



HAL
open science

Effect of phosphatation and calcination on the environmental behaviour of sediments

Moussa Dia, R. Zentar, Nor Edine Abriak, Ange Nzihou, Guy Depelsenaire,
Alain Germeau

► **To cite this version:**

Moussa Dia, R. Zentar, Nor Edine Abriak, Ange Nzihou, Guy Depelsenaire, et al.. Effect of phosphatation and calcination on the environmental behaviour of sediments. *International Journal of Sediment Research*, 2019, 34, pp.486-495. 10.1016/j.ijsrc.2018.10.002 . hal-01942707

HAL Id: hal-01942707

<https://imt-mines-albi.hal.science/hal-01942707>

Submitted on 31 Jan 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of phosphatation and calcination on the environmental behaviour of sediments

Moussa Dia^{a,b}, Rachid Zentar^{a,*}, Nor-edine Abriak^a, Ange Nzihou^b, Guy Depelsenaire^c, Alain Germeau^d

^a Department of Civil & Environmental Engineering, 941 rue Charles Bourseul, BP 10838, 59508 Douai, France

^b Toulouse University, Mines Albi, CNRS, RAPSODEE Center, Campus Jarlard, F-81013 Albi cedex 09, France

^c SOLVAY SA, DCRT, rue de Ransbeek 310, B-1120 Bruxelles, Germany

^d PRAYON SA, rue J. Wauters, Engis, Belgium

A B S T R A C T

Dredging operations produce considerable quantities of materials, to be managed and this opens an opportunity for valorization in civil engineering. However, the contamination of the dredged sediments has become a major problem to solve. The major contaminants are heavy metals and organic compounds. This study focuses on the use of phosphoric acid (H_3PO_4) to stabilize heavy metals from sediments and destroy organic matter by calcination at 650 °C with a goal of using sediments in roadworks. Several studies have been conducted in this field. The stabilized materials obtained have been used in civil engineering. The main purpose of this work is to discuss the environmental behavior of marine sediment treated by phosphatation and calcination. Two types of phosphoric acids were used. The pH dependence leaching test has been used as the basic characterization to evaluate the effect of the type of phosphoric acid on the metals behavior in a valorization scenario. The standard leaching test and the Toxicity Characteristic Leaching Procedure (TCLP) were conducted as compliance tests. In regards of the obtained results, the environmental assessment has also shown a reduction in the availability of targeted heavy metals in alkaline environment whatever the type of acid used for treatment. This opens opportunities for co-valorization.

Keywords:

Polluted sediments

Heavy metals

Phosphatation

Calcination and environmental behaviour

1. Introduction

Dredging operations generate around 50 million tons of sediments every year in France (Alzieu, 1999). About 90% concern the maritime dredging. These materials could be used in civil engineering to address the limitations of available natural materials and in line with the sustainable development approach. The civil engineering sector uses more than 400 million tons of aggregates each year and about half of this amount is consumed in road sector (UNPG, 2013). However, in few situations, the pollution of sediments by industrial activities (Bartoli et al., 2012; Davutluoglu et al., 2011) is a major obstacle that prevents their utilization. The main pollutants in sediments are heavy metals (Darwish, 2013; Sakan et al., 2013) and organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (Hursthouse, 2001; Miller et al., 2004). In addition, the dredged sediments are not certified for use

in building and public works. During the last two decades, several studies have been conducted for the valorization of these materials in civil engineering with or without treatment (Achour et al., 2014; Ali et al., 2014; Wang et al., 2013; Zentar et al., 2008, 2009a, 2009b, 2012). In this context, the Novosol[®] process (Patent no 8246836, 2012) was developed by Solvay Company in order to treat the polluted sediments. This process is divided into two distinct phases. The first step consists of phosphate treatment by mixing raw sediment with phosphoric acid. This method is currently used to stabilize heavy metals by capturing them in a calcium phosphate matrix ($[Ca_{10}(PO_4)_6(OH)_2]$) (Kribi et al., 2012). The sediments are then dried to decrease water contents and allow their maturation since well-crystallized calcium phosphates have a more stable structure. The second step is a thermal treatment. It consists of calcination of the phosphated sediment at 650 °C in order to destroy the organic matter (PAHs and pesticides) (Ramaroson et al., 2009, 2012). This reduces the volume of processed materials after treatment and allows better stabilization of metal phosphates. Gas emission resulting from the treatment

* Corresponding author.

E-mail address: rachid.zentar@imt-lille-douai.fr (R. Zentar).

process (essentially H₂S and CO₂, traces of heavy metals and dust) are removed to comply with the European emission standards. A number of studies have already been performed on the effect of such treatment on the valorization of sediments in bricks (El Fgaier et al., 2013; Lafhaj et al., 2007, 2008; Mezencevova et al., 2012) mortar (Agostini et al., 2007), and road material (Duan et al., 2011; Nguyen, 2008; Tribout et al., 2011). However, as mentioned above, one type of phosphoric acid has been used in the studies. In this paper, the ability of Novosol[®] process to treat polluted sediments is applied using two types of phosphoric acid with various composition and origin. To understand the mechanisms induced by Novosol[®] in the depollution process, the study has been carried out on the raw sediment, the phosphated sediments (using the two different types of acids) and phosphated calcined sediments. In the first part of this work, chemical characterizations have been carried out to determine the main properties of the sediment. In the second part, the environmental behaviour of metals has been assessed by the pH dependence leaching test (XP CEN/TS 14429, 2006), the Toxicity Characteristic Leaching Procedure (TCLP) (EPA METHOD 1311, 1998) and the standard leaching test using demineralized water (NF EN 12457-2, 2002).

2. Materials, methods and experimental program

2.1. Materials

The studied sediment was dredged from Dunkirk harbor (north of France) in a region called Nord-Pas-de-Calais. The phosphatation has been done with two phosphoric acids. The first, called in the following A6, is a technical acid of Prayon. It contains 20% of phosphoric acid (H₃PO₄) and proportion of sulfuric acid (H₂SO₄). The A7 acid is a purified acid composed of 80% phosphoric acid. It is used in the Novosol[®] process presented in Fig. 1. The samples treated with the different types of acids are calcined for two hours. The environmental characterizations have been carried out on raw sediment, phosphated sediment with A6 and A7 acids and phosphated and calcined sediment. The studied samples according to the different treatments are presented in Table 1.

2.2. Method and Experimental program

The preparation of samples for the environmental characterization was conducted according to the French test standard NF ISO 114 64 (NF ISO 11464, 2006). It consists of drying the sediments at 40 °C until the water is completely evaporated and its mass is stable. This is followed by grinding and sieving at 2 mm. For the analyses requiring a mass lower than 2 g, the particle size was reduced to 250 µm. For the characterizations of the described

Table 1
Designation of samples according to different treatments.

Designation		
Acids (%H ₃ PO ₄)	A6 (20)	A7 (80)
Raw sediment	DB	
Phosphated sediment	DA6P	DA7P
Phosphated and calcined sediments	DA6C	DA7C

samples (Table 1), several tests were carried out. The crystalline phases were identified by X-ray diffraction measurements (XRD) with CuK α radiation generated at 40 mA, in the 3° < 2 θ < 60° range and at a scanning speed of 5°/min. The total contents of organic matter were determined via test standard NF EN 15169 (NF EN 15169, 2007) which consists in the measurement of loss on ignition at 550 °C. Regarding the chemical characteristics, the tests performed combine the measurement of the pH value in accordance with the test standard NF X 31-103 (NF X 31-103, 1988), the Carbon, Hydrogen, Nitrogen and Sulphur were obtained by NA 2100 Protein analyzer (CE instrument) and the metal concentration was determined according to the total digestion as proposed in the NF ISO 14869-1 (NF ISO 14869-1, 2001). A pretreatment is necessary for the samples containing organic components. A mass of 0.25 of the sample is introduced into a crucible and calcined at 450 °C for 3 h to reduce the risks associated with acid splashes due to the violent oxidation of organic matter. The solid residue is transferred to a PTFE tube then 5 ml of hydrofluoric acid (40%) and 1.5 ml of perchloric acid (75%) are added to the pretreated test portion. The mixture is heated using a hot plate until the dense fumes of perchloric acid cease. This step is followed by an addition of 3.5 ml of hydrochloric acid (38%) and 1.25 ml of nitric acid (65%). After heating to facilitate dissolution, the mixture is introduced into a 50 ml graduated flask and completed with demineralized water and mixed. The samples are then ready for analysis.

