in the secondary swelling phase. These measurements suggest that zinc adsorption mainly occurs during the first phase. Comparing the kinetics of infiltration, i.e. the slope of the three curves during primary swelling, shows that the highest infiltration rate is obtained with water and the lowest rate, with the zinc solution at the 2.97 g/l concentration.

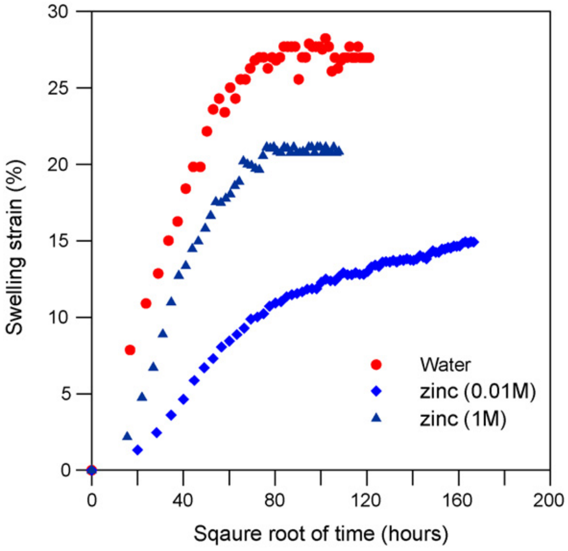

Fig. 3. Swelling strain versus square root of time during the wetting of the specimens by water or zinc solutions.

3.3. Characterization of the soil after the leaching tests

3.3.1. Retention of zinc derived from acid digestion and selective sequential extraction

The results of the selective sequential extraction (SSE) tests are shown in Fig. 4. The total amount of zinc extracted from the samples by selective sequential extraction is equal to 76.7 and 27.2 mg/g for the samples hydrated with the 2.97 and 297 g/l solutions, respectively. The total amount of zinc fixed in the soil was also measured by acid digestion and led to values of 82.6 mg/g and 29.4 mg/g for the two concentrations. The agreement between these values is good, with relative differences of 7.7% and 8.1% for the two concentrations. This, and similar results found by Cabral and Lefebvre [33] and Yong et al. [7]; partly confirm the validity of the method.

In the case of the sample hydrated with the 2.97 g/l zinc solution, the total retention of zinc is higher than in the case of the sample

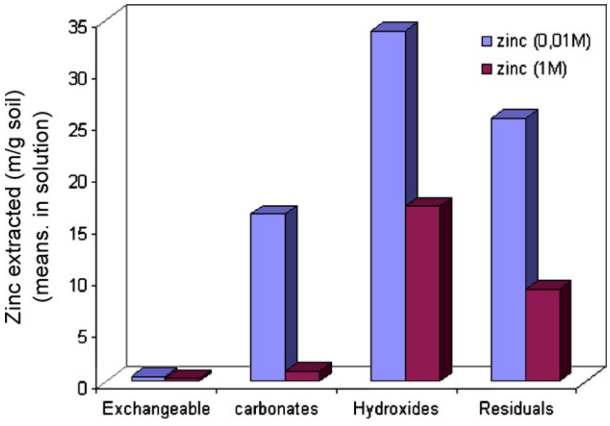

Fig. 4. Zinc extracted from soil sample using SSE.

hydrated with the 297 g/l solution. In pure clays, retention is usually related to the pH value. Indeed, many researchers (Bradbury and Bayens [34], Nasseem and Tahir [2], Kara et al. [35], Bradl [36] showed that the amount of heavy metals fixed on clays increases with the pH value. Considering the fact that the studied soil is a mixture of clay and carbonates, the retention mechanisms cannot be analysed without understanding the role of each constituent of the soil. In our study, the influence of each constituent will be analysed more closely by looking at the results of the SSE. Many authors agree that, when the soil presents an acidic pH (usually ≤ 4), the main absorption mechanism is cationic exchange; when the pH is basic, heavy metals precipitate with carbonates and hydroxides.

