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ScienceDirect
Journal of Hazardous Materials 148 (2007) 606–612
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

The use of the Novosol process for the treatment of polluted marine sediment

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Received 22 January 2007; accepted 6 March 2007
Available online 14 March 2007

Abstract

The work presented in this article concerns polluted marine sediments. The article is divided into three parts. The first part discusses existing industrial procedures of treatment. The second part introduces the Novosol® process, which was used for the treatment of polluted marine sediments. This process is based on the stabilization of heavy metals in the solid matrix by phosphatation and the destruction of organic matter by calcination. Finally, after a comparison had been made between environmental results obtained on both polluted marine sediments and inert ones, treated sediments were introduced in the production of clay bricks. The results obtained show that the Novosol process leads to the immobilization of most heavy metals and can be considered as an efficient tool for the stabilisation of polluted marine sediment. Thus, the results of physical and mechanical tests as compressive strength and water absorption indicate that performances obtained were comparable to standard brick values. These results confirm that, once treated, polluted sediments can be recycled.

Keywords: Marine sediment; Heavy metals; Phosphatation; Stabilization; Recycling

1. Introduction

Over the last few years, the protection of the environment and sustainable development has become increasingly important in all sectors of activity. This tendency, linked to a growing public awareness, can be seen in numerous measures and legislations concerning the environment. These laws are not only national but also European and concern companies, authorities and citizens alike. The companies, aware of their obligations, have anticipated the arrival of these elements in order to optimise the economic factor. Their strategy is in the first place to anticipate the consequences of the presence of pollution and in the second place to reduce the production source of these pollutants.

Amongst the various problems that for a long time have affected not only France but also several other countries, one of the most important is that of the silting up of harbour and of estuaries by sediments and sludge. Currently, 50 million m^3 of sludge are dredged each year in France and indeed 10% of this volume is dredged in the five major maritime harbours. This represents both an economic and an ecological problem. On the one hand, this silting effect slows down the development of harbour activities: the dredging of harbours is a necessity to aid navigation and is regularly carried out. Moreover, the sediments pollute the marine environment with negative effects on the biomass.

There are two types of polluting substances in these sediments: those known as organic and those known as inorganic. The organic pollutants, which are composed of a high number of carbon atoms, are essentially hydrocarbons and derived products (PAH, PCB, etc.). The main parameters governing the behaviour of hydrocarbons in soil are solubility, volatility and their electronic structures [13]. The inorganic pollutants are mainly heavy metals, nitrates, phosphates and salts. As an example of heavy metals, we can mention lead, cadmium, zinc and copper. These heavy metals can have serious direct consequences not only on humans but also on the flora and fauna. The second characteristic of heavy metals is their interaction with each other. Indeed, Richter [12] has shown that in a saturated soil, cadmium is adsorbed 80 times less than in the absence of lead. Colandini [11] has shown that heavy metals absorbed by the soil can be

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doi:10.1016/j.jhazmat.2007.03.029

released in the presence of water carrying salt. The principal characteristic that distinguishes organic pollutants from inorganic ones is that the latter have a longer life. The present article is divided into three parts. The first part introduces the issue of the silting up of ports by polluted sediments and proposes a comparative study of the different existing industrial processes. The second part includes a presentation of the Novosol® process, which was used in this study. Finally, the third part outlines the performance of this process when used on polluted marine sediment and describes the recycling method, which consists in the production of hot bricks.

2. Remediation methods

Different processes of treatment of polluted sediments have been developed. Generally, they consist of reducing, immobilising, confining or suppressing the action of a contaminant. The techniques underlined here are the most widely used, particularly physico-chemical and biological techniques. However, other less well known techniques, such as thermal or acoustic techniques, which are more effective for particular waste, must not be ignored. Amongst the different physico-chemical techniques, the processes of stabilisation/solidification and of separation/recuperation can be mentioned. The latter includes the process of vacuum extraction, which is a technology used for soil decontamination. Its objective is to eliminate volatile contaminants. After passing through a vacuum chamber, the volatile pollutants flow through a cooling system, which dries them, and compress them into gas canisters. Other techniques exist and are based on processes which wash the sediments or which use acido-basic reactions in the polluted area. The process of stabilisation/solidification is based on the trapping of contaminants in their matrix. Thus, the spread of the contaminant is rendered impossible. Examples of this process are vitrification, biofixation, phosphatation, pyrolysis or processes based on oxydo/reduction or hydraulic binding.

