

Formulation of Mortars with Marine Sediments

Nor-Edine Abriak, Mouhamadou Amar, Mahfoud Benzerzour

Abstract—The transition to a more sustainable economy is directed by a reduction in the consumption of raw materials in equivalent production. The recovery of byproducts and especially the dredged sediment as mineral addition in cements matrix represents an alternative to reduce raw material consumption and construction sector's carbon footprint. However, the efficient use of sediment requires adequate and optimal treatment. Several processing techniques have so far been applied in order to improve some physicochemical properties. The heat treatment by calcination was effective in removing the organic fraction and activates the pozzolanic properties. In this article, the effect of the optimized heat treatment of marine sediments in the physico-mechanical and environmental properties of mortars are shown. A finding is that the optimal substitution of a portion of cement by treated sediments by calcination at 750 °C helps to maintain or improve the mechanical properties of the cement matrix in comparison with a standard reference mortar. The use of calcined sediment enhances mortar behavior in terms of mechanical strength and durability. From an environmental point of view and life cycle, mortars formulated containing treated sediments are considered inert with respect to the inert waste storage facilities reference (ISDI-France).

Keywords—Sediment, calcination, cement, reuse.

I. INTRODUCTION

THE term sediment indicates the elementary deposits at the bottom of aquatic environments and is composed of unit particles (various sizes, forms and mineralogical compositions) of diverse origins (endogenous and exogenous). The accumulation of sediments in seas and river beds is a natural phenomenon often amplified by human activities which can disrupt maritime activities as well as the physicochemical balance of large masses of water. Therefore, dredging is often essential to restore the required depth for navigation and indeed the natural environment.

In France, about 50 million m³ of sediments are annually dredged, stored, treated or salted overseas, while this figure is 300 million for whole Europe [1] and near 300 million in the USA.

According to EU Council Directive 91/271/EEC of 21 March 1991, "Sustainable sludge handling may be defined as a method that meets requirements of efficient recycling of resources without supply of harmful substances to humans or the environment". In order to save natural resources and regarding the increase of environmental regulations, the use of alternative material in construction sector [2], the recycling and the use of sediment as resource (USAR, SETARMS, SEDIBET project, etc.) are considered as a suitable solution

Mouhamadou Amar and Mahfoud Benzerzour are with the Ecole des Mines de Douai, GCE, 764 Bd Lahure, BP 10838, 59508 Douai, France.

Nor-Edine Abriak is with the Ecole des Mines de Douai, GCE, 764 Bd Lahure, BP 10838, 59508 Douai, France (e-mail: nor-edine.abriak@mines-douai.fr).

for a sustainable development [3]-[5]. For several years, a core subject for world environmental policies (Kyoto Protocol (1995); COP 21 (2015)) has been the optimized and efficient use of by-products such as sediments [6]-[8].

The construction sector in France uses a huge volume of concrete amounting to over 20 million tons a year. Also, concrete possesses a high carbon footprint, being responsible for 7% of CO₂ emissions of industrial origin worldwide. Nowadays, much mineral addition is used in cement based material to reduce cost or involve performance (metakaolin, silica fume, fly ash, etc.) [1], [13]-[15].

Sediments, because of their mineralogical and chemical constitution (siliceous, clayey, limestone, etc.), they can be used in cementitious mixture. However, the effective use of this product often requires an adequate treatment process particularly aimed at eliminating the organic fraction and certain pollutants. The aim of this study covers heat treatment of dredged sediments and their use as supplementary cementitious material. It has been established that, for the substitution rate in the order of 10% to 20%, cementitious matrix based on this calcined sediment compared to a standardized mortar (cement, sand, water), has mechanical, physical, and chemicals at least equal to those of standard reference mortar.

II. MATERIAL AND METHODS

A. Materials

For formulation of mortars, a Portland cement has been used, which complies with European standard EN 197-1 (2012). It is composed of over 95% clinker and less than 5% of secondary components. The initial setting time is greater than 45 minutes. At 28 days, the simple compression strength according to EN 196-1, is greater than 52.5 MPa.

In our study, we used a CEN siliceous sand, with rounded grains, and the diameter of the largest aggregate is less than 2 mm (D_{max} = 2 mm). Its silica content is at least 98%.

B. Material Characterization

The sediments used are from the Grand Port Maritime de Dunkerque (GPMD) located in the North of France. This port dredges about 4 million m³ sediments each year. A sample of 500 kg was taken in February 2015 in a storage lagoon located at the port site. These sediments were homogenized and dried in an oven at 60 °C to stabilize the sample's mass. After the drying phase, sediments were crushed in a jaw crusher to have the finest granular material to be characterized and to be used in the mortar's formulation.

