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Characterization and valorisation of dredged harbours sediments from Tangier and Larache (Morocco)

Laïla BEN ALLAL [1], Mohammed AMMARI [1], Ikram FRAR [1], Amina AZMANI [1], Nour Eddine BELMOKHTAR [1]

1. Laboratoire de Génie Chimique et Valorisation des Ressources (LGCVR), Université Abdelmalek ESSAADI, Faculté des Sciences et Techniques, Tanger, Maroc.
l.benallal@fstt.ac.ma

Abstract:
This work falls under the process of sustainable management of dredged harbour sediments by studying the behaviour of these materials for valorising them effectively in the construction sector, the interesting field in this study. A complete characterization of sediments dredged from the ports of Tangier and Larache was carried out from chemical, physical and environmental analyses. The study of the physical properties of these sediments revealed that these sediments are generally fine material 0/1mm. Chemical characterization of these sediments was used to evaluate potential pollutant. The absence of metal pollution was noted. The first sector of valorisation is the field of building materials which has involved mortars by replacing the sand by dredged sediments. The values of compressive strength obtained have confirmed that a partial substitution of sand by dredged sediments from the ports of Tangier and Larache in mortars is satisfactory for a strength of 20%. The valorisation of sediments in bricks manufacturing is the second track explored. Technological feasibility of bricks containing sediments from the port of Larache was demonstrated by preliminary tests in a brickyard. For these bricks, the composition chosen was 70% of sediment. Two valorisation processes are potentially possible. Therefore, the dredged harbour sediments can constitute a source of interesting raw materials for the sector of construction that consumes aggregates and developed materials.

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1. Introduction

Dredged harbour sediments are the product of the extraction of sediments deposited on the bed, including port docks. They are commonly called vessels and are composed of mineral phases and organic liquid. Sustainable management of dredged sediments remains an important issue; the volume of dredged sediments is considerable. In Morocco 3.4 Mm^3 are dredged annually.

This study focuses on the valorisation of dredged gross sediments from the ports of Tangier and Larache in construction materials such as bricks and mortars. It fits into an overall management approach of dredged harbour sediments which requires knowledge of sediments, in a way, their identity card (LEVACHER *et al*., 2011). To do this, it is first necessary to determine different sediments properties and therefore realize their physical, chemical, mineralogical and environmental characterization. We are interested in this study with sediments from two ports in northern Morocco: Tangier port and Larache port. Both sediments were incorporated into mortars by partial substitution of standard sand and cement. The mechanical strengths were measured and compared to the resistance of a control mortar.

2. Knowledge of sediment

2.1 <u>Presentation of sampling sites</u>

The sediments studied in this work were collected from the ports of Tangier and Larache (figure 1). Thanks to its strategic location between the Atlantic and the Mediterranean Tangier port is Morocco's leading port in passenger traffic and international transit roads.

Figure 1. Zones of sampling of sediments.

Larache port is located on the north Atlantic coast of Morocco, 90 km south of Tangier. It is a river port located in a basin on the left bank of the wadi Loukkos, 750 m from its mouth. The port of Larache now focuses exclusively on fishing.

2.2 Characterization of raw sediments

It involves the study of physical properties (state parameter and nature, water contents, granulometric distribution, mineralogy), chemical properties (pH, conductivity, carbonate content, organic matter and hydrocarbons, sulphate content, trace elements and major elements) and environmental characteristics (leaching tests). The methods and materials for determining these quantities are described and results presented. A discussion ensued on all the characterization results which are in themselves the identity card of the sediments. This identity card will reveal the impact of sediments on the environment and the proposal of appropriate valorisation methods.

2.2.1 Physical characterization

First, the absolute and apparent densities of the two sediments were determined according to NF P18-555. The results are summarized in table 1.
Particle size analysis was performed on a wet sieve of 63 microns in order to separate the fine fraction and coarse fraction (> 63 microns). The results are presented in table 1. For the coarse fraction which corresponds to the refusal, it was dried in an oven at 110 ° C until constant weight and sieved by using a series of screens according to NF P 18-560.
These are two fine sediments, however, in figure 2, we clearly observe that the sediment from Larache port is much finer than the sediment from Tangier port.