The approach taken to assess the environmental behavior of metals present in sediments is based on the prioritization defined by the CEN/TC 292 framework (Van der Sloot & Kosson, 2012) and the previous studies (Tribout et al., 2011). Since the pH is a key parameter to determine the mobility of pollutants, the pH dependence test is chosen as a principal characterization test. This test was used in several studies to assess the environmental behavior of pollutants present in waste (Van der Sloot & Kosson, 2012), recycled concrete (Engelsen et al., 2012) and contaminated soils and sediments (Cappuyns & Swennen, 2008). The test consists of maintaining the sample at a given pH by adding nitric acid or sodium hydroxide at a liquid to solid ratio (L/S) of 10 (l/kg) for 48 h. The suspensions were filtered throughout 0.45 µm and the filtrates were analyzed by ICP-AES. The acid neutralization

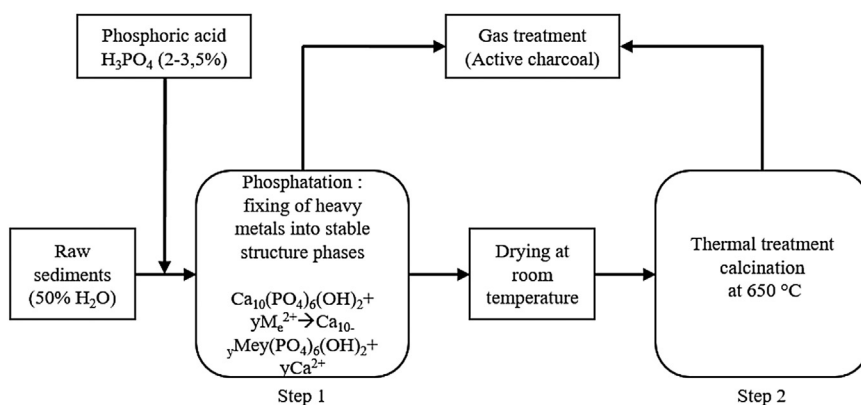


Fig. 1. Schematic representation of Novosol[®] process.

capacity (ANC) and the basic neutralization capacity (BNC) can be derived from the amount of acid or base used to reach a given pH.

The toxicity characteristic leaching procedure (TCLP) has been chosen as the first compliance test. This test uses the acid CH_3COOH . It is described in the United States Environmental Protection Agency Publication SW-846 (U.S EPA, 1998). The aggressive nature of acids will allow us to see the maximum release from sediments in extreme conditions. The extraction liquid depends on the alkalinity of the matrix studied. The pH of the extraction liquid employed is 2.88 ± 0.005 . Following the extraction, The sediments were extracted for $18 \text{ h} \pm 2 \text{ h}$ at liquid to solid ratio (L/S) of 20 (l/kg). Following the extraction, the liquid extract was separated from the solid phase by filtration through-out $0.45 \mu\text{m}$ and analyzed by ICP-AES.

French environmental characterization (NF EN 12457-2, 2002) has been selected as the second compliance test. This test is frequently used to assess the environmental impact of wastes by comparing the release of heavy metals with predetermined thresholds values (JORF no 0046, 2013). The test consists of contacting the waste material with demineralized water on a vertical rotary shaker. The sediments were subject to an agitation period of 48 h at room temperature at liquid to solid ratio (L/S) of 10(l/kg). Then the suspension was filtered at $0.45 \mu\text{m}$ and analyzed by ICP-AES.

3. Results and discussion

3.1. Mineralogical composition

The crystalline phases identified by XRD are presented in Figs. 2 and 3. For all sediments, the main minerals were Quartz (SiO_2) and Calcite (CaCO_3). These crystallized phases are commonly found in dredged sediments (Veerasingam et al., 2014).

Some minor phases were detected such as:

- Halite (NaCl),
- Pyrite (FeS_2),
- Muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F,OH})_2$),
- Illite ($(\text{K,H}_3\text{O})(\text{Al,Mg,Fe})_2(\text{Si,Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$),
- Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$),
- Montmorillonite ($(\text{Na, Ca})_{0.3}(\text{Al, Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$).

The clays such as Illite, Kaolinite and Montmorillonite were not detected for the treated sediments. The treatment had certainly changed the clay's structure. Phosphoric acid provokes

consolidation and stabilization of clay materials by agglomeration of the clay particles (Ghazali et al., 1991). Moreover, the X-ray diffraction has shown the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) for phosphated sediments with A6 Acid (DA6P). The A6 acid contains proportions of sulfuric acid and it has probably reacted with the calcium (from CaCO_3) to produce gypsum. This form has changed shape into Anhydrite (CaSO_4) during calcination. The low quantity of Anhydrite detected for the phosphated and calcined sediment (DA7C) is certainly related to the sulfate initially present in raw sediment (Nguyen, 2008).

3.2. Physicochemical characterizations

The results of organics, carbon, hydrogen, nitrogen and sulfur content and the pH value are summarized in Table 2. The amount of organic matter in the raw sediment is about 11%. For the phosphated sediments (DA6P, DA7P), organics content is on the same order of magnitude as the raw sediment. Hence, the phosphatation has no effect on the organics. After calcination, the amount of organics is close to zero. This confirms that the calcination has destroyed almost all organics. Indeed, it's known that thermal treatment at temperatures between $550 \text{ }^\circ\text{C}$ and $600 \text{ }^\circ\text{C}$ is sufficient to destroy more than 99% of organics (Ramaroson et al., 2008). For the total carbon hydrogen and nitrogen, the values are in the same order of magnitude for raw and phopsphated sediments. These values are close to zero after calcination. This is expected as these elements are related to the organics. However, the sulfur content is higher for the sediments phosphated with the A6 acid. After calcination, the pH of sediments increases to 11, which is probably due to the decarbonation of calcite which produces lime. This is in accordance with previous studies (Piantone et al., 2005; Tribout, 2010).

The major and minor elements determined by ICP-AES are presented in Figs. 4 and 5. The average composition is on the same order of magnitude for all materials except phosphorus and sulfur. This was expected because the treatment was carried out with phosphoric acid. The difference in sulfur content is in accordance with the XRD results. It can be related to the presence of sulfur in A6 Acid. After calcination, we can see a slight increase of the total content of heavy metals. This is due to the loss of mass related to the degradation of organics. The raw sediment is considered to be polluted if the concentration of heavy metals such as As, Cu, Pb and Zn, exceed the limits designated by French authorities (JORF no 0046, 2013). It should be noted that this analysis provides information on the pollution and not on the environmental behavior of

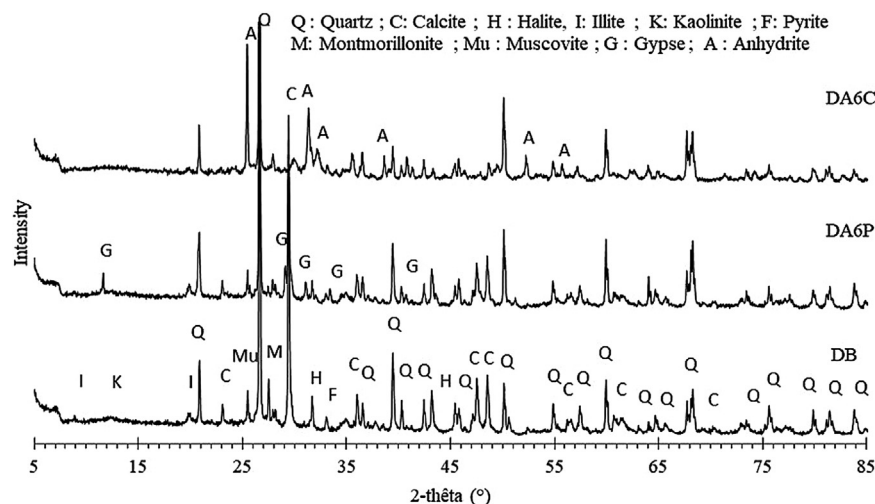


Fig. 2. X-ray diffractogram of raw sediment (DB), treated sediment with A6 acid (DA6P), and treated sediment with A6 acid then calcined (DA6C).