C. Physical Characterization

Concerning the physical characterization, the measurement of the density of the materials has been taken with a helium

pycnometer type Micromeritics AccuPyc 1330. This test was performed in accordance with the EN 1097-7 standard. The BET surface area is determined according to the NF EN ISO 18757. The particle size distribution was conducted by laser particle size analysis. The measurement of organic matter was produced by the calcination test 450 °C according to standard XP P94-047.

The methylene blue absorption test (VBS) in order to evaluate the clay content was also conducted according to the French standard NF P94-068. The evaluation of Atterberg limits (liquid limit: W_L and W_p and plastic limit) was done according to standard NF P94-051. These analyses revealed that the sediments of this study were A2 class materials: sandy, silty, clayey soil to the GTR French guide.

D. Mineralogical Characterization

The mineralogical characterization of dredged sediments is performed through X-ray diffraction analysis (XRD) (Fig. 1). The test is conducted using a Siemens D5000 type apparatus

and is a measure of the intensity and diffraction angles in order to establish an electronic mapping of crystalline phases in presence. The major elements present are: calcite (CaCO₃), quartz (SiO₂), anhydrite (CaSO₄), pyrite (FeS₂), but also clay fraction: kaolinite in particular. For Roux and Unikowski [10], the presence of fine clay in general may cause four kinds of effects: water absorption, shielding effects, swelling and shrinkage, chemical activity (pozzolanic activity). Also, according to Rodríguez et al. [9], it appears that the fine sediments, with finely crystallized clays, could have a relatively high pozzolanic activity.

The chemical analysis consisted of determining the proportion of each chemical element by X-Ray Fluorescence XRF (Table I). It has revealed the presence of oxygen (~50%), silicon (~16.6%) and calcium (~15%). These values are close to those found in the previous studies [11], [12] conducted on sediments GPMD. These results confirm the findings from the XRD analysis.

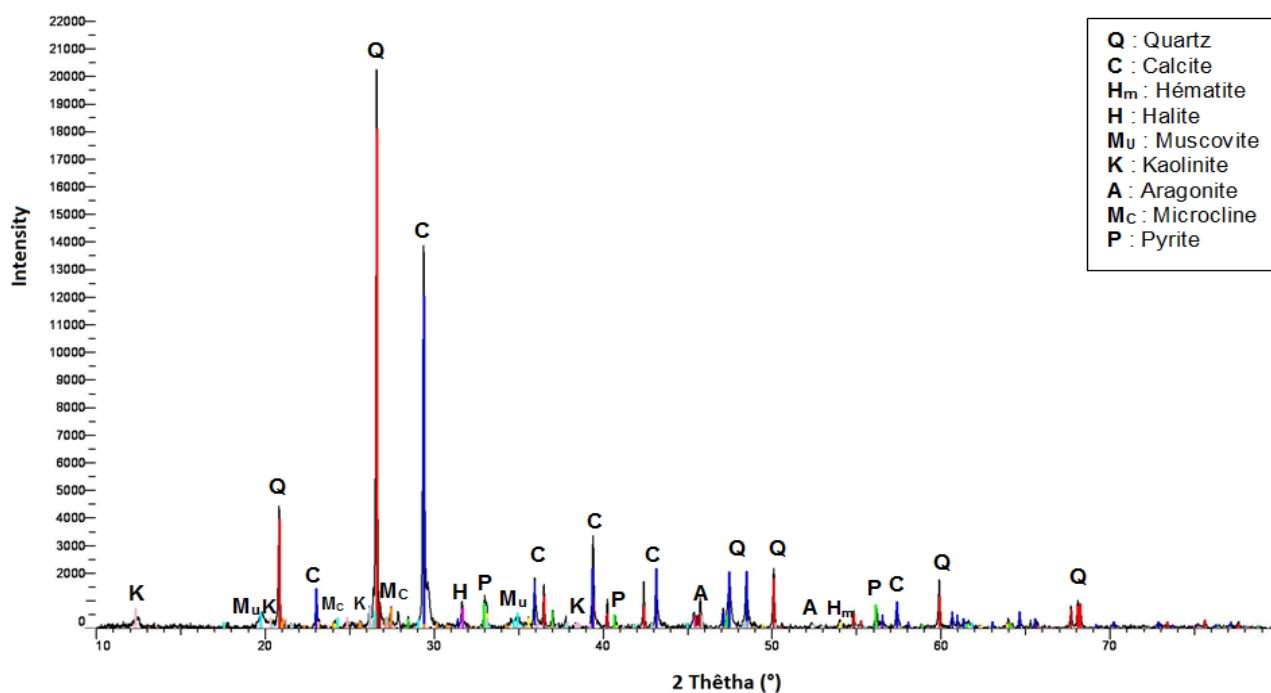


Fig. 1 XRD mineralogic analysis

Characteristics	Raw sediment
Specific weight (g / cm ³)	2.48
Water content %	80
VBS (g/100g MS)	2.8
Specific surface BET (m ² /g)	10.92
Liquid limit W _L (%)	45.3
Calcination 450°C (%)	9.10
Ignition loss 550°C (%)	12.80
D50 (µm)	23
D90 (µm)	161
GTR class (1992)	A2
Soluble fraction (g/kg MS)	3083