- For the sample saturated with the 2.97 g/l zinc solution, the pH remains relatively high (pH 6.5) and the quantity of metal adsorbed as exchangeable cations appears to be negligible, corresponding to 0.6% of the total amount of zinc extracted from the sample. This result means that the double layer effect observed by some authors in the case of pure clays does not play a significant role in this case [37–39]. Owing to these pH conditions, the quantity of zinc fixed on the carbonate is large (21.3% of the total amount extracted by SSE. The adsorption of zinc on the oxides/hydroxides is also important. Indeed, the SSE results show that 66% of the total amount of zinc fixed by the sample precipitates either with carbonates or oxides/hydroxides. These results confirm those of several authors working on carbonated clays who observed that a major amount of the heavy metals retained by the soil is fixed on the carbonates. At this concentration, the pH of the samples allows the formation of $ZnCO_3$ and $Zn(OH)_2$ precipitates [40–43].
- For the sample saturated with the 297 g/l zinc solution, the SSE results show that the metal is mainly adsorbed on the hydroxides, constituting 63% of the total zinc amount. As in the case of the 2.97 g/l solution, the quantity of zinc adsorbed as exchangeable cations is negligible (less than 1% of the total) whereas the amount of zinc fixed on the carbonates decreases dramatically, constituting only 3.6% of the total amount of zinc extracted from the sample. At this concentration, the pH of the soil suspension becomes very low (pH 4), which leads to the dissolution of carbonate. In order to confirm this result, additional measurements of the total carbonate content were carried out according to the procedure indicated in Section 2.1. The result shows that the amount of carbonate in the sample decreases from 22% in the initial state to 10%, confirming the dissolution of carbonate.

3.3.2. Porosity and pore size distribution derived from mercury intrusion porosimetry

The aim of this section is to evaluate the influence of the metals on the changes that occur in the pore size distribution during the leaching tests and to determine which pores were influenced by this process. To analyse the results of mercury intrusion porosimetry (MIP), Sala and Tessier [44] proposed to distinguish two families of pores: the inter-aggregate pores with diameters larger than 1.5 μm and the intra-aggregate or inter-particular pores with diameters smaller than 1.5 μm.

Comparison of the total cumulative pore volumes of the specimens submitted to leaching by water and zinc solutions with the pore volume of the compacted sample in the initial state shows an increase from the initial state value (0.090 ml/g) to 0.127 ml/g for the sample hydrated with the 297 g/l zinc solution, 0.330 ml/g for the sample hydrated with the 2.97 g/l solution and 0.363 ml/g for the sample hydrated with water (Fig. 5a). Table 3 shows the contributions of the inter-aggregate and inter-particular pores to the total pore volume measured by MIP. The main conclusion is that the contribution of the two pore families remains nearly unchanged in the case of water and the 2.97 g/l zinc solution, compared to the initial state, with approximately 60% of the total pore volume for the inter-particular pores and 40% for the inter-aggregate pores. This proportion is completely inverted in the case of the 297 g/l zinc solution as the proportion of inter-aggregate pores rises to 69% whereas that of inter-particular pores decreases to 31%.