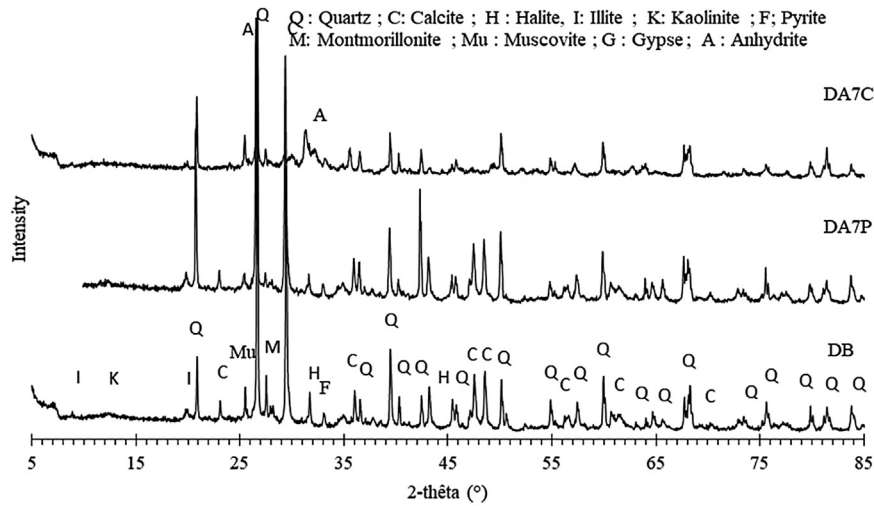


Fig. 3. X-ray diffractogram of raw sediment (DB), treated sediment with A7 acid (DA6P), and treated sediment with A7 acid then calcined (DA6C).

Table 2
Physicochemical properties of sediments.

Treatment	Sediments	O.M (%)	SD	C (%)	SD	H (%)	SD	N (%)	SD	S (%)	SD	pH	SD
Raw	DB	11.13	0.67	5.94	0.20	0.68	0.13	0.38	0.08	1.33	0.18	8.06	0.28
Phosphatation	DA6P	11.58	0.22	5.29	0.17	1.04	0.24	0.46	0.10	2.68	0.33	7.08	0.70
	DA7P	11.38	0.20	5.62	0.25	0.77	0.02	0.35	0.03	1.30	0.09	7.07	0.25
Calcination	DA6C	0.13	0.06	0.00	0.00	0.21	0.19	0.00	0.00	3.26	0.27	10.56	0.35
	DA7C	0.22	0.02	0.37	0.01	0.22	0.04	0.00	0.00	1.25	0.17	10.94	0.19

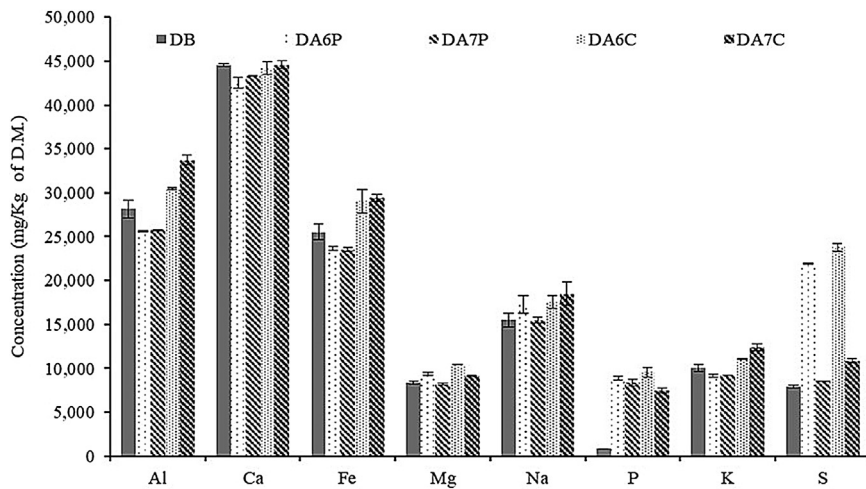


Fig. 4. Majors elements in the sediments.

sediments. N1 and N2 are thresholds fixed by French authorities for the immersion of dredged sediments. Below the N1 level, immersion is authorized while above these thresholds further study is needed. Immersion above the N2 level is prohibited. The units used in the graphs are in mg per kg of Dry Material (D.M.).

3.3. Environmental assessment

3.3.1. Acid-base neutralization capacity

The pH dependence test has been used to assess the behavior of sediments and metals under various pH. Figs. 6 and 7 present the curves of acid and base neutralization capacity of raw (DB) and treated sediments (DA6P, DA7P, DA6C and DA7C). The added acid or base are expressed in milliequivalents (meq) of the amount of

$H^+(OH^-)$ /g of dried sediments. The positive and negative milliequivalents correspond to acid and base added respectively. The presented curves reveal several phenomena. Firstly the interpretation of the acid-base neutralization curves will be carried out on the raw sediment then a comparative analysis will be undertaken for treated sediment.

3.3.1.1. Raw sediment (DB). As seen in the acid-base neutralization curve, the natural pH of the raw sediment (DB) determined in demineralized water is about 7.4. This is in line with the value from the pH measurement (see Table 2). Under this natural value, the presence of a plateau is observed. This is due to the carbonate dissolution which neutralizes acid according to the Eq. (1) and Eq. (2). The pH of the mixture is buffered until the carbonates are

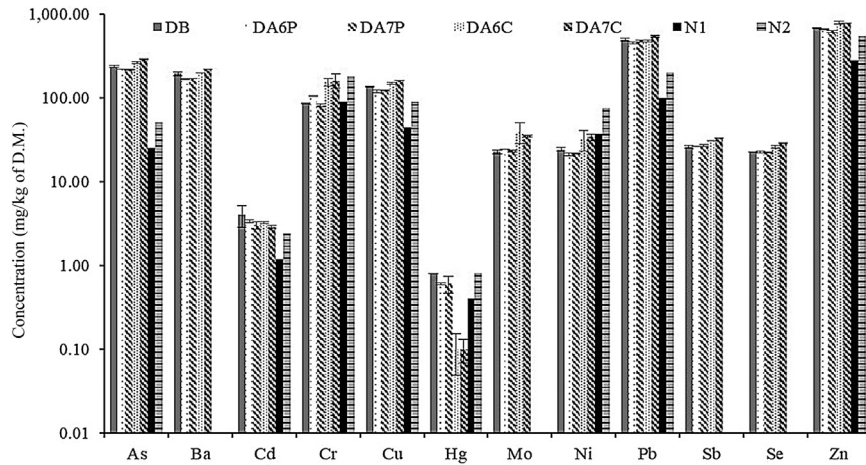


Fig. 5. Comparison of minor elements with thresholds in use by French authorities.

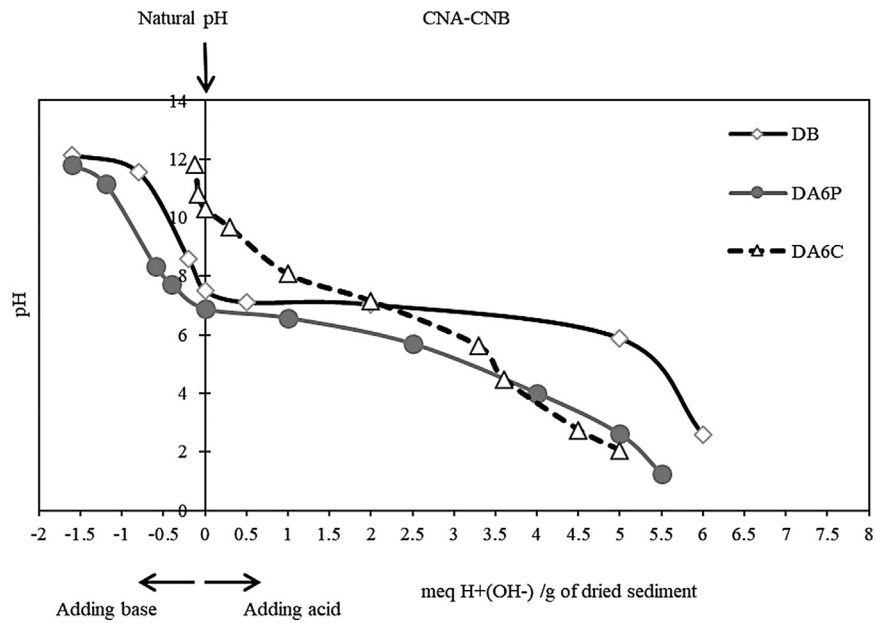


Fig. 6. A N C (acid neutralization capacity) for the sediments DB, DA6P and DA6C.