Table 1. Physical and chemical characteristics of studied sediments.

Sediment	***Larache***	***Tanger***
Absolute density (g/cm^3)	*2.20*	*2.28*
Apparent density (g/cm^3)	*1.53*	*1.30*
Fraction < 63 µm (%)	*94*	*41*
Fraction > 63 µm (%)	*6*	*59*
Dryness at 40 °C (%)	*49.4*	*58.6*
pH	*7.8*	*8.0*
Conductivity (mS/cm^2)	*6.5*	*6.6*
Carbonates content (%)	*8.0*	*10.5*
Organic matter (%)	*4.2*	*7.0*
Hydrocarbons (%)	*1.3*	*5.1*
Sulphates (%)	*0.7*	*1.1*

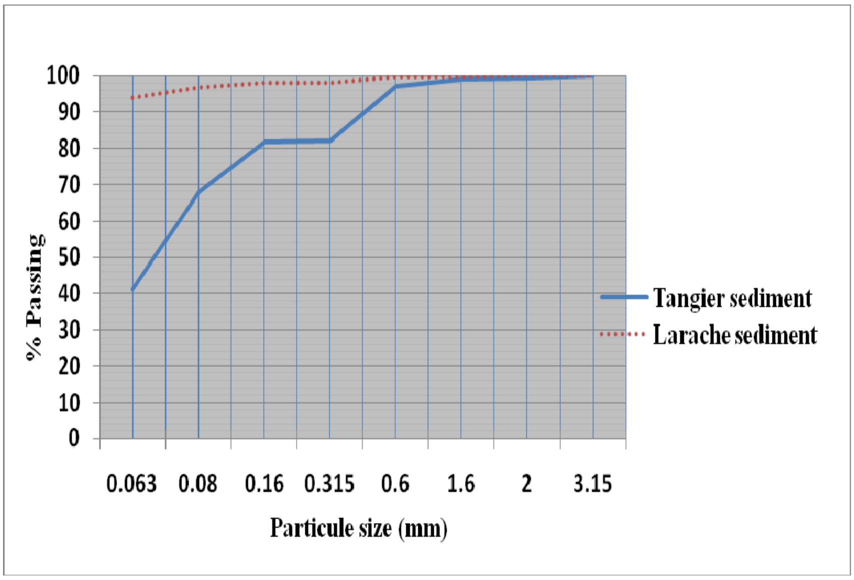

Figure 2. Particle size distribution curve of studied sediments.

We proceeded to measure the dryness sediment at 40 °C. The principle is based on drying the sample in an oven at 40 °C until constant weight according to standard NF ISO 11464. The measures on sediments (average of 3 samples) are shown in table 1. These values depend heavily on dredging conditions. This removal of moisture is used into the case of the preparation of samples for physical and chemical analysis. The temperature is 40 °C to avoid any alteration of organic matter (KRIBI, 2005). A mineralogical analysis of sediments studied was carried out using qualitative analysis by XRD performed on a crushed portion of the order of 80 microns for both sediments using a Spinner PW 3064 device. As a result, calcite and quartz are the two principal crystalline phases.

2.2.2 Chemical characterization

It includes some useful chemical properties to select methods of valorisation (valorisation in cementitious materials or ceramics) and the determination of certain levels of the constituents which by their very presence may contribute to or disrupt the implementation of any process.

The pH determination is an indicator in the case of treatment of sediments by an hydraulic binder. An acidic pH causes the dissolution of metal salts, the desorption of cations and anions adsorption (LIONS, 2004). When using a hydraulic binder, the metal cations precipitate as metal hydroxides not very soluble because of the high alkalinity of cement matrix (CONNER, 1990).

The pH value expresses the real acidity and takes into account the free H_3O^+ in the liquid phase.

The pH of the two sediments were determined according to NF X 31-103, see table 1.

Another property assessed is electrical conductivity which is a good assessment of the overall concentrations of dissolved solids in sediments.

Standard NF ISO 11265 is used. The average values of conductivity are measured in table 1.

The evaluation of different levels of the constituents concerns first carbonates, organic matters and sulphates. The chemical compositions were obtained from the measurement of heavy metals and major elements. Stabilization with hydraulic binders is one of the most popular methods for stabilizing and solidifying wastes rich in heavy metals such as sediments. Presence of organic matter may influence the hydration of cement and reduce resistance.