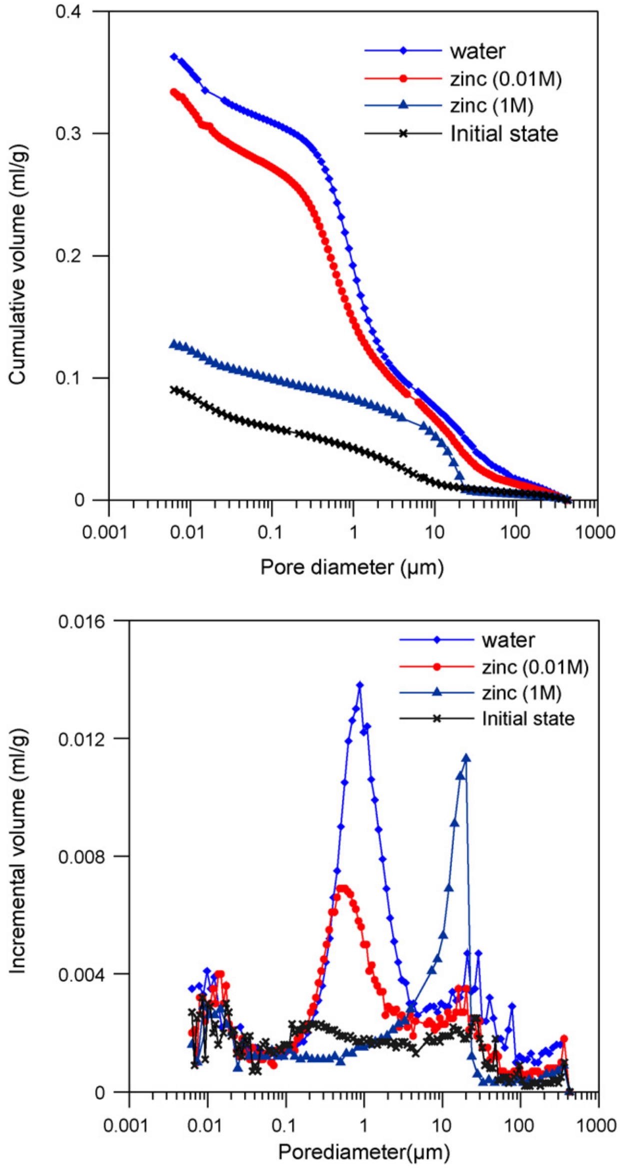

Fig. 5. MIP tests on soil specimens after leaching test: (a) cumulative volumes for specimens equilibrated with water and zinc solutions (2.97 and 297 g/l); (b) incremental volumes for specimens equilibrated with water and zinc solutions (2.97 and 297 g/l).

These differences in cumulative pore volumes are associated with significant differences in the pore diameters in the four cases (Fig. 5b). In the initial state, the sample presents two families of pores, the first one located around 10 μm and the second one around 0.2 μm. As expected, the swelling of the sample with water or with the zinc solutions modifies the size of the pores: Saturation with water increases the size of the inter-aggregate pores to 30 μm and that of the inter-particular pores to 1 μm. In the case of the 2.97 g/l zinc solution, the pore size distribution is similar to that with water, with slightly smaller diameters: 20 μm for the inter-aggregate pores and 0.7 μm for the inter-particular pores. The change is much more important in the case of the sample saturated with the 297 g/l zinc solution, where only inter-aggregate pores remain, with a mean diameter of 20 μm. Therefore, the MIP measurements confirm the deep change that happens between the specimens hydrated with the 2.97 g/l zinc solution, whose behaviour is grossly similar to that of those hydrated with water, and the behaviour of the specimens hydrated with the 297 g/l zinc solution, the latter presenting only inter-aggregate pores but with a small increase in total pore volume with respect to the initial state before saturation.

4. Discussion and conclusion

The following conclusions can be derived from this study:

- Hydration of the sample with zinc solutions results in a decrease in the swelling strain from 27%, when the sample is saturated with water to 16% and 21% when saturation is carried out with solutions containing zinc at 2.97 and 297 g/l concentrations, respectively.
- The total retention of zinc in the material derived from SSE and acid digestion decreases when the zinc concentration of the solution is increased. Selective sequential extraction (SSE) results show that, for the solution at the 2.97 g/l zinc concentration, zinc is mainly fixed on calcite and oxides–hydroxides. On the contrary, at the highest zinc concentration, the amount of zinc fixed on calcite becomes very small. In both cases, the quantity of zinc fixed as exchangeable cations is negligible.
- Mercury intrusion porosimetry shows that the swelling process is accompanied by an increase in the total pore volume and a reorganisation of the pore size distribution. An important observation is that the contribution of the inter-particular and inter-aggregate pores (60% and 40% of the pore volume, respectively) changes very little between the compacted samples and the samples hydrated with water and with the 2.97 g/l zinc solution, whereas the proportion changes significantly for the 297 g/l zinc solution. In that case, inter-particular pores represent 30% of the pore volume and inter-aggregate pores, 70%.

  By combining the results obtained by mercury intrusion porosimetry, pH measurements and selective sequential extraction, it appears that the swelling capacity is directly related to the adsorption mechanisms and to the pH value changes:
- For the sample saturated with the 2.97 g/l zinc solution, during the swelling process, the pH value decreases from 7.5 to 6.5. SSE results suggest that, under these conditions, zinc precipitates with carbonates and hydroxides. The formation of precipitates contributes to the obstruction of the pores and to the reduction of the inter-aggregate spaces and, as a consequence, leads to an increase in the contribution of the interparticular pores. The obstruction of the pores explains the lower swelling capacity of the sample compared to the sample saturated with water, as the free space available for water infiltration is reduced. This interpretation is also confirmed by the lower swelling rate.
- For the sample saturated with the 297 g/l zinc solution, the swelling capacity is higher than that of the less concentrated zinc solution. The pH of the soil falls to 4. The selective sequential extraction tests and carbonate content measurements highlight the effect of carbonate dissolution. This behaviour is at the origin of the widening of the pores and of the increase in the proportion of inter-aggregate pores. On the other hand, the dissolution of carbonate enhances the swelling phenomenon. Indeed, the carbonate plays a cementation role in the soil; its dissolution creates spaces between the clay particles and allows an increase in the swelling capacity.