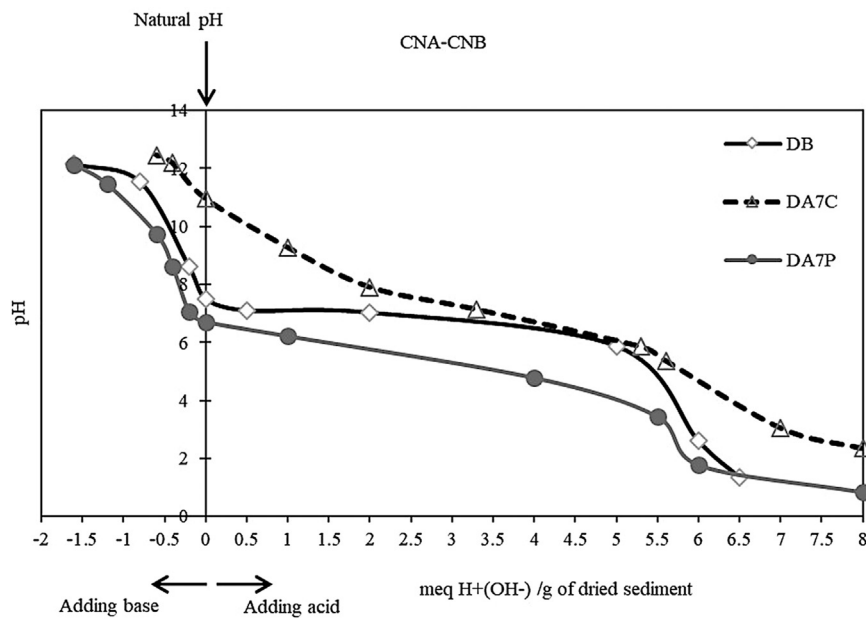
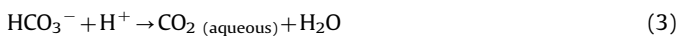


Fig. 7. A N C (acid neutralization capacity) for sediments DB, DA7P and DA7C.

completely consumed. Then the hydrogen carbonate ions react with the acid to form carbon dioxide which reduces the pH to 4 according to the Eq. (3). The sharp decrease in pH was observed after adding 5 meq H⁺/g of raw sediment. This means that a tone of sediment can neutralize 5 m³ of 1 mol/l acid. This corresponds to a high acid buffer capacity (Brons-Laot, 2002). Concerning the base added, we can see an increase in the alkaline values (pH ≈ 12) after adding 0.8 meq OH⁻/g of raw sediment. This shows that raw sediment has a low base neutralization capacity. This is beneficial for the treatment with the hydraulic binder.



3.3.1.2. *Raw sediment (DB) versus treated sediments (DA6P, DA7P, DA6C, DA7C).* By comparing the acid-base neutralization curve obtained for the raw sediment with those obtained from treated sediment with A6 Acid (DA6P, DA6C), we can see that the curves are more or less similar. However, we can observe that the curves are shifted along the y-axis. This shift is related to the difference between the initial pH of the sediments. Phosphatation led to a drop in pH due to the addition of acid while the calcination process increases the pH. This rise of the pH is due to the decarbonation of calcite which produces lime (Kribi, 2005). The pH values are respectively 6.9 and 10.3 for the sediments DA6P and DA6C. These values are close to those determined from the pH measurement (see Table 2). It can be seen that the acid buffer capacity of raw sediment is higher than that of treated sediments with A6 acid (DA6P and DA6C). This could be due to A6 acid reaction with the carbonates. This is confirmed by X-ray diffraction which revealed a small amount of calcite in the sediments DA6P and DA6C. In addition, the basic buffer capacity of the calcined sediment (DA6C) is even lower than that of the sediments DB and DA6P. The sediments treated with the A7 Acid (DA7P, DA7C) exhibit the same trend as the sediments treated with the A6 Acid (DA6C and DA7C) in term of the global rate in curves. The difference lies in the acid buffer capacity. The plateau of the sediment DA7P is between pH 7.6 and 4. Obviously, the A7 acid had consumed a part of carbonate but this reaction is susceptible to produce the phosphated calcium that is stable at pH lower than that

of calcite. Regarding the sediment DA7C curve, there is no observable plateau pH but the acid buffer capacity is the same as the raw sediment. In summary, the sediments DA6P and DA6C are more sensitive to the acid attack than the sediments DB, DA7P and DA7C. That should be not problematic for the use of sediments in basic environments such as cement matrix in general.

A simulation has been conducted using the United States Geological Survey public domain PHREEQC geochemical package in order to determine the pH zone of acid buffer capacity of calcite, calcium phosphate (hydroxyapatite) and gypsum. The results are illustrated in Fig. 8. We can see that the acid buffer capacity of calcite is reached at a pH higher than that of hydroxyapatite. It could be argued that the quantity of acid required to dissolve all of the hydroxyapatite is twice as much as calcite. In addition, we can see gypsum has a low acid buffer capacity. This may explain the reduction in acid buffer capacity for the sediment after treatment with A6 acid. These results are in line with those obtained by the pH dependence test and the study on acid buffer capacity of gypsum (Raii, 2012).

3.3.2. Chemical elements availability of metals

The availability of metal elements depends on the pH and their solubility. Only metal elements which greatly exceed the thresholds in use by Geode (GEODE, 2000) were selected. In Fig. 9 the pH-dependent release of As, Cu, Pb and Zn is shown. In general, these heavy metals present an amphoteric behavior. Their maximum release is achieved for the very acidic or alkaline pH. The latter affects the sorption of metals in soils directly or indirectly. The preferential sorption of hydrolyzed metal species governs the pH-dependent reaction of cationic metals. The concentration of hydrolyzed metal species increases with pH. In addition, adsorption sites in soils are pH-dependent, and the number of negative sites for cation sorption decreases with decreasing pH. Moreover, in an alkaline environment, metals can precipitate as oxides, hydroxides, carbonates and phosphates.

3.3.2.1. *Zinc.* The solubility of zinc as function of pH exhibits similar trends for all sediments. We can see that for a pH higher than 6, the release of zinc for raw sediment is higher than that of the treated sediments. The solubility at alkaline pH is 0.8% for the raw sediment (DB), 0.02% for the phosphated sediment (DA6P, DA7P) and 0.009% for the phosphated calcined sediment (DA6C, DA7C). The leaching of zinc at pH lower than 6 is similar for raw and phosphated sediments. The percentages are 53%, 50%, 54% for

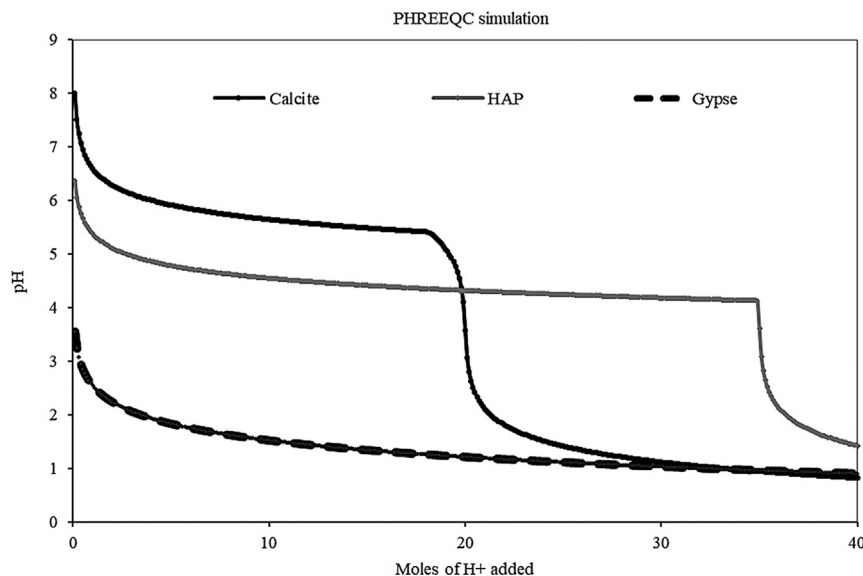


Fig. 8. Simulation by PHREEQC of acid buffer capacity of calcite, hydroxyapatite and gypsum.

