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Effect of chemical and thermal treatment on the geotechnical properties of dredged sediment

M. Dia^{a, b*}, J. Ramaroson^a, A. Nzihou^a, R. Zentar^b, N.E. Abriak^b, G. Depelsenaire^c, A. Germeau^d

^a Université de Toulouse, Mines Albi, CNRS, Centre RAPSODEE, Campus Jarlard, F-81013 Albi cedex 09, France.

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

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

^d PRAYON SA, rue J. Wauters Engis Belgium

Abstract

Dredging of sediments is necessary in order to maintain maritime activities and for flood prevention. However the increased industrial activities are causing accumulation of pollutants in the sediments. The main contaminants are heavy metals and organic compounds. Because of the cost of storage, treatment and valorization can be economically sound. This study focuses on the technology to treat heavy metals from dredged sediments using phosphoric acid (H₃PO₄) (the Novosol® process developed by Solvay company) with a goal to stabilize heavy metals by capturing them in calcium phosphate matrix and to destroy organic matter by calcination at 650°C. Several studies have been conducted in this field. The stabilized materials obtained have been used in civil engineering. However these studies have never assessed the effect of the composition of the phosphoric acid on the treatment. In this paper the effect of two types of phosphoric acids with various composition and origins were compared. The investigation focuses on the effect of the phosphoric acids on the environmental behavior of metals and on the geotechnical properties of the dredged sediment.

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1. Introduction

Harbors, rivers and lakes require ongoing dredging to maintain the navigability and for flood prevention. These dredging operations generate a considerable quantity of sediments which is close 50 million tonnes per year in France for marine sediments (1). The dredging materials open an opportunity to valorization in civil engineering. However a large proportion of dredged sediments is considered as polluted with heavy metals (As, Pb, Cr, Cd, Zn and Cu.) and organic compounds (such as PAHs) (2) according to the thresholds in use by French authorities (3). Due to the cost of storage, treatment and recovery can be an economic issue. That is why the Novosol® process (patent n° EP 1341 728 B1) was developed by Solvay Company in order to treat the sediments. This process is a combination of physicochemical (heavy metal stabilization) (4) and thermal treatment (degradation of organic matter) (5).

* Corresponding author. Tel.: +33563493240; fax.: +33563493243

E-mail address: jocelyn.ramaroson@mines-albi.fr; moussa.dia@mines-albi.fr

A number of studies have already been performed on the effect of such treatment on the valorization of sediments in bricks (6), mortars (7), and road materials (8). In this paper the study is carried out on the effect of the phosphoric acid composition on the physicochemical characteristics and on the geotechnical behavior of sediments.

2. Materials and methods

The marine sediment used in this study was dredged from Dunkirk harbor (north of France) in region called Nord-Pas-de-Calais. The different treatments defined in this work were performed by Solvay. The phosphatation has been carried out using the 2 phosphoric acids. The A6 is a technical acid of Prayon. It contains 20% phosphoric acid (H_3PO_4) and proportion of sulfuric acids. The A7 acid is a purified acid composed of 80% phosphoric acid. It is typically used in the Novosol[®] process presented in Fig.1. The phosphatation with each type of acid, in accordance with the Novosol[®] process, is followed by 650° C calcinations for 2 hours. Characterizations have been carried out to determine the main properties of the raw and treated sediments (raw sediment, 2 phosphated, 2 phosphated and calcined). The acids and sediments that were studied are presented in Table 1.

Table 1.Designation of material characterised in this work

Acids (% H_3PO_4)	A7(80)	A6(20)
Raw sediment	DB	
Phosphated sediments	DA7P	DA6P
Phosphated and calcined sediments	DA7C	DA6C

The methods used are standard. The water content is obtained by drying at 40°C and 105°C in accordance with standard NF P 94050. Before any measurement the sediments are mixed for homogenization. In order to determine their characteristics, the French standard AFNOR (NF ISO 114 64) method was used. It consists of drying the sediment 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 2g, the particle size must be reduced at 250 μm . All the samples for the physicochemical analyses were prepared according to this method. For the characterizations several tests were carried out.