References

[1] D.G. Strawn, N.E. Palmer, L.J. Furnare, C. Goodell, J.E. Amonette, R.K. Kukkadapu, Copper soption mechanismes on smectites, Clays Clay Miner 3 (2004) 321–333.

[2] R. Nassem, S.S. Tahir, Removal of Pb(II) from aqueous/acidic solutions by using bentonite as an adsorbent, Water Res. 16 (2001) 3982–3986.

[3] R.N. Yong, W.Z.W. Yaacob, S.P. Bentley, C. Harris, B.K. Tan, Partitioning of heavy metals on soil samples from column tests, Eng. Geol. 60 (2001) 307–322.

[4] R.A. Griffin, N.F. Shimp, J.D. Steele, R.R. Ruch, W.A. White, G.M. Hughes, Attenuation of pollutants in municipal landfill leachate by passage through clay, Environ. Sci. Technol. 10 (1976) 1262–1268.

[5] R.N. Yong, Y. Phadungchewit, pH influence on selectivity and retention of heavy metals in some clay soils, Can. Geotechnol. J. 30 (1993) 821–833.

[6] J.E. Maskall, I. Thornton, Chemical partitioning of heavy metals in soils. clays and rocks at historical lead smelting sites, Water Air Soil Pollution 108 (1998) 391–409.

[7] R.N. Yong, W.Z.W. Yaacob, S.P. Bentley, C. Harris, B.K. Tan, Portioning of heavy metals on soil samples from column tests, Eng. Geol. 60 (2001) 307–322.

[8] A.L. Lafuente, C. González, J.R. Quintana, A. Vázquez, A. Romero, Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region, Geoderma 145 (2008) 238–244.

[9] C.D. Shackelford, C.H. Benson, T. Katsumi, T.B. Edil, L. Linc, Evaluating the hydraulic conductivity of GCLs permeated with non-standard liquids, Geotextiles Geomembranes 18 (2000) 133–161.

[10] V.R. Ouhadi, R.N. Yong, M. Sedighi, Influence of heavy metal contaminants at variable pH regimes on rheological behaviour of bentonite, App. Clay Sci. 32 (2006) 217–231.

[11] A. Jullien, Proust Ch, L. Le Forestier, P. Baillif, Hydro-chemio-mechanical coupling effects on permeability and swell behaviour of a Ca smectite soaked Cu solutions, Appl. Clay Sci. 21 (2002) 143–153.

[12] AFNOR, Qualité des sols – Sols, sédiments - Mise en solution totale par attaque acide, AFNOR NF X 31 (1996) 147.

[13] F. Bergaya, M. Vayer, CEC of clays. Measurement by adsorption of a copper ethylenediamine complex, Appl. Clay Sci. 12 (1997) 275–280.

[14] J.P. Quirk, R.S. Murray, Appraisal of the ethylene glycol monoethyl ether method for measuring hydratable surface area of clays and soils, Soil Sci. Soc. Am. J. 63 (1999) 839–849.

[15] Standard NF P 94-048, 2003, Sols: Reconnaissance et Essais–Détermination de la teneur en calcite – Méthode du calcimètre. 2nd ed. January, AFNOR, Paris, 11p.

[16] D. Tessier, J. Berrier, Utilisation de la microscopie électronique à balayage dans l'étude des sols; Observations de sols humides soumis à différents pF, Sci. Sol. Bull. l'AFES. 1 (1979) 67–82.

[17] AFNOR, 2002, Qualité des sols – Détermination du pH. AFNOR NF ISO 10390.

[18] Standard NF P 94-051, Sols: Reconnaissance et Essais–Détermination des limites d'Atterberg–Limite de liquidité à la coupelle–limite de plasticité au rouleau. AFNOR, Paris, March 1993, 15 p.

[19] Standard NF P 94-057, Sols: Reconnaissance et Essais–Analyse granulométriques des sols–Méthode par sédimentation. May, AFNOR, Paris, May 1992, 17 p.

[20] Standard NF P 94-048, Sols: Reconnaissance et Essais–Détermination de la teneur en calcite–Méthode du calcimètre. 2nd ed., AFNOR, Paris, January 2003, 11 p.

[21] Standard ISO 17313, Qualité du sol. Détermination de la conductivité hydraulique de matériaux poreux saturés à l'aide d'un perméamètre à paroi flexible. AFNOR, Paris, July 2004, 22 p.