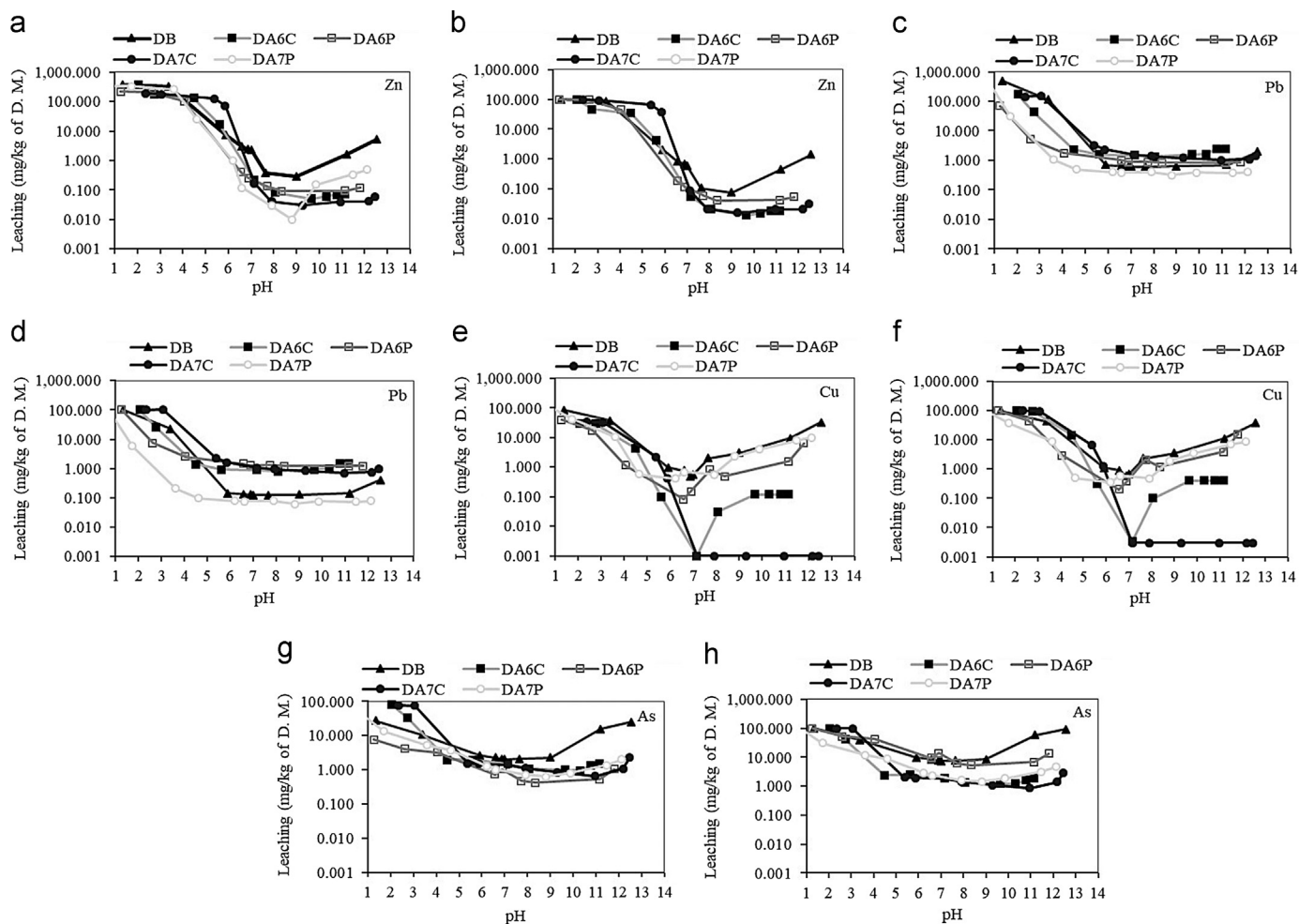


Fig. 9. pH dependent leaching of Zn, Pb, Cu and As, from sediments.

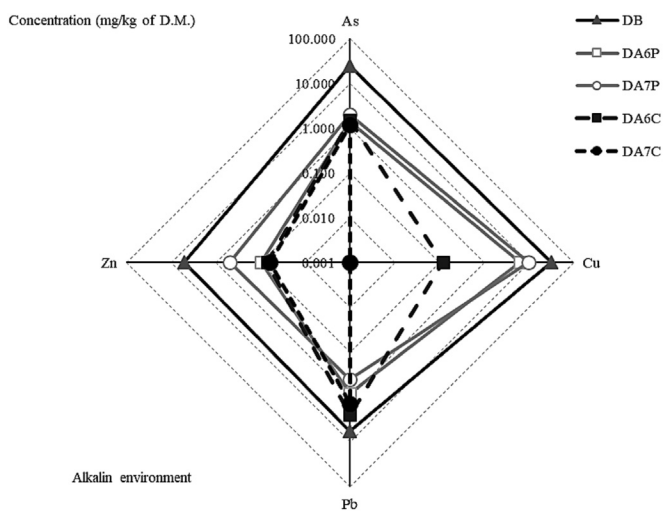


Fig. 10. Leachability of As, Cu, Pb, and Zn in very alkaline pH.

the sediments DB, DA6P and DA7P respectively. The release of calcined sediments is about 20%. This is in line with the previous studies on the sediments treated by Novosol[®] process. It has been shown that phosphatation does not stabilize zinc while calcination stabilizes it by capturing this metal in a silicate matrix (Kribi, 2005).

3.3.2.2. *Lead (Pb)*. In the case of lead, the release of treated sediments is less than the raw sediment. Several authors have highlighted the precipitation of hydroxypyromorphite ($Pb_5(PO_4)_3OH$) in the stabilization by phosphate in a polluted soil. The good stability of this phosphate may explain the decrease in lead leaching after phosphatation (Hettiarachchi et al., 2001). The decrease in the amount of lead in the residual fraction of sediments after calcination has also been shown (Kribi, 2005). The rates of lead release in the acidic pH were 98% for the raw sediment and 15%, 6%, 35% and 26% for the sediments DA6P, DA7P, DA6C, and DA7C respectively. The release for alkaline pH is about 1% for the raw sediment 0.5% for the phosphated sediments and 0.1% for the calcined sediments.

3.3.2.3. *Copper (Cu)*. For copper, the highest concentrations obtained at acidic pH values are 62% for raw sediment, 35% for the phosphated sediments and 20% for calcined sediments. After calcination and pH between 7 and 12 the copper leachability decreases to achieve a minimum of 0.08% for the sediment DA6C and values below the detection limit for the sediment DA7C. In the most alkaline pH the leached contents for the sediments DAB, DA6P, DA7P are 23%, 6% and 5% respectively. These results are consistent with the literature. Indeed it has been shown that the phosphatation induces the increase of the residual fraction of lead while calcination reduces more than 50% of the mobilisable fraction (Kribi, 2005).

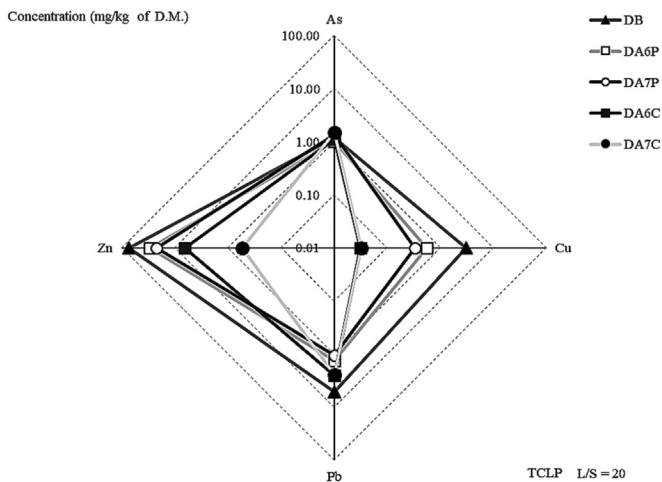


Fig. 11. Leachability of As, Cu, Pb and Zn in acidic environment (TCLP).

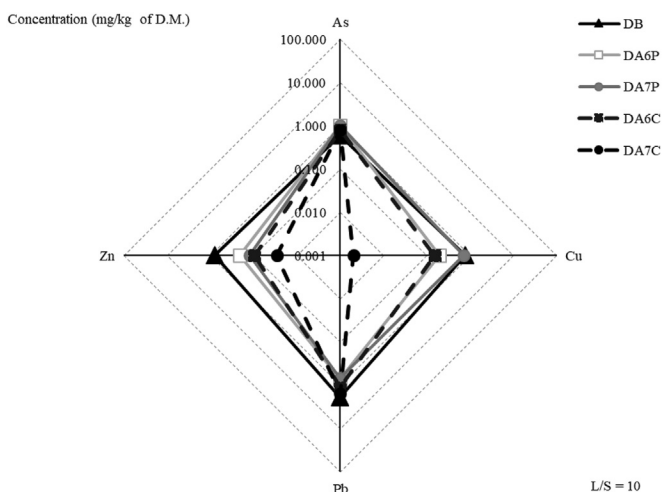


Fig. 12. Leachability of As, Cu, Pb and Zn in neutral environment.