For the physical characterizations several analyses were conducted. The total contents of organic matter were determined via standard NF EN 15169 (Determination of loss on ignition in waste, sludge and sediments). The sample is heated in a furnace up to (550°C \pm 25°C). The difference in mass before and after heating is used to calculate the loss on ignition. The true density was determined by a helium pycnometer (MICROMETRICS, accupy 1330). The specific surface area of the samples was carried out using nitrogen adsorption with BET method (MICROMETRICS Gemini Vacprep 061). The particle-size distribution was determinate using a laser granulometry (Coulter LS 230) in accordance with NF ISO 13320-1. The methylene blue value was determined in accordance with the standard NF P 94 068. The liquid limit (w_L) of sediments which is the water content at which a soil changes from plastic to liquid behavior was measured by a percussion-cup method. The plastic limit (w_P), which represents the limit between the plastic state and solid state, was determined by the rolling test method. Then the plasticity index that determines the plasticity of soil was obtained by the difference between the limit liquid and the plastic limit.

Regarding the mineralogical and chemical characteristics, the following tests were performed. X-ray diffraction measurements (XRD) were carried out with $\text{CuK}\alpha$ radiation generated at 40 mA, in the $3^\circ < 2\theta < 60^\circ$ range and at a scanning speed of 5°/min. The pH values were measured in accordance with standard NF X 31-103. The Carbon, Hydrogen, Nitrogen and Sulphur were obtained by NA 2100 Protein analyzer (CE instrument). The metal concentration was determined according to the total digestion as proposed in the NF X 31 151 followed by the dissolution of the solid with 50 ml of distilled water.

To explore the effect of type of acids and treatment on the compaction and the ability of the studied sediments to be used as base-course material, the modified proctor compaction test in combination with I-CBR were used to determine the optimal water content which corresponds to the maximum dry density according to the standard NF P 94-093.

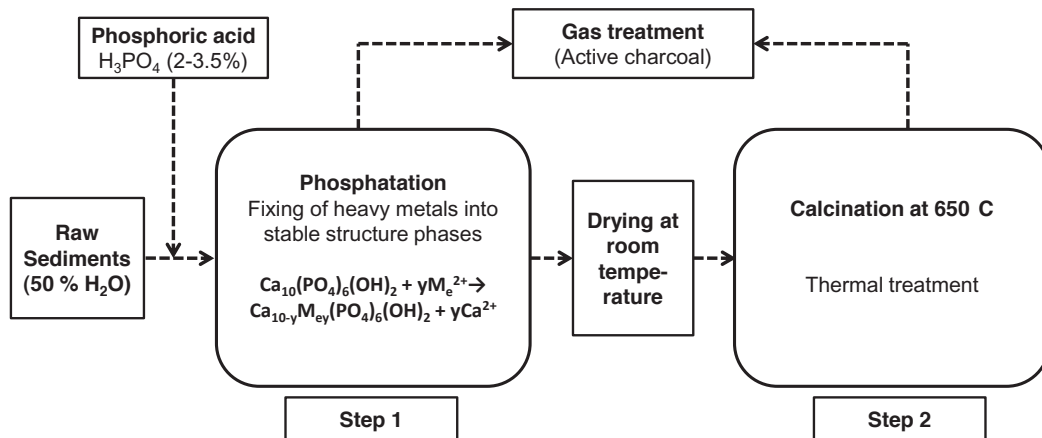


Fig. 1. Schematic representation of the Novosol® process

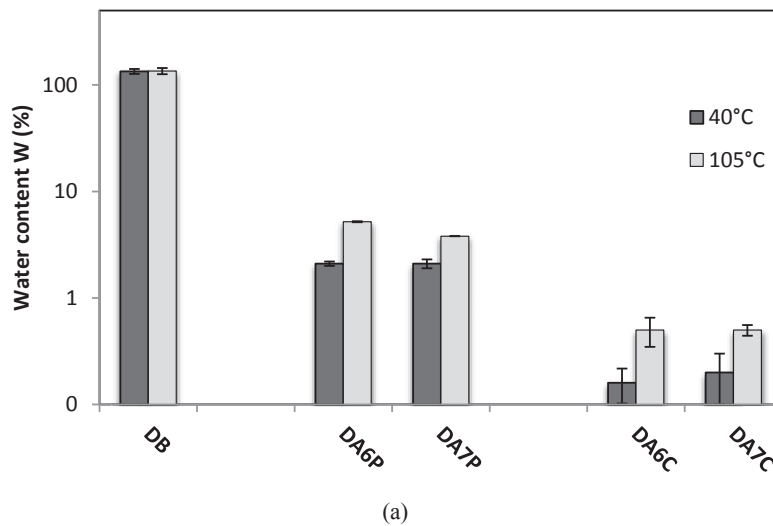
3. Results and discussion

3.1. Physical characteristics

Water and organics contents are presented in Fig.2

Initial water content is very useful data before treatment and characterization. The values obtained by drying at 105°C are slightly higher than those obtained at 40°C. This is probably due to the presence of volatile organic substances that degrade between 40 °C and 105 °C. The assumption of residual water can also be advanced. We can also observe that the step of phosphatation has considerably reduced the amount of water in the sediment (135 to 5%). The water contents of the calcined sediment are close to zero. This can be explained by the fact that moisture (from ambient air) is absorbed by sediments. This removal of water is advantageous, since its presence is an obstacle for the sediment's transport and valorization.