Biological techniques in most cases consist of using microorganisms to break down the organic substances in order to accelerate the natural decomposition of the contaminants. Among these techniques, phytoremediation and biodegradation are the most often used.

2.1. Comparative study of the processes of inertage

This section deals with an inventory of existing industrial processes, which are used to decontaminate polluted materials. This list is not exhaustive but will present the main types of treatment currently used. Such treatment processes are based on the destruction, on the stabilisation and finally on the separation/recovery of the pollutants.

(a) The destruction process is biological treatment. This process accelerates natural reactions to bring about the destruction of the pollutant materials. In the case of Patent FR2774980 [1], the effluents are treated by a biomass which increases while the treatment progresses. This requires the elimination of excess sediments. Thus, the process treats these sediments through a humid oxidation where the temperature varies between 80 °C and 200 °C and under a pressure value ranging from 1 to 40 bars. This operation is done before re-injection of treated sediments into the biological reactor.

Furthermore, processes using destruction can be distinguished as far as combustion is concerned. Incineration is the result of destruction by the combustion under high-temperature (more than 500 °C) of organic material. Water is expelled into the atmosphere as steam. Mineral matter (ashes) remains, as some vapour cleaning residues, which must be removed to monitored dumps.

For technical and economic reasons, incineration remains an option for large quantities of sediments and for self-combusting sediments (rich in organic materials and not humid), which, when burnt liberate sufficient heat to maintain the temperature in the furnace.

The EBARA Corp process [2] proposes the combustion of a wide range of solid waste products without producing heavy residues (tar). The second one is that of the CNIM [3], which proposes a system to treat ashes, obtained from incineration. Before the fusion operation, solid residues are mixed with an additive. The dry mass of the additive composed of silicium, aluminium and calcium oxides represents 60% of the mix.

(b) In the range of stabilisation processes, the one of Saint-Gobain [4] concerns the stabilisation of the waste products by vitrification. A recycling solution into bottles or glass wool was proposed. However, this process remains expensive and cannot be used for large volumes as polluted marine sediment. It could, nevertheless, be used following the separation stage of the most dangerous elements of some waste products.

The second process in this category is that based on phosphatation perfected by Solvay [10].

It is known as the Novosol® process and will be described in the next section.

The third process [5] proposes a method of stabilisation of the blast-furnace slag by trapping it in concrete. This raises two problems: how to make sure that the concrete sets quickly and how to guarantee the long-term reliability of the process of stabilisation?

The first problem is solved by adding silica-based composites. The second, by compressing the concrete after it has finished setting. This guarantees a major reduction in the micro porous volume and a better resistance to lixiviation. This patent can be coupled with patent EP1076048 [6] which proposes to use the lixiviates that are necessary for maturing the slag in order to make the concrete set. The heavy metals present in the lixiviates are therefore trapped in the concrete.

Mention can also be made of the CEA patent [7], which proposes a process, which contains radioactive waste products in a confining matrix based on $Al_2O_3/SiO_2/CaO$. This is sufficient to prove the high resistance of stabilised matrices. However, in order to create the matrix it is necessary to reach temperatures of 1100–1300 °C.

(c) Another technique can be mentioned, as the method based on the separation/recuperation of the pollutants. Treatments using metallic salts have been perfected, in order to precipitate the wastes, such as process EP0968138 [8]. This process involves the precipitation of phosphates composites by metallic ions Fe/Al. The sediments are then treated by centrifugation. Metallic salts treat the solution, which contains the dissolved precipitate, in order to remove heavy metals.

Finally, patent EP0903325 [9] proposes to treat sediments using ozone. The objective is to fix organic residues. The latter appear during the biological treatment of aqueous waste products.

A series of reactors allows the organic residues to be put in contact with a gas composed of ozone under pressure. These residues pass through all the reactors, for which a supply system allows the quantity of gas to be regulated. An appropriate pressurisation and agitators placed in each reactor allow an equal absorption of ozone in each reactor Table 1.

2.2. Presentation of Novosol® process

This process was developed and patented by the Solvay Company [10]. It consists of two major phases: phosphatation and calcination. Heavy metals are stabilised in the solid matrix during the phosphatation process, while organic matter is eliminated by calcination.