3.3.2.4. *Arsenic (As)*. The leachability curve of arsenic shows that the concentration of arsenic for raw sediment (DB) at neutral pH is lower than the treated sediments (DA6P, DA7P, DA6C and DA7C). It has been shown for soils that the addition of phosphoric acid causes a slight increase in the mobilized fraction of arsenic (Theodoratos et al., 2002). The hypothesis of chemical similarity between arsenate and phosphate ions has been used to explain this phenomenon. Indeed the partial substitution of phosphate by arsenate causes the formation of soluble salt as $Pb_2(AsO_4)Cl$. Moreover, in the most acidic pH, the leachability of this metal is on the same order of magnitude as raw sediment (6%) and phosphated sediment (12%). However, the extraction yield of arsenic at very alkaline pH is about 10% for raw sediment and 0.5% for treated sediments.

Leachability of As, Cu, Pb, and Zn in very alkaline pH corresponding to the future environment of sediment is illustrated in Fig. 10. This diagram, established from pH dependence tests shows that the release of heavy metals from raw sediment is higher than that of treated sediments. This could be due to stabilization of metals in the phosphate matrix for treated sediment and dissolution of organic matter complexed to the heavy metals for raw sediment. Indeed the dissolved organic carbon is composed of organic species such as sugars, organic acids lignin, amino acids, humic acids and fulvic acids. For the sediments, humic and fulvic acids control the binding of heavy metals. Fulvic acids are soluble in the acidic and basic medium while humic acids only dissolve in an alkaline environment. Generally, the solubility of dissolved organic carbon increases with increasing pH (Cappuyens & Swennen, 2008). This can explain the release of heavy metal in alkaline environments. But metals with no organic matter (zinc, lead and others) can also dissolve at high pH values, as zincate or $[Pb(OH)_4]^{2-}$. Binding to organic matter is best evaluated according to a Tessier like speciation test.

3.3.2.5. *Toxicity characteristic leaching procedure*. The leachability of As, Cu, Pb and Zn obtained by TCLP is presented in Fig. 11. This diagram shows that the highest release is observed with the raw sediment. The highest reduction in availability is that of Zn which

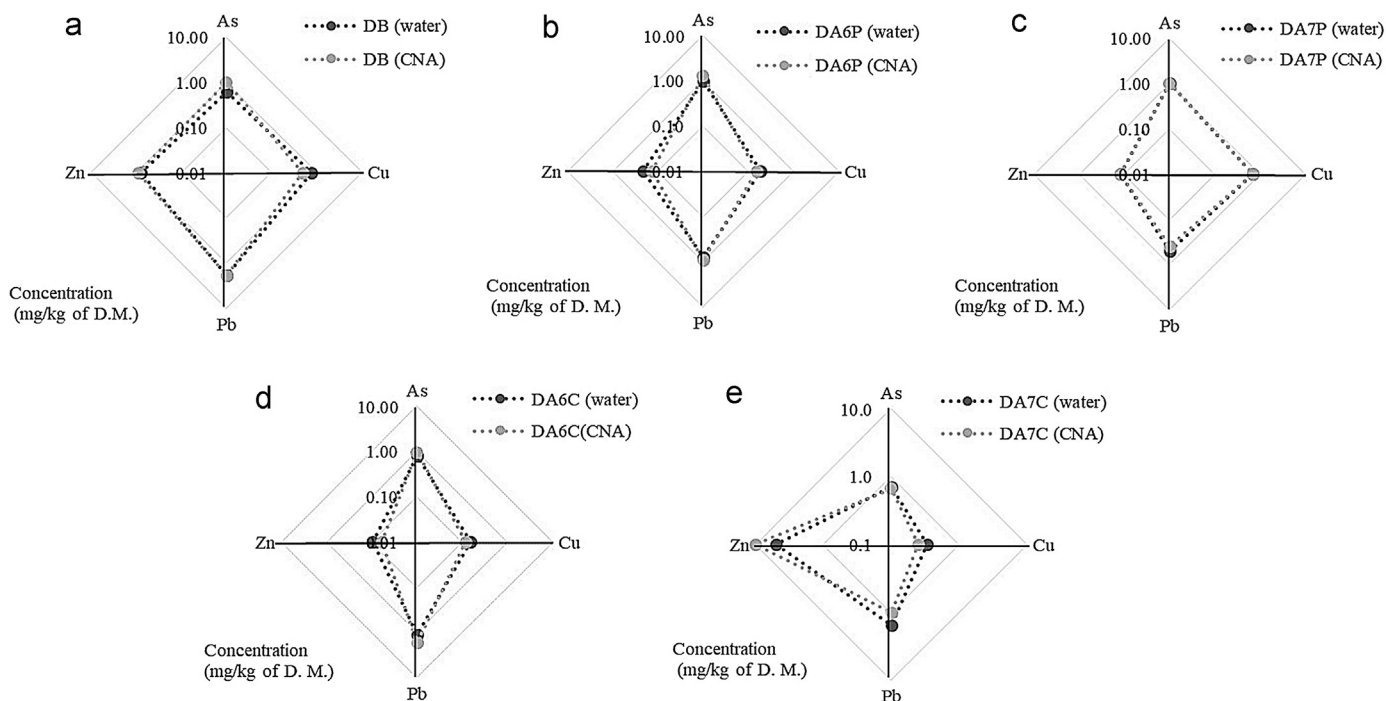


Fig. 13. Comparison of the pH dependence test with leaching test using water.

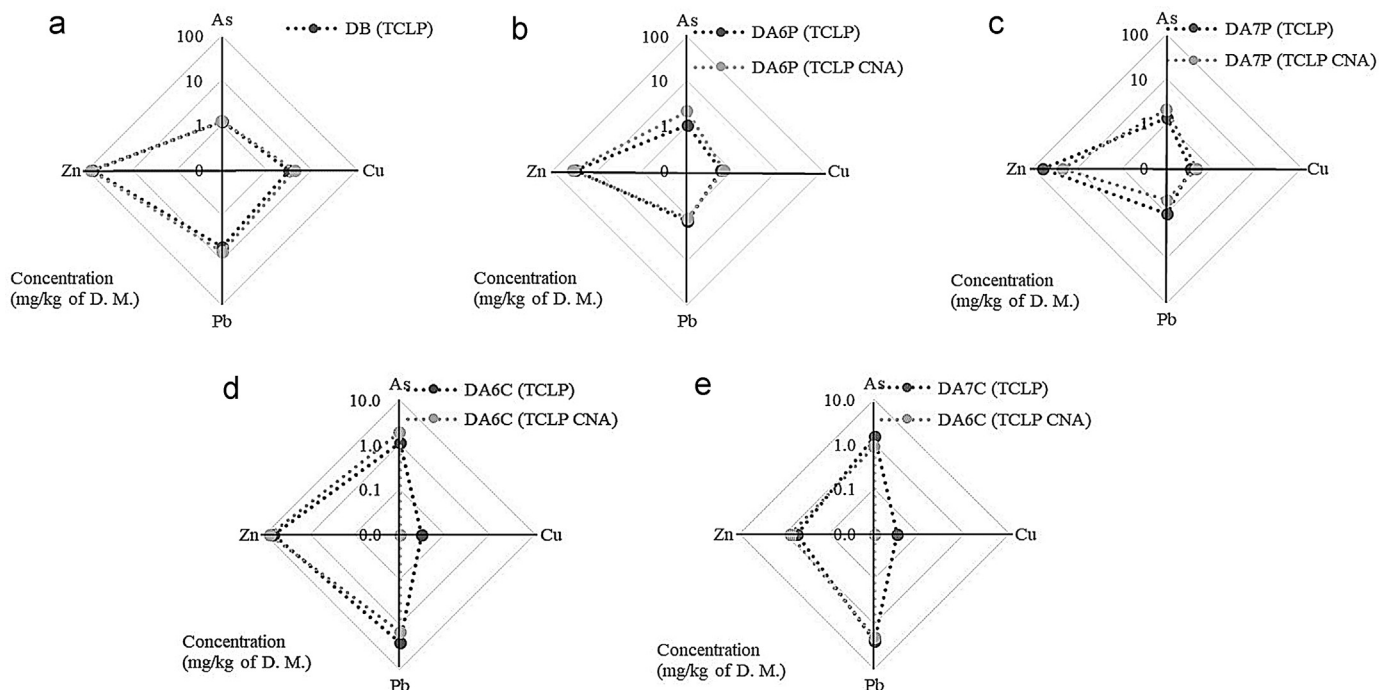


Fig. 14. Comparison of the pH dependence test with TCLP.

is a major pollutant in the studied sediments. This demonstrates the stability of heavy metals after treatment in acidic environment except for As, which has the same leachability for all materials.