The amount of organic matter in the raw and phosphated sediment is around 10%. We can see that the phosphatation has no effect on the organic matter content. According to the minimum standard in use by the technical guide road (9) the sediments can be considered as high organics. After calcination the organics are also close to zero. These results are aligned with the values of water content. The difference is mainly due to the absorption of moisture (of ambient air) by sediment.



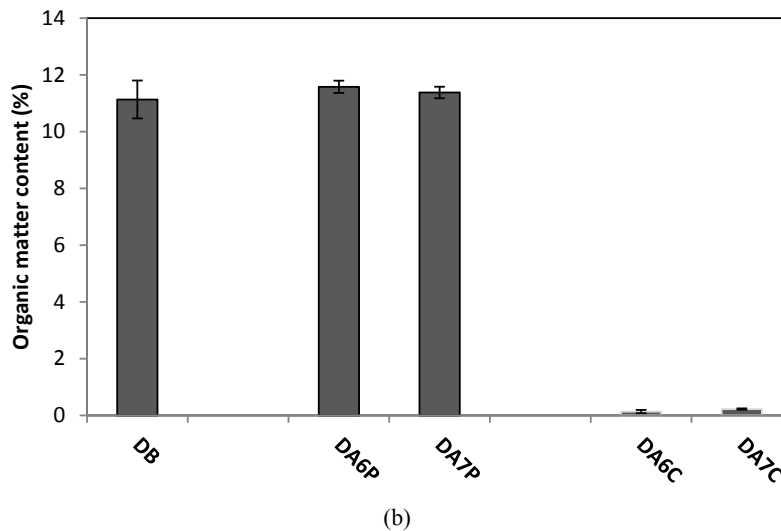
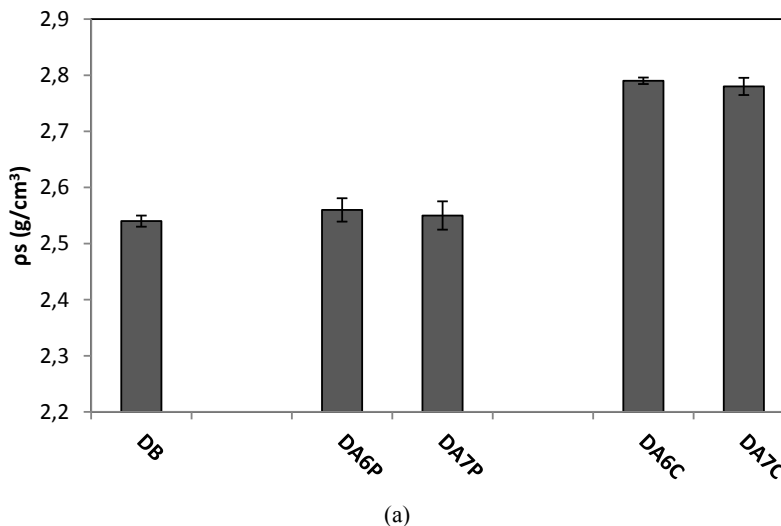


Fig. 2. (a) Initial water content of sediments (b) Organic matter content of sediments

The absolute densities of raw and phosphated sediments (DB, DA6P, and DA7P) are of the same order of magnitude. We can observe that the densities increase after calcination. This might be related to the degradation of organic matter. The remaining mineral phase is denser than the amorphous compounds. After calcination, all the sediments' densities are in the same range and comparable to those of inorganic sand. The phosphatation did not have any effect on the sediment density.

For the specific surface area we can observe the same tendency in terms of density for the raw and phosphated sediments (DB, DA6P, and DA7P). After calcination we can see a decrease in the specific surface area. This trend was also observed by Ramaroson (5). This could be explained by the total organic degradation which has a high specific surface area and the sintering of phosphate mineral matrices well known in the literature at temperatures higher than 600°C (10).