The phosphatation phase involves mixing the polluted sediments, once drained off, with phosphoric acid H_3PO_4 (2–3.5%). Addition of phosphoric acid allows, in presence of calcite, the formation of insoluble metal phosphates. This process takes place in a tubular reactor, where heavy metals are trapped and fixed into stable crystal phases as apatite.

$$10Me^{2+}(aq) + 6H_2PO_4^{-}(aq) + 2H_2O \rightarrow Me_{10}(PO_4)6(OH)_2 + 14H^{+}(aq) \quad (1)$$

Me: Ca, Pb, Cd, Cu, Zn, As.

The calcination phase consists in calcining the phosphated sediments at >650 °C in a rotary kiln, in order to destruct the organic matter (polycyclic aromatic hydrocarbons, dioxins and pesticides). It increases product toughness and reduces the volumes of the processed materials after treatment and allows a better stabilization of metal phosphates.

Gaseous emissions resulting from the treatment process are chemically treated using active charcoal and sodium bicarbonate. The fumes are cleaned as follows:

$$2NaHCO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 + H_2O + 2CO_2 \quad (2)$$

$$2NaHCO_3 + 2SO_3 \rightarrow SO_3Na_2SO_4 + H_2O + 2CO_2 \quad (3)$$

This treatment is based on heat activating sodium bicarbonate. Once in contact with the fumes at high temperature, sodium bicarbonate is quickly transformed into sodium carbonate with a high specific surface and porosity, which reacts with SO_2 and SO_3. The treatment is efficient for neutralising acids (hydrochloric, hydrofluoric acids, sulphur dioxide, etc.) and absorbing heavy metals.

Active charcoal, available in two forms (powder and granules), is the most absorbent composite material known today. Its high specific surface (500–1500 m^2 per gram) gives it a high level of absorption so the substance to be filtered sticks to its surface without any chemical reaction. Active charcoal is used to fix substances that are difficult to eliminate using traditional treatments.

Finally, the Novosol® process remains innovative for a certain number of points [15]. First, it is a chemical process, which links phosphatation to burning. Moreover, it allows a mass stabilisation of the matter, and finally is polyvalent in the variety of polluted products, which are treatable. Indeed, it has the advantage of being able to treat in one process different types of pollution, whether chemical or biological.

3. Recycling of marine polluted sediment after stabilisation

The main methods of reducing sludge and sediments are the agricultural muck-spreading or in some countries the dumping at sea, which is very practical. This method of elimination has been illegal since 1999 (EEC decree 97/277). The second method consists in stocking in a dump. This tends to be ruled out. The last method of elimination is the incineration, which accounts for about 20% of the total tonnage. Given the difficulties and the limitations of these methods of reduction, it seems necessary to find new issues of recycling.

Table 1
Summary of different processes: advantages and disadvantages

Process	Advantages	Drawbacks
Vitrification	Large list of composites. Long-term resistance	High energy cost
Combustion	Easy to undertake	Limited and polluting treatment
Biological	Attractive solution because of efficiency (contaminants are made inoffensive or less toxic)	Targeted treatment
Stabilisation	Efficient fixing of pollutants (notably by phosphatation)	Recent treatment with limited standardization
Trapping in concrete	Large array of products to treat and possibility to recycle waste products	Difficult to undertake. Requires guarantee of stabilisation reliability through resistance, compression and lixiviation tests

Table 2
Total concentrations of pollutants of two types of marine sediments (mg/kg dry)

	Sediment from Dunkerque	Sediment from Calais	Soil norm
Cadmium (Cd)	12	16	2
Chromium (Cr)	118	62	150
Copper (Cu)	493	56	100
Lead (Pb)	456	120	100
Zinc (Zn)	2090	1978.8	300

3.1. Characterisation of raw material

The polluted sediments, which make up this study, come from the north region of France. Organic materials and heavy metals are the main pollutants identified in these sediments. Their pollution is diverse and it is linked mainly to the industrial history and to the paints used on ships' hulls. The following Table 2 sets out a comparison of the concentrations of main heavy metals for sediments coming from sites in Dunkerque and Calais with French standard limit, the NFU44–041 (soil norm) serving as a benchmark for the sediments.