For the determination of carbonate contents, see table 1, it was performed using the calcimeter Bernard. This measure is described by NF ISO 10693. Then the organic matter content OM was analysed using the method of sulfochromic oxidation. The principle of this test is based on the oxidation of organic matter by potassium dichromate and titration of excess dichromate by Mohr's salt as the standard: NF ISO 14235. The average values derived are in table 1.

The potential presence of PAH hydrocarbons justified the measurement of hydrocarbon content. Hydrocarbons such as organic matter are soluble in organic solvents. The principle of this test is based on the extraction of hydrocarbons in sediments with an organic solvent, toluene was used. Values shown in table 1 clearly indicate the presence of PAH for the Tangier port.

The determination of sulphates has been advocated since the sulphates are disturbing elements in the methods of treatment with hydraulic binders. Sulphates are compounds necessary to regulate the setting time. However, if the content becomes too high, degradation of the treated material by hydraulic binders can occur (significant swelling, development of a significant cracking, decreased mechanical strength), (BARYLA *et al*., 2000). The sulphates were measured in both sediments by gravimetric method. Values are shown in table 1.

To get a clearer idea about the chemical composition of the studied sediments, we proceeded to the measurement of heavy metals and major elements. Major elements were determined by atomic absorption spectrometry and trace elements (heavy metals) were measured by mass spectrometry coupled plasma (ICP-MS). The results are summarized in tables 2 and 3.

Table 2. Chemical composition of major elements in sediments in %.

Major elements	***SiO_2***	***Al_2O_3***	***Fe_2O_3***	***CaO***	***MgO***	***SO_3***	***K_2O***	***Na_2O***
Larache sediment	*49.6*	*14.5*	*9.1*	*11.2*	*0.5*	*0.6*	*1.7*	*2.0*
Tangier sediment	*48.5*	*11.9*	*7.4*	*11.7*	*1.2*	*1.1*	*1.7*	*2.0*

Table 3. Concentrations of trace elements in sediments mg/kg of dry sediment.

Trace elements	***Larache sediment (mg/kg)***	***Tangier sediment (mg/kg)***
Chrome (Cr)	*0.22*	*0.10*
Arsenic (As)	*0.02*	*0.01*
Nickel (Ni)	*0.06*	*0.07*
Zinc (Zn)	*0.01*	*0.39*
Copper(Cu)	*0.08*	*0.38*

Table 4: Levels relative to trace elements (mg/kg of dry sediment analysis on the fraction below 2 mm), GEODE (2000).

Trace elements	***Level N_1***	***Level N_2***
Arsenic (As)	*25*	*50*
Chrome (Cr)	*90*	*180*
Copper (Cu)	*45*	*90*
Nickel (Ni)	*37*	*74*
Zinc (Zn)	*276*	*552*

2.2.3 Clarification on the definition of levels N_1 and N_2

For the N_1 level, below which dredging and disposal would be allowed without further studies, the potential impact is considered neutral or negligible, see table 4. The observed values are comparable to the environmental "background noise".

For the N_2 level, above which the dumping would likely be prohibited provided that such prohibition is the least damaging management solution to the environment, see table 4. Further investigation is generally necessary because the indices may be predictive of potential impact of the operation. A thorough impact assessment is then deemed essential.

Between levels N_1 and N_2, further investigation may be necessary depending on the particular project and the degree of tolerance level N_1. Tests are then performed to assess the overall toxicity of the sediments.

2.2.4 Environmental study: leaching of raw sediments

Leaching tests are conducted according to European Standard EN 12457. The samples are in contact with distilled water under stirring for 24 h. The liquid/solid ratio is 10. They produce the desired dosages for chlorides and sulphates.

The chlorides were determined by titration with silver nitrate. The results are summarized in table 5.

For sulphate, they were determined by UV spectrophotometry. The results are summarized in table 5.

Table 5. Chlorides and sulphates content (mg/kg).