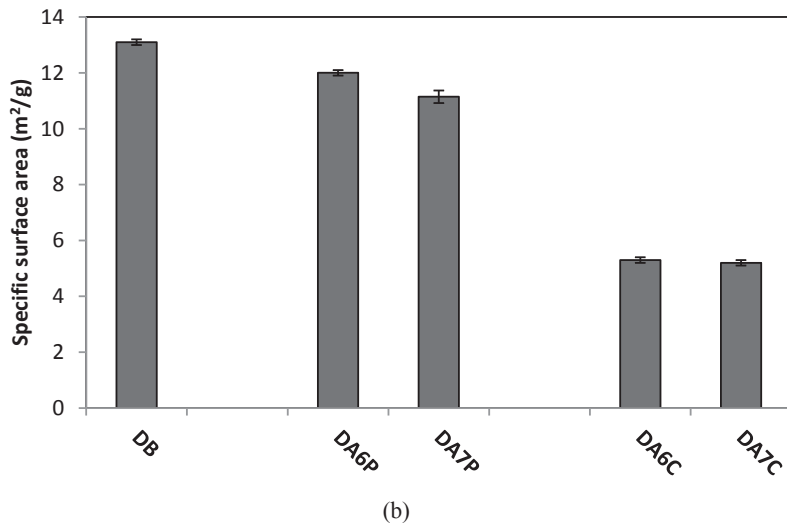


Fig. 3. (a) True density of sediments (b) Specific surface area of sediments

The grain size of sediments is highly variable. Their texture can vary from clay to block. The gradation of all the samples presented in Fig.4 are distributed between 0.4 μm and 1000 μm . Granulometric tests conducted on raw (DB) and treated sediments (DA6P, DA7P, DA6C, DA7C) show that there is no significant change in the shape of the granulometric distribution curves and the all sediments are relatively close. We noticed that the sediments are mainly composed of silt and sand around 50 and 40% respectively. Clay fraction represents approximately 10-15 %. The treatment (phosphatation and calcination) has no effect on the size distribution of sediments. The previous works (5) have shown that the calcination had no effect on the size distribution of two sediments up to a temperature of 700°C.

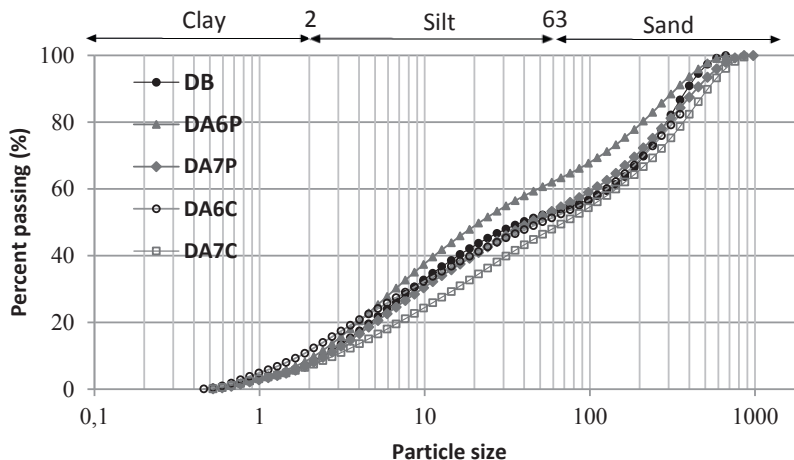


Fig.4. Granulometric distribution of the sediments

The methylene blue value measured for the raw sediment is 3.2 g/100g of D.M. According to the guide road (9), the raw sediment can be considered as a clay-loam soil with a high water absorption capacity. After phosphatation we can observe the decrease in this value. It went to around 0.7-0.9 g/100g of D.M. This is due to the addition of phosphoric acid. Acids were frequently used as chemical processing agent for soil stabilization (11). It can agglomerate the clay particles. For the calcined sediments the methylene blue value is close to zero. We can conclude that calcination destroys the clays in the sediment.

The consistency limits for raw sediments are 82% for the liquid limit (W_L) and 38% for the plastic limit (W_P). This induces a plasticity index of 44%. After phosphatation we can see a decrease in the liquidity limit. It is 55% and 58% for DA6P and DA7P respectively. We can also observe an insignificant increase in the plastic limit. The values are 45 % for DA6P and 50% for DA7P. These variations have resulted in the decrease of the plasticity index to around 10%. This confirms that the acid treatment significantly reduces the plasticity of the sediment. The Atterberg limits could not be measured for the calcined sediments. This is certainly related to the degradation of organics and clays. This confirms that the calcined materials are not plastic.