3.3.2.6. *Leaching test using water (NF EN 12457-2)*. The availability of As, Cu, Pb and Zn obtained by leaching test using water is presented in Fig. 12. We can see that the concentrations of Cu, Pb and Zn leached from raw sediment (DB) are higher than those of treated sediments (DA6P, DA7P, DA6C and DA7C) and especially phosphated calcined sediments. Concerning As, its release is little lower for raw sediment than treated sediment. The reasons underlying this trend were confirmed previously by the pH dependence test.

3.3.2.7. *Comparison of the pH dependence test with TCLP and leaching test using water (Figs. 13 and 14)*. The environmental assessment of sediments was carried out with the pH dependence test, the TCLP and the leaching test using demineralized water. It is essential to note that we can account for the difference between the results due to inequality of the liquid to the solid ratio by expressing the results in mg/kg of Dry Material (D. M.). The results of the pH dependence test with TCLP and leaching test using demineralized water are presented in Fig. 11. There is no doubt in the compliance of data whatever considered element. We can, therefore, find the results of TCLP and the leaching test using demineralized water from the pH dependence test. This shows that the pH dependence is important because it allows finding many of the routine testing results. Therefore the amount of testing can be reduced by choosing tests in line with that proposed by CEN TC 292 while getting a thorough knowledge of the waste (Figs. 13 and 14).

4. Conclusions and prospects

The methodology adopted has allowed us to understand the mechanisms of heavy metals release and to predict the behaviour of sediments in different scenarios. The pH dependence test was

used as a basic characterization test as the pH is an important parameter for the heavy metals availability. This test has shown that the acid buffer capacity of raw sediment and treated sediment with A7 acid is higher than that of the sediments treated with the A6 acid. Also, it should not be a problem to use sediments in basic environments such as cementitious materials. The simulation conducted by PHREEQC showed that calcium phosphate has a good stability only down to pH 4. This test has also shown a reduction in the availability of targeted heavy metals in alkaline environments such as a future matrix of sediment for any type of acid. Two compliance tests have been performed with the goal to confirm the results obtained by the pH dependence test in accordance with the hierarchy established by European community for harmonization of leaching/extraction tests and standardization in relation to the use of alternative materials in construction. The agreement between these tests has been demonstrated. This will provide the release of pollutants while optimizing the number of tests. Furthermore, it was clearly shown that the acids types selected for this work with a different level of purity gave equivalent results in term of stabilization of targeted heavy metals in dredged sediments. This finding is important as it demonstrates the robustness of the treatment process of dredged sediment and the cost-effectiveness of treated sediments. The next step of this work is to study the effect of treatment on the mechanical characteristics of dredged materials in relation with their valorization in civil engineering works.

Acknowledgements

The authors would like to thank Solvay Company and Prayon for the financial support for this research.

References

Achour, R., Abriak, N.-E., Zentar, R., Rivard, P., & Gregoire, P. (2014). Valorization of unauthorized sea disposal dredged sediments as a road foundation material.