Sediment	***Larache***	***Tangier***
Average content chlorides (mg/kg)	*940*	*1020*
Average content sulphates (mg/kg)	*885*	*1268*

2.2.5 Discussion and results interpretation

Comparison of concentrations of trace elements in the studied dredged sediments at GEODE (2000) baseline (table 4) allows to conclude to an absence of metal pollution. The organic content for sediment dredged from Tangier port is higher than the sediment of Larache port. This result can be explained by the intensity of urban waste in the port of Tangier. The determination of oil shows a high rate for the sediment from Tangier port, this because of the nature of the great activity of that port. We can conclude that the two sediments are polluted with hydrocarbons when compared to the rates obtained for threshold values allowed in landfills Waste (EUC, 2003), (table 6).

Table 6. Respective threshold concentrations of pollutants for different classes of waste (CUE, 2003).

Settings	***Class III Storage of inert waste***	***Threshold values (mg/kg of dry matter)***	***Class II Storage of not dangerous waste***	***Threshold values (mg/kg of dry matter)***	***Class I Storage of dangerous waste***	***Threshold values (mg/kg of dry matter)***
			On raw material			
COT	<	*30 000*	< - <	*50 000*	< - <	*60 000*
BTEX	<	*6*	-	-	-	-
PCB	<	*1*	-	-	-	-
Hydrocarbons	<	*500*	-	-	-	-
HAP	<	*50*	-	-	-	-

Sulphates content (in the solid phase) obtained by atomic absorption are almost equal to those obtained by gravimetry method, are respectively 0.6 and 0.7% for Larache sediment and the same value at 1.1% for Tangier sediment. Sediment grain size of Larache shows its silty nature (that fraction is 94%) while the sediment of Tangier has a slightly sandy loam character.

3. Valorisation of dredged sediments as building materials

3.1 Valorisation of sediments

Most studies have shown the feasibility of substituting natural materials by waste or by-products and the relative quality of the obtained materials (AUBERT, 2002; BOUCARD, 2006). Inspired by these studies, we chose to study the behaviour of sediments in mortars by partially replacing on the one hand, the standard sand, and the other hand, the cement.

3.1.1 Substitution of 20% of standard sand by sediments

This study aims to highlight the influence of partial substitution of sand by raw sediments on strength resistance of mortars. The cement used is a Moroccan cement CPJ 45, with a water to cement ratio (W/C) of 0.5. The dosages selected were from 1350 kg of sand per 450 kg of cement.

Thus, specimens of 4×4×16 cm were produced, according to EN 196-1 and then tested. The compressive strength and flexural R_{cj} and R_{tfj} were measured at 7 days and 28 days. The reference values are those obtained for a standard mortar.

All the average values of resistance are summarized in table 7

Table 7. Compressive strength and tensile bending mortars for a 20% substitution of standard sand.

R_{c7} (MPa)	R_{c28} (MPa)	R_{tf7} (MPa)	R_{tf28} (MPa)	Reference mortars
32.0	45.0	5.6	6.4	Normal mortar CPJ 45
18.0	28.5	3.9	5.8	Mortar of Tangier sediment
19.3	30.3	4.1	6,0	Mortar of Larache sediment

3.1.2 Substitution of 20% cement CPJ 45 by sediments

In this section, the mortars were made by replacing 20% of cement CPJ 45 by sediments. The ratio of water to binder, *ie* cement and sediment (E/L), was 0.5. As before, compressive strength and bending strength Rcj and R_{tfj} were measured on specimens 4×4×16 cm and tested at 7 and 28 days. The results are summarized in table 8.

Table 8. Compressive strength and tensile bending mortars for a 20% substitution of cement.

R_{c7} (MPa)	R_{c28} (MPa)	R_{tf7} (MPa)	R_{tf28} (MPa)	Reference mortars
32.0	45.0	5.6	6.4	Normal mortar CPJ 45
14.2	23.4	3.3	5.4	Mortar of Tangier sediment
14.2	24.6	3.4	5.5	Mortar of Larache sediment

3.1.3 Discussion and interpretation of results

The sediment from the port of Larache gives a mortar stronger than the sediment from the port of Tangier where both raw sediments replace 20% of standard sand. This result can be explained by the high rate of organic matter present in the sediment from the port of Tangier. From (KUJALA *et al.*, 1996), the presence of high organic matter may prevent proper hydration of cement paste. Organic matter would capture calcium ions released by the cement during the hydration and would no longer form hydrates needed to manufacture strong bonds between particles. The strength decrease can be caused by the presence of organic matter which has an inhibitor character. According to (FANTOZZI-MERLE, 2003), the presence of organic pollutants can also affect the mechanical strength.