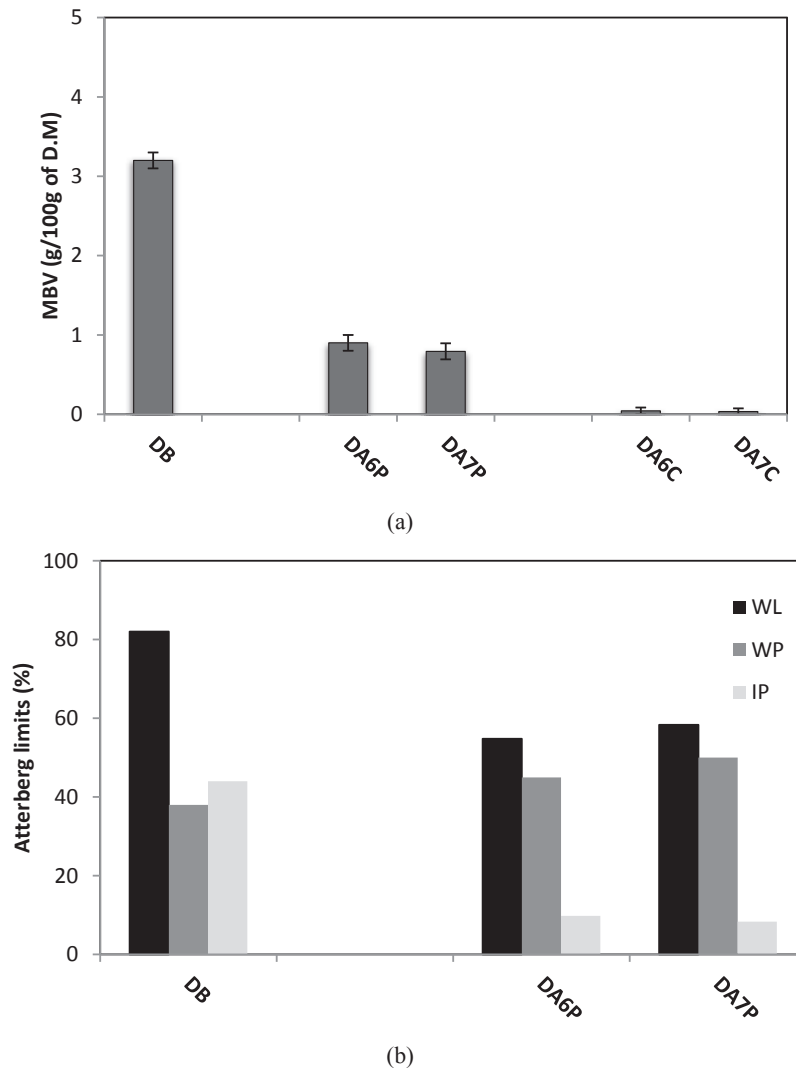


Fig.5. (a) Methylene blue values of the sediments (b) Atterberg limits of the sediments

3.2. Chemical characteristics

The crystalline phases identified by XRD are presented in Fig.6.

For all sediments the main minerals were:

- Quartz (SiO_2),
- Calcite (CaCO_3).

Some minor phases were detected such as:

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

The clays such as Illite, Kaolinite and Montmorillonite were not detected for the treated sediments. This is aligned with the methylene blue value and the plasticity index. 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 source of calcium (CaCO_3) to produce gypsum. This form has changed shape into anhydrite (CaSO_4) during calcination.