From the above table, it can be observed, that sediments from Dunkerque exhibit high concentrations in heavy metals. The measured concentrations strongly exceed the usual limits and norms currently in place. Complementary results are presented in Table 3 The main parameters measured are the pH, the electrical conductivity, the carbonates and finally the sulphate content. The pH indicates the degree of acidity or alkalinity. The pH value herein indicates that the marine polluted sediment is alkaline. It can be noted, that the high level of conductivity indicates the presence of high quantities of chlorides, mainly in the form of sodium salts NaCl and potassium KC1. Carbonates give important information, they are the first to react with acid to form calcium, which becomes soluble and forms metallic phosphates with heavy metals. Therefore, they indicate the degree of interaction with heavy metals. Finally, it can be observed, that the sulphate content is high and polluted sediment exhibit 4% of organic materials. Tables 2 and 3 shows that the Dunkerque marine sediments are very polluted and cannot be used as they are because they are dangerous and can cause serious problems. These sediments must be treated and stabilised before any action or re-use. In order to stabilise these polluted sediments, the Novosol® process was used after a period of dryness and maturity of these sediments. Only the first phase of the process (phosphatation) was undertaken. Calcination, was not used because this phase will be carried out in the recycling process. The latter involves making bricks using a hot process. Photo lc presents the treated sediments obtained after the phosphatation phase.

The environmental characterisation of the treated sediments was carried out. This characterisation is a necessary and obligatory phase in the recycling process. It allows checking the efficiency of the Novosol® treatment. Different leaching tests exist in literature and they generally consist in extracting leachable fractions of a sample with an aqueous solution. The standard test, which has been used in this study, is the French standard XP X31–210 [14]. In Table 4 results of lixiviation tests performed on sediments from Dunkerque were presented. Regulatory limits were reported in this table [16]. This good result clearly shows the efficiency of the Novosol® process with regards reducing the pollution.

3.2. Composition of the brick

After stabilizing the polluted sediment using the Novosol® process, the treated sediments were used as raw material in order to manufacture clay bricks. The recycling method proposed here consists of producing bricks by hot process. This

Table 3
Characteristics of polluted sediment from Dunkerque

pH	Conductivity (m/S)	Density	Carbonates (% of mass)	Sulphates (mg/kg dry)	Organic matter (% of mass)
8	12	1.4	2.7	12,500	4

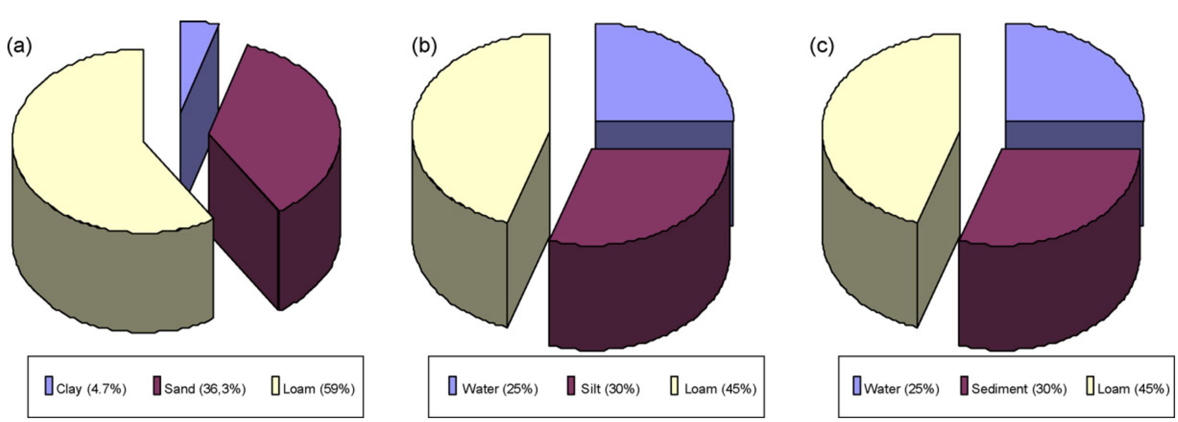

Fig. 1. Granular distribution of treated sediment and average composition of bricks: (a) Granular distribution of treated sediment; (b) composition of standard brick; (c) composition of new brick with treated sediment.