[22] A.S.T.M., Test Method for laboratory compaction characteristics of soil using standard effort (600 kNm/m3), Am. Soc. Test. Mater., D698-91, vol. 04–08, 1998.

[23] Standard XP P 94-091, Sols: Reconnaissance et Essais–Essais de gonflement à l'œdomètre – Détermination des déformations par chargement de plusieurs éprouvettes. AFNOR, December 1995, 13 p.

[24] E.K. Yanful, R.M. Quigley, H.W. Nesbitt, Heavy metals migration at a landfill site, Sarnia, Ontario, Canada -2: metal partitioning and geotechnical implications, Appl. Geochem. 3 (1988) 623–629.

[25] A. Tessier, P.G.C. Campbell, M. Bison, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–850.

[26] S.K. Gupta, K.Y. Chen, Partitioning of trace metals in selective chemical fractions of nearshore sediments, Enviro. Lett. 10 (1975) 129–158.

[27] M.B. Seed, R.J. Woodward, R. Lundgren, Prediction of swelling potential for compacted clays, J. Soil. Mech. Found Eng. Div. ASCE. 88 (1962) 107–131.

[28] V. Dakshanamurphy, V. Raman, A simple method of identifying an expansive soil, Soils Found 13 (1973) 97–104.

[29] A.B. Williams, G.W. Donaldson, Developments related to building on expansive soils in South Africa: 1973-1980, in: Proc. 4th Int. Conf. Expansive Soils, Denver, 2, 1980, pp. 834–844.

[30] F.H. Chen, Foundations on expansive soils Developments in Geotechnical Engineering, 54, Elsevier Publishing Co., Amsterdam, 1988.

[31] J.M. Marcoen, D. Tessier, J. Thorez, A. Monjoie, C. Schroeder, Manuel relatif aux matières naturelles pour barrières argileuses ouvragées pour C.E.T. (centres d'enfouissement technique) et réhabilitation de dépotoirs en Région Wallonne. Version 1, 2000, 14p.

[32] G. Brown, G.W. Brindley, X-ray procedures for clay mineral identification, in: G.W. Brindley, G. Brown (Eds.), Crystal Structures of Clay Minerals and their X-ray Identification, Monograph 5, Mineralogical Society, London, 1980, pp. 305–360.

[33] A.R. Cabral, I. Lefebvre, Use of sequential extraction in the study of heavy metal retention by silty soils, Water, Air, Soil Pollution 102 (1998) 329–344.

[34] M.H. Bradbury, B. Bayens, Modelling the sorption of Zn and Ni on Ca montmorillonite, Geochimica Cosmochimica Acta 63 (1999) 325–336.
[35] M. Kara, H. Yuzer, E. Sabah, M.S. Celik, Adsorption of cobalt from aqueous solutions onto sepiolite, Water Res. 37 (2003) 224–232.
[36] H.B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, J. Colloid interf. Sci. 277 (2004) 1–18.
[37] H. Farrah, W.F. Pickering, The sorption of zinc species by clay minerals, Aust. Chem. 29 (1976) 1649–1656.
[38] Y. Kitano, N. Kanamori, S. Yoshioka, Adsorption of zinc and copper on calcite and aragonite and its influence on the transformation of aragonite to calcite, Geochem. J. 10 (1976) 175–179.
[39] J.M. Zachara, J.A. Kittrick, J.B. Harsh, The mechanism of Zn adsorption on calcite, Geochim. Cosmochim. Acta 52 (1988) 2281–2291.
[40] S. Puppala, A.N. Alshawabkeh, Y.B. Acar, R. Gale, Enhanced electrokinetic remediation of high sorption capacity soils, J. Hazard. Mater. 55 (1997) 203–220.
[41] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation: critical overview, Sci. Total Environ. 289 (2002) 97–121.
[42] J.C. Echeverría, I. Zarranz, J. Estella, J.J. Garrido, Simultaneous effect of pH, temperature, ionic strength, and initial concentration on the retention of lead on illite, Appl. Clay Sci. 30 (2005) 103–115.
[43] D. Wenming, G. Zhijun, D. Jinzhou, Z. Liying, T. Zuyi, Sorption characteristics of Zn(II) by calcareous soil-radiotracer study, Appl. Radiat. Isot. 54 (2001) 371–375.
[44] G.H. Sala, D. Tessier, Importance de l'état énergétique de l'eau sur l'aptitude au tassement de matériaux argileux non saturés, CR Acad. Sci. Paris. 316 (1993) 231–236.