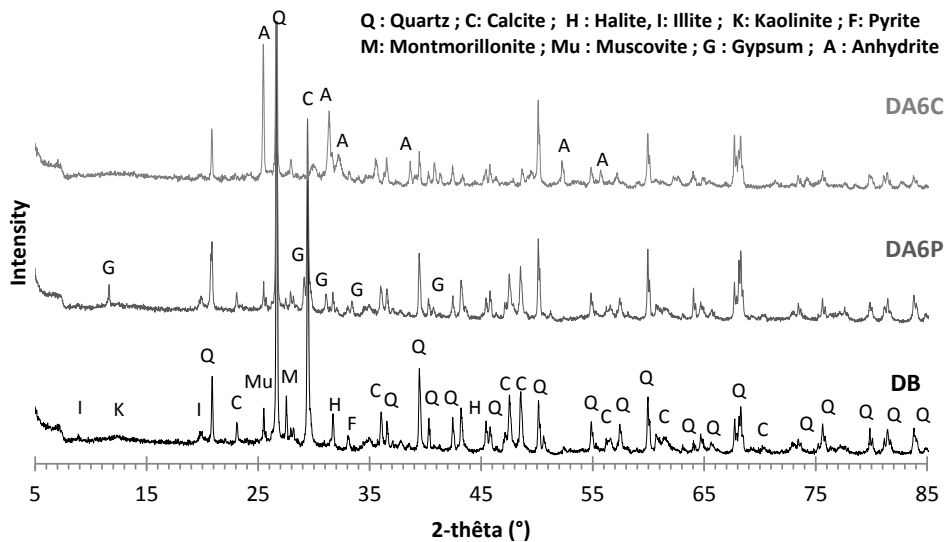
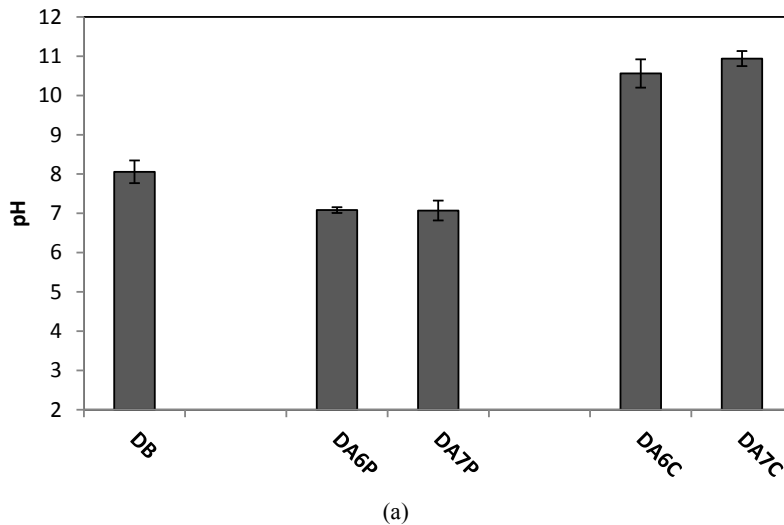


Fig.6. X-ray diffractogram of the raw and treated sediments with A6 acid

The pH of the studied sediments is presented in Fig 7. The natural pH of the raw sediment is 8.1. This value decreases to around 7 for the phosphated sediments due to the addition of phosphoric acid. After calcination, the pH of the sediments increases around 11, which is probably due to the decarbonation of calcite which produces lime (CaO).

The Carbon, Hydrogen, Nitrogen and Sulphur content are presented in Fig.3. The total carbon, Hydrogen and Nitrogen contents are in the same order of magnitude for the raw and phosphated sediments. These values are close to zero after calcination. This is expected because these elements are related to the organics. However the sulphur content is higher for the sediments treated with the A6 acid.



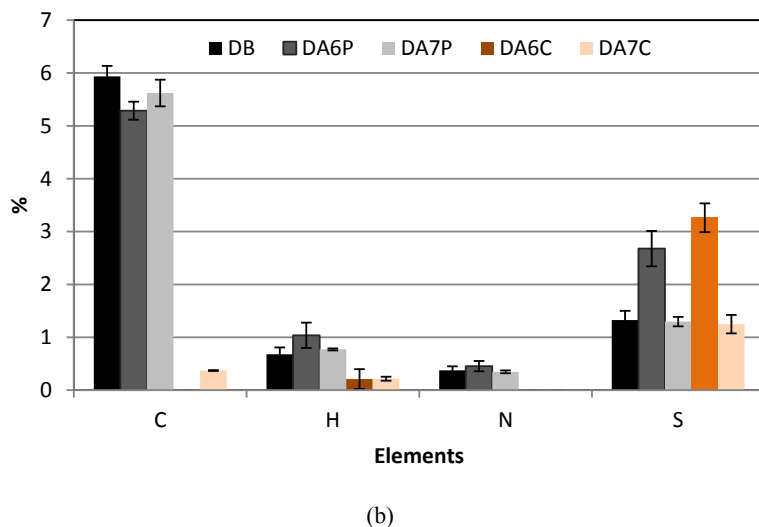


Fig.7. (a) pH of the sediments (b) C-H-N-S content of the sediments

The major and minor elements are presented in Fig.8 and Fig.9 respectively. For the major elements, the sediments are essentially composed of calcium Aluminium and iron. This is in accordance with the XRD results. Concerning the minor elements, the chemical composition reveals a high quantity of heavy metals. The main pollutants are zinc and lead. After calcination we can see a slight increase of the total content of the elements. This is due to loss in mass related to the degradation of organics. We can conclude that the treatment had no effect on the elemental composition of sediment. It should be noticed that, this analysis provide information on the pollution and not on the environmental behavior of the sediments. The environmental aspect was addressed in previous studies (12).