In the case of the substitution of cement by 20% of sediment, the resistance obtained for the two mortars are comparable. But this resistance remains far below the resistance of the reference mortar. The result can be explained by the decrease in the amount of cement. A decrease of resistance is inevitable.

The predictive Bolomey model confirms the experimental results:

$f_{cj} = k_b . f_{mj} [C / (E + V) - 0.5]$

f_{cj} = strength (MPa) of mortar j days.

k_b = coefficient that depends on the granular aggregate used (we take $k_b = 0.50$).

f_{mj} = true resistance cement j days, measured on standard mortar (EN 196-1).

C, E, V: respective densities of cement, water and air (kg/m^3).

We determined the theoretical compressive strength:

After 7 days $f_{c7} = 15.3$ MPa.

After 28 days $f_{c28} = 21.5$ MPa.

So overall, the partial replacement of cement by the two sediments leads to the strength variation predicted by the Bolomey model.

3.2 Valorisation of sediments in the development of bricks: feasibility stage

The chemical composition (% of major elements) of both raw sediments and the chemical composition of clays used for making clay products are comparable (ALVISET, 1994). This analogy of composition has directed our research towards the development of sediments as raw material for bricks. This is a feasibility study for this type of valorisation. Sediments were used in bricks manufacturing by partial substitution of the clay used in the formulation. The making of bricks was performed within the brickyard Al Andalous Tangier.

Sample preparation of bricks is a mixture of 70% sediment and 30% clay. After drying in open air, the three materials (Larache sediment, Tangier and clay sediment) were ground and sieved to 1 mm. After kneading, moulding and drying the dough, the brick samples are dried at a cooking temperature of 920 °C for 32 hours. The initial findings are encouraging because the brick has proved possible. The photos in figure 3 show the appearance of bricks by replacing 70% of the clay used by the dredged sediments.

One point is clear for the feasibility stage. The texture and appearance of bricks obtained are comparable to brick reference of the company. The idea of assigning studied sediments in the manufacture of bricks can be envisaged. At this stage, it is necessary to verify the mechanical and environmental performance of these bricks incorporating sediments.

Larache sediment

Tangier sediment

Figure 3. Bricks manufactured with a substitution rate of 70% of sediments, the same size 2.5×5.0×7.5 cm.

4. Conclusions

The physical characterization of sediments dredged from ports of Tangier and Larache revealed that these sediments are fine to very fine materials. Their main constituents are silts and fine sands in grain size. Chemical characterization of sediment was used to evaluate potential pollutant. It was especially noted the absence of metal pollution. However, the sediment dredged from Tangier port has a high rate of oil due to the nature of port activity.

The impact on the environment, measured through leaching tests, shows a moderate level of chlorides and sulphates in sediments compared to the two thresholds of acceptance in landfills.

It turns out that these sediments are fine grained materials and are attractive to local Moroccan construction enterprises, including brickworks.
The values of compressive strengths of mortars have shown that partial substitution of sand by sediment dredging of the ports of Tangier and Larache is satisfactory, but with a rate of strength reduction of about 30%. With such resistance, the potential uses relate to mortar plaster or manufactured masonry blocks. For these products, we can accept a partial replacement of standard sand by these sediments.
Partial replacement of cement by sediments has led to a drop in strength of 45%. Part of this drop in resistance is explained by the fact that the quantity of cement was reduced by 20%: a discussion based on an analysis by Bolomey law had been proposed. From (SEMCHA, 2006), thermal activation of dredged sediments (high fines content) could give those pozzolanic properties and better mechanical performance in the long run. Heat treatment transforms the mineralogical composition of the material and the combination of new structures with lime results in the formation of a hydraulic binder.
Valorisation of sediments in the bricks is a feasibility stage which is promising. This "brick" die is more than potential and work to optimize production is to continue.
Finally, we can conclude that these two dredged harbour sediments can be a source of very interesting local raw materials, especially for the construction sector, strong consumer of aggregates.

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