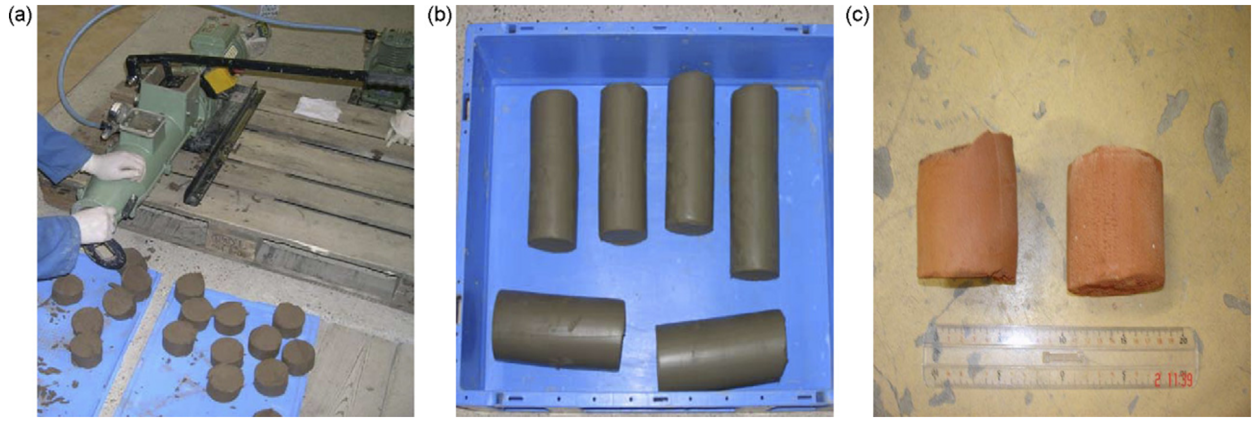

Fig. 2. Laboratory scale brick manufacturing: (a) extruder set up; (b) samples obtained before burning; (c) valorised bricks.

Table 4
Lixiviation test in deionised water on raw and treated sediments (mg/kg)

	Cd	Cr	Cu	Pb	Zn
Raw sediment	<0.03	0.06	6.2	0.15	1.3
Treated sediment	<0.03	13.34	0.87	<0.2	0.3
Regulatory limit for non dangerous waste [16]	1	10	50	10	50

recycling method has two major advantages. First, making bricks using a hot process avoids calcination during the treatment of the sediments with the Novosol® process, since the brick undergoes baking, which guarantees the elimination of all organic matter. Moreover, the industrial brick-making industry is not necessarily disturbed by the use of sediments as raw material. As shown in Fig. 1 treated sediments can replace a considerable part of a standard brick as raw material.

The grain-size distribution (Fig. la) of the treated sediment classify it as clayey, sandy silt. Any composition of a standard brick contains clay and silt because these materials give cohesion and plasticity, which are necessary to the mixture in order to be extrusion shaped. Currently, bricks are made with a mixture of 75% clay (45% loam and 30% Silt) (Fig. lb). The composition of the new brick is as follows: inerted sediments replace the loam, as these are composed of 60% loam, and no sand is used (Fig. 1c and Photo 1). It can be noted that treated sediment looks like brown, light and porous aggregate. The cohesion is very low and it can easily be crushed with a finger. The main result concerns their porosity, which is very high (48%).

After mixing the raw materials (Clay from Lille and sediments from Dunkerque, which are phosphatised but not, calcinated), the mix is introduced into an extruder (Fig. 2a). The latter is a laboratory device, which is similar to the industrial device used in brick factories. This laboratory device allows the production of a homogenous cylindrical sample (Fig. 2b). These samples were burnt in an industrial furnace at a temperature of 1100 °C as with any standard bricks. The first bricks produced with treated sediment were obtained and samples are presented in Fig. 2c.

Even if the first results can be considered as good, since that treated sediment could be used as raw material for brick production, the brick's physical characteristics such as compressive strength and water absorption were measured. The experimental