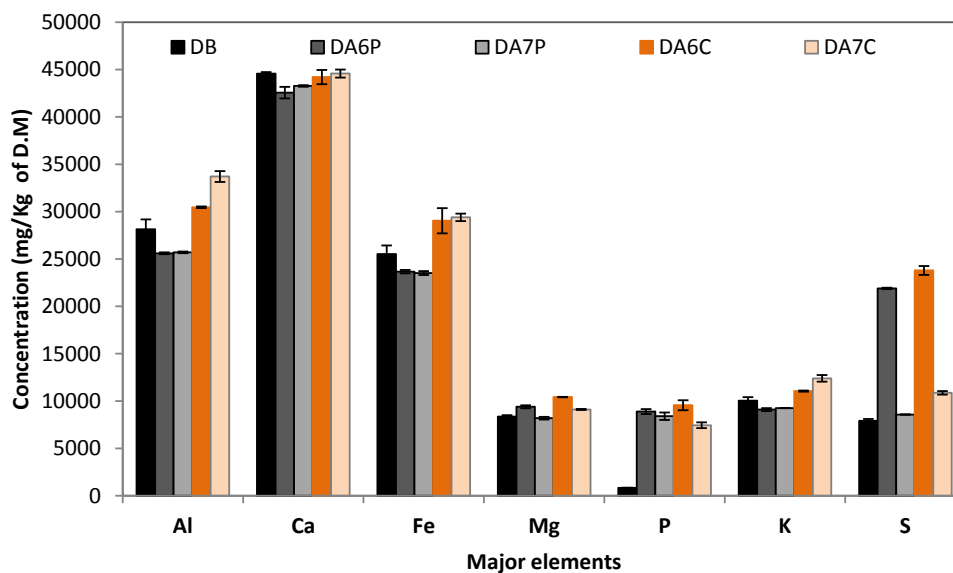


Fig.8. Major elements in the sediments

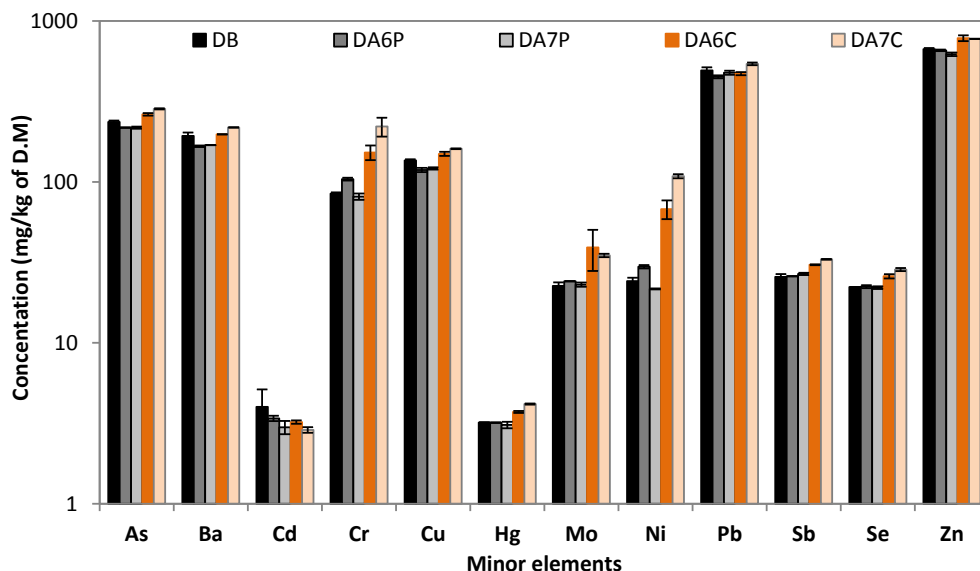


Fig.9. Minor elements in the sediments

3.3. Compaction of the sediments

The optimum level of compaction is evaluated by following the evolution of dry density. According to the corresponding value of moisture content, is determined. The CBR is a test of suitability of materials to withstand the loads of fill and layers of compacted forms of road works. This is determined experimentally healthy index (IPI CBR) that allows establishing a classification of soils (GTR), to assess the trafficability of machines (IPI) and to determine the thickness of the pavement. The compaction and CBR index curves are presented in fig.10. The values of dry densities and the CBR indexes at the optimum moisture content of the modified Proctor are presented in table 2.