- Environmental Technology*, 35(16), 1997–2007. <http://dx.doi.org/10.1080/09593330.2014.889758>.
- Agostini, F., Skoczylas, F., & Lafhaj, Z. (2007). About a possible valorisation in cementitious materials of polluted sediments after treatment. *Cement and Concrete Composites*, 29(4), 270–278. <http://dx.doi.org/10.1016/j.cemconcomp.2006.11.012>.
- Ali, I. B. H., Lafhaj, Z., Bouassida, M., & Said, I. (2014). Characterization of Tunisian marine sediments in Rades and Gabes harbors. *International Journal of Sediment Research*, 29(3), 391–401. [http://dx.doi.org/10.1016/S1001-6279\(14\)60053-6](http://dx.doi.org/10.1016/S1001-6279(14)60053-6).
- Alzieu, C. (1999). Dragages et environnement marin: état des connaissances = Dredging and marine environment: state of the art. Retrieved from (<http://www.vliz.be/imis/imis.php?Module=ref&refid=17902>).
- Bartoli, G., Papa, S., Sagnella, E., & Fioretto, A. (2012). Heavy metal content in sediments along the Calore river: Relationships with physical–chemical characteristics. *Journal of Environmental Management*, 95(Supplement(0)), S9–S14. <http://dx.doi.org/10.1016/j.jenvman.2011.02.013>.
- Brons-Laot, G. (2002). *Evaluation environnementale de la valorisation de mâchefers d'incinération d'ordures ménagères en remplissage de carrière (Doctoral dissertation)*. France: INSA Lyon.
- Cappuyens, V., & Swennen, R. (2008). The application of pHstat leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials. *Journal of Hazardous Materials*, 158(1), 185–195. <http://dx.doi.org/10.1016/j.jhazmat.2008.01.058>.
- Darwish, M. A. G. (2013). Geochemistry of the High Dam Lake sediments, south Egypt: Implications for environmental significance. *International Journal of Sediment Research*, 28(4), 544–559. [http://dx.doi.org/10.1016/S1001-6279\(14\)60012-3](http://dx.doi.org/10.1016/S1001-6279(14)60012-3).
- Davutluoglu, O. I., Seckin, G., Ersu, C. B., Yilmaz, T., & Sari, B. (2011). Heavy metal content and distribution in surface sediments of the Seyhan River, Turkey. *Journal of Environmental Management*, 92(9), 2250–2259. <http://dx.doi.org/10.1016/j.jenvman.2011.04.013>.
- Duan, Z., Lafhaj, Z., Ali, I., & Duceillier, S. (2011). Valorization of stabilized river sediments in self compacting Materials. *Geo-Frontiers 2011* (pp. 1355–1364) American Society of Civil Engineers. (<http://ascelibrary.org/doi/abs/10.1061/41165%28397%29139>).
- El Fgaier, F., Lafhaj, Z., & Chapiseau, C. (2013). Use of clay bricks incorporating treated river sediments in a demonstrative building: Case study. *Construction and Building Materials*, 48, 160–165. <http://dx.doi.org/10.1016/j.conbuildmat.2013.06.030>.
- Engelsen, C. J., Wibetoe, G., van der Sloot, H. A., Lund, W., & Petkovic, G. (2012). Field site leaching from recycled concrete aggregates applied as sub-base material in road construction. *Science of The Total Environment*, 427–428, 86–97. <http://dx.doi.org/10.1016/j.scitotenv.2012.04.021>.
- EPA METHOD 1311 (1998). *Toxicity characteristic leaching procedure, SW-846: Test method for evaluating solid waste - physical/chemical methods*.
- GEODE (2000). A. du 14 juin 2000 (JO du 10 A. 2000) relatif aux niveaux de référence à prendre en compte lors d'une analyse de sédiments marins ou estuariens présent en milieu naturel ou portuaire.
- Ghazali, F. M., Baghdadi, Z. A., & Khan, A. M. (1991). Overconsolidated behavior of phosphoric acid and lime-stabilized kaolin clay. *Transportation Research Record*, (1295). Retrieved from (<http://trid.trb.org/view.aspx?id=359116>).
- Hettiarachchi, G. M., Pierzynski, G. M., & Ransom, M. D. (2001). In situ stabilization of soil lead using phosphorus. *Journal of Environment Quality*, 30(4), 1214. <http://dx.doi.org/10.2134/jeq.2001.3041214x>.
- Hursthouse, A. S. (2001). The relevance of speciation in the remediation of soils and sediments contaminated by metallic elements—an overview and examples from Central Scotland, UK. *Journal of Environmental Monitoring*, 3(1), 49–60.
- JORF no 0046 (2013). Arrêté du 8 février 2013 complémentaire à l'arrêté du 9 août 2006 relatif aux niveaux à prendre en compte lors d'une analyse de rejets dans les eaux de surface ou de sédiments marins, estuariens ou extraits de cours d'eau ou canaux relevant respectivement des rubriques 2.2.3.0, 3.2.1.0 et 4.1.3.0 de la nomenclature annexée à l'article R. 214–1 du code de l'environnement. Retrieved from (<http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT00002709733&dateTexte=&categorieLien=id>).
- Kribi, S. (2005). *Décomposition des matières organiques et stabilisation des métaux lourds dans les sédiments de dragage (Doctoral dissertation)*. France: INSA Lyon.
- Kribi, S., Ramarosan, J., Nzihou, A., Sharrock, P., & Depelseinaire, G. (2012). Laboratory scale study of an industrial phosphate and thermal treatment for polluted dredged sediments. *International Journal of Sediment Research*, 27(4), 538–546. [http://dx.doi.org/10.1016/S1001-6279\(13\)60011-6](http://dx.doi.org/10.1016/S1001-6279(13)60011-6).
- Lafhaj, Z., Saliceto, A., Laurent, C. S., Coudray, Y., Huynh, T. T., Le, G. B., & Anguoni, F. (2007). The use of the Novosol process for the treatment of polluted marine sediment. *Journal of Hazardous Materials*, 148, 606–612. <http://dx.doi.org/10.1016/j.jhazmat.2007.03.029>.
- Lafhaj, Z., Samara, M., Agostini, F., Boucard, L., Skoczylas, F., & Depelseinaire, G. (2008). Polluted river sediments from the North region of France: Treatment with Novosol® process and valorization in clay bricks. *Construction and Building Materials*, 22(5), 755–762. <http://dx.doi.org/10.1016/j.conbuildmat.2007.01.023>.
- Mezencevova, A., Yeboah, N. N., Burns, S. E., Kahn, L. F., & Kurtis, K. E. (2012). Utilization of Savannah Harbor river sediment as the primary raw material in production of fired brick. *Journal of Environmental Management*, 113(0), 128–136. <http://dx.doi.org/10.1016/j.jenvman.2012.08.030>.
- Miller, J., Hudson-Edwards, K., Lechler, P., Preston, D., & Macklin, M. (2004). Heavy metal contamination of water, soil and produce within riverine communities of the Rio Pilcomayo basin, Bolivia. *Science of The Total Environment*, 320(2–3), 189–209. <http://dx.doi.org/10.1016/j.scitotenv.2003.08.011>.
- NF EN 12457-2 (2002). Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: one stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).
- NF EN 15169 (2007). *Characterization of waste - Determination of loss on ignition in waste, sludge and sediments*.
- NF ISO 11464 (2006). *Soil quality - Pretreatment of samples for physico-chemical analysis*.
- NF ISO 14869-1 (2001). *Soil quality - Dissolution for the determination of total element contents - Part 1: dissolution with hydrofluoric and perchloric acids*.
- NF X 31-103 (1988). Soils quality. Determination of ph-value in H₂O. Electrometric method.
- Nguyen, T.B. (2008). *Valorisation des sédiments de dragage traités par le procédé NOVOSOL(R) dans des matériaux d'assises de chaussée: comportement mécanique et environnemental (Doctoral dissertation)*. Retrieved from (<http://www.theses.fr/2008T0U30338>).
- Patent no 8246836 (2012). Process for treating substances contaminated by heavy metals, 8/21/2012, Solvay.
- Piantone, P., Bodéan, F., & Lassin, A. (2005). *Evaluation environnementale de sédiments phosphatés et calcinés (Rapport d'avancement (Projet DEMOROUTE) No. BRGM/RC-54355-FR)*.
- Raii, M. (2012). *Formulation, caractérisation et mise en œuvre des barrières perméables réactives à base de phosphate de calcium, utilisation pour la fixation de polluants (Doctoral dissertation)*. Retrieved from (<http://jethesis.inp-toulouse.fr/archive/00002325/>).
- Ramarosan, J., Dia, M., Dirion, J.-L., Nzihou, A., & Depelseinaire, G. (2012). Thermal treatment of dredged sediment in a rotary kiln: Investigation of structural changes. *Industrial Engineering Chemistry Research*, 51(21), 7146–7152. <http://dx.doi.org/10.1021/ie203023k>.
- Ramarosan, J., Dirion, J.-L., Nzihou, A., & Depelseinaire, G. (2009). Characterization and kinetics of surface area reduction during the calcination of dredged sediments. *Powder Technology*, 190(1–2), 59–64. <http://dx.doi.org/10.1016/j.powtec.2008.04.094>.
- Ramarosan, J., Dirion, J.-L., Nzihou, A., Sharrock, P., & Depelseinaire, G. (2008). Calcination of dredged sediments: investigation of the behaviour of heavy metals and the organic compounds. *High Temperature Materials and Processes*, 27(5), <http://dx.doi.org/10.1515/HTMP.2008.27.5.327>.
- Sakan, S. M., Sakan, N. M., & Dordevic, D. S. (2013). Trace element study in Tisa River and Danube alluvial sediment in Serbia. *International Journal of Sediment*, 28, 234–245. [http://dx.doi.org/10.1016/S1001-6279\(13\)60034-60037](http://dx.doi.org/10.1016/S1001-6279(13)60034-60037).
- Theodoratos, P., Papassiopi, N., & Xenidis, A. (2002). Evaluation of monobasic calcium phosphate for the immobilization of heavy metals in contaminated soils from Lavrion. *Journal of Hazardous Materials*, 94(2), 135–146.
- Tribout, C. (2010 November 10). *Valorisation de sédiments traités en techniques routières: contribution à la mise en place d'un protocole d'acceptabilité*. (Doctoral dissertation) Université Toulouse III - Paul Sabatier. Retrieved from (<http://thesups.ups-tlse.fr/1277/>).
- Tribout, C., Husson, B., & Nzihou, A. (2011). Use of treated dredged sediments as road base materials: environmental assessment. *Waste and Biomass Valorization*, 2(3), 337–346. <http://dx.doi.org/10.1007/s12649-1011>.
- UNPG (2013). *Union nationale des productions de granulats*. Retrieved from (<http://www.unpg.fr>).
- Van der Sloot, H. A., & Kosson, D. S. (2012). Use of characterisation leaching tests and associated modelling tools in assessing the hazardous nature of wastes. *Journal of Hazardous Materials*, 207–208, 36–43. <http://dx.doi.org/10.1016/j.jhazmat.2011.03.119>.
- Veerasingam, S., Venkatchalapathy, R., & Ramkumar, T. (2014). Distribution of clay minerals in marine sediments off Chennai, Bay of Bengal, India: Indicators of sediment sources and transport processes. *International Journal of Sediment Research*, 29(1), 11–23. [http://dx.doi.org/10.1016/S1001-6279\(14\)60018-4](http://dx.doi.org/10.1016/S1001-6279(14)60018-4).
- Wang, D., Abriak, N. E., & Zentar, R. (2013). Strength and deformation properties of Dunkirk marine sediments solidified with cement, lime and fly ash. *Engineering Geology*, 166, 90–99. <http://dx.doi.org/10.1016/j.enggeo.2013.09.007>.
- XP CEN/TS 14429 (2006). *Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with initial acid/base addition*.
- Zentar, R., Abriak, N.-E., & Dubois, V. (2009b). Fall cone test to characterize shear strength of organic sediments. *Journal of Geotechnical and Geoenvironmental Engineering*, 135(Issue 1), [http://dx.doi.org/10.1061/\(ASCE\)1090-0241\(2009\)135:1\(153\)](http://dx.doi.org/10.1061/(ASCE)1090-0241(2009)135:1(153)).
- Zentar, R., Abriak, N.-E., Dubois, V., & Miraoui, M. (2009a). Beneficial use of dredged sediments in public works. *Environmental Technology*, 30(8), 841–847. <http://dx.doi.org/10.1080/09593330902990139>.
- Zentar, R., Dubois, V., & Abriak, N. E. (2008). Mechanical behaviour and environmental impacts of a test road built with marine dredged sediments. *Resources, Conservation and Recycling*, 52(6), 947–954. <http://dx.doi.org/10.1016/j.resconrec.2008.02.002>.
- Zentar, R., Wang, D., Abriak, N. E., Benzerzour, M., & Chen, W. (2012). Utilization of siliceous-aluminous fly ash and cement for solidification of marine sediments. *Construction and Building Materials*, 35(0), 856–863. <http://dx.doi.org/10.1016/j.conbuildmat.2012.04.024>.