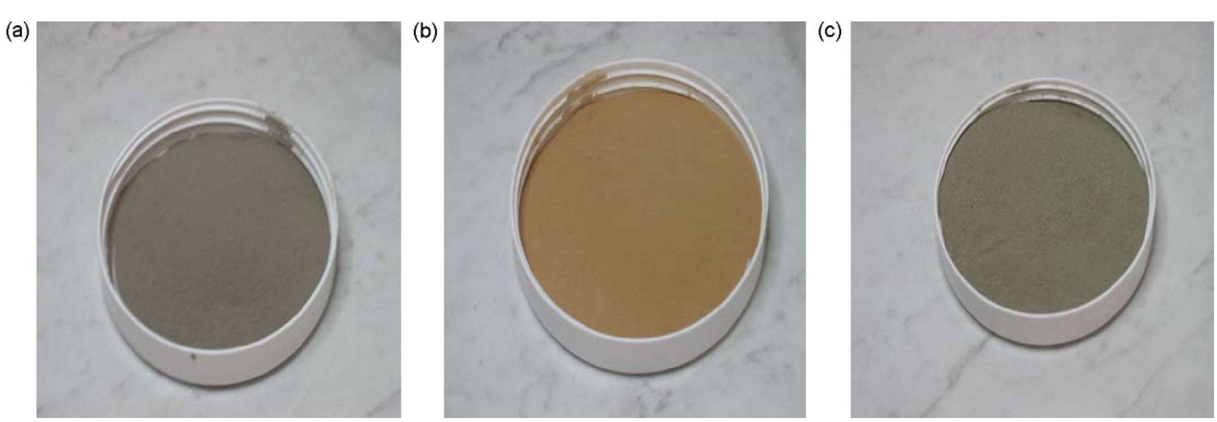

Photo 1. Visual aspect of components of the brick: (a) silt; (b) loam; (c) treated sediment.

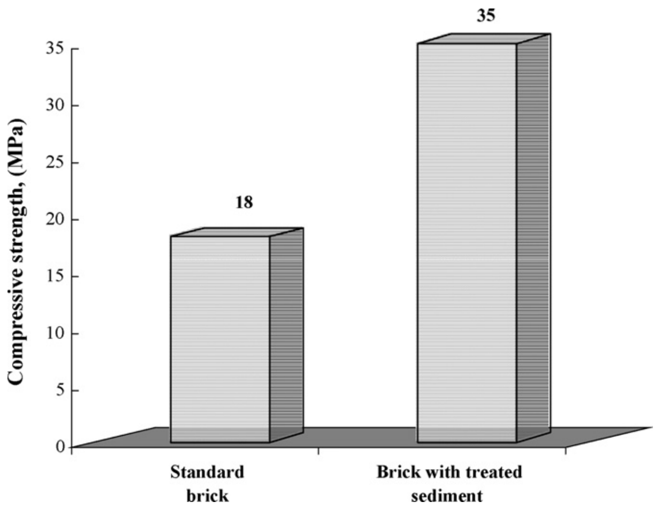

Fig. 3. Comparison between compressive strength values obtained for standard brick and brick with treated sediment.

results obtained were systematically compared to those obtained on standard bricks.

3.3. Physical characterisation of new brick

3.3.1. Compressive strength

Resistance to compression is a key parameter to evaluate the suitability of the material to be used in construction. The compressive strength of cylindrical specimens, cored in substituted bricks, was measured using a 30 kN Instron mechanical press.

The results obtained are shown in Fig. 3 These results indicate that when compared to the standard brick, the compressive strength of brick samples with treated sediment is higher than that of the standard brick.

3.3.2. Water absorption

Water absorption is a key parameter for the durability of a material. A high water absorption may facilitate the ingress of aggressive species in the material and accelerate its deterioration. Low water infiltration into the brick indicates good durability of the brick. Brick samples were oven-dried at 110 °C for more than 24 h. After drying, samples were cooled in a drying room at 25 °C, with a relative humidity of 40%. The next phase involves submerging the sample in distilled water at 16 °C. This operation was stopped when full saturation of the sample is achieved. Finally, the sample is removed and weighed. Table 5 shows the results of the water absorption test.

We can note an increase of water absorption for bricks with treated sediment when compared to standard brick. However, water absorption value obtained is inside regulatory limits.

Table 5
Comparison between water absorption coefficient values

Standard brick	Brick with treated sediment	Regulatory limits
6.5	9.3	40

4. Conclusion

The first objective of the work presented in this article is to study the use of Novosol® process for the treatment of polluted marine sediments. After a brief description of existing procedures of treatment, an introduction to the Novosol® process was presented. This process is based on the stabilization of heavy metals by phosphatation and the destruction of organic materials by calcination. The polluted sediment, which was studied, came from the harbour of Dunkerque in the north of France. These sediments exhibit high concentrations of pollution and the results show that once treated by the Novosol® process, the content of pollutants respected standard norm limits. As a result, Novosol® process can be considered as an efficient tool for the stabilisation of polluted marine sediments.

Finally, the method of recycling of treated sediment undertaken consists in making bricks by a hot process. The physical characterization of these bricks, mainly their compressive strength and water absorption, was undertaken. The results obtained were compared to values obtained on standard bricks. The latter confirm the industrial feasibility of this valorization.

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