Table 2. The values of dry densities and the CBR indexes at the optimum moisture content of the modified Proctor

Treatment	sediments	W (%)	$\rho_d(\text{Kg/m}^3)$	I-CBR (%)
Raw	DB	22.4	1.57	25
Phosphatation	DA6P	25.1	1.53	26
	DA7P	24.0	1.51	25
Calcination 650°C	DA6C	31.5	1.40	55
2h	DA7C	33.0	1.42	58

The optimum moisture contents for the phosphated sediments are higher than the raw sediment. We can also observe the decrease of the dry density at optimum for phosphated sediments. This might be related to the clay flocculation. However the CBR indexes are similar. We can notice that the phosphatation did not have a significant affect on the CBR index.

For the calcined sediment we can see a decrease in dry density and significant increase of the water content and the CBR indexes. This behavior is currently observed with lime treatment soil. These high CBR values ensure the trafficability of machines during the road works. These results give an opportunities to use calcined sediments in road materials.

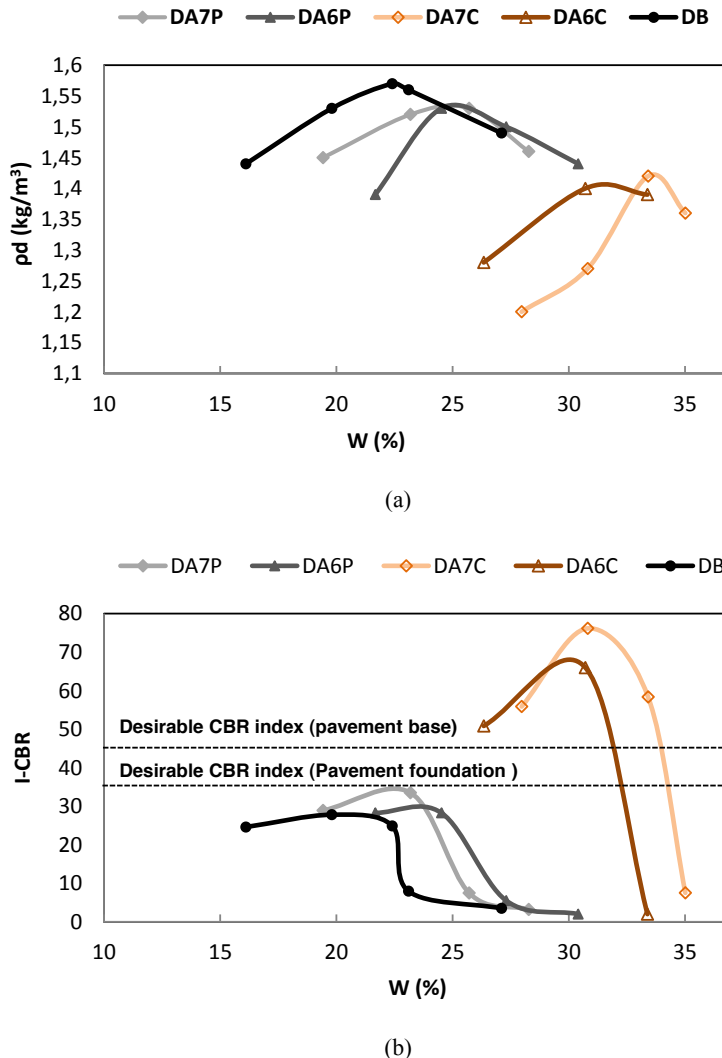


Fig.10. (a) Compaction curves of the sediments versus content of the modified Proctor; (b) CBR index curves of the sediments versus content of the modified Proctor.

4. Conclusions and prospects

In this paper the effect of changing the acid type for the Novosol[®] process on the evolution of the physicochemical and geotechnical behavior is investigated in order to find an efficient way of valorisation in road materials. It was shown clearly that the acid type gives a similar results.

The physical characterization shows that the raw sediment has high water content (around 130%); this can constitute a major obstacle to valorization of the sediment. This value decreases considerably after treatment, to around 5% for the phosphated sediments. The phosphatation did not have any effect on the absolute density. After calcination the specific surface area decreases and the sediments true densities increase. These values are in the same range and comparable to those of inorganic sand (around 2.6 and 2.8g/cm³). The plasticity index and the methylene blue value decrease after treatment especially for the calcined sediments.

The chemical characterization shows that for all sediments the main minerals were quartz and calcite. Moreover the X-ray diffraction has shown the presence of gypsum for the treated sediments with A6 acid and the clay were not detected. The treatment had no effect on the elemental composition of sediment.

The bearing capacity of the calcined sediments ensure the trafficability of machines during the road work. These results give an opportunities to use calcined sediments in road materials.

The next step of this work is to study the the mechanical behavior of road material based on treated sediments. In this field, complementary tests are in progress.

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