E. Thermogravimetric Analysis: TGA

This thermal method enables to assess a relationship between mass loss of a sample and temperature treatment. The TGA is performed in a controlled environment with Aragon flow (75 ml/min) and where samples are exposed to a range of temperature (105 °C to 1100 °C; ramp rate = 2 °C/min). The results are presented in Fig. 2.

The TAG highlights a peak in mass loss corresponding to the dehydration phase. This mass loss appears from 380 °C to 600 °C. This loss of H₂O is probably due to intergranular water and constitution water from clay minerals as identified by Teklay et al. [28]. The release of carbon monoxide and carbon dioxide between 350 °C and 550 °C temperatures

could originate from the combustion reactions of organic matter and organic pollutants (PAHs, PCBs, TBT) present in sediments according to Dia et al. [29]. A CO₂ peak appears between 600 °C and 750 °C and is induced by the

decarbonation of calcite [9]. This probably originates from the shells of marine species. According to this analysis, the temperature which allows for optimum calcination sediment must be greater than 730 °C.

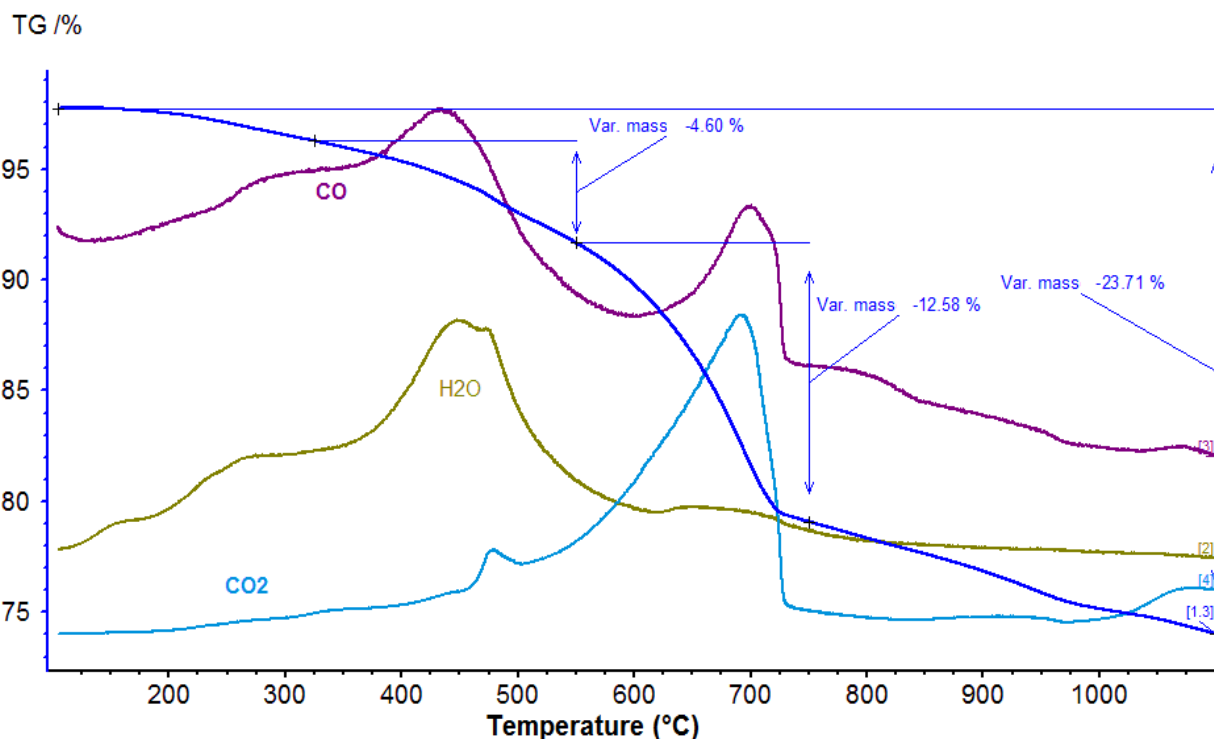


Fig. 2 TGA result on raw sediment (RS120)

F. Formulation

The reference mortar (RM) is prepared in accordance with NF EN 196-1 French standard. For its formulation, the following proportions are considered: one part of cement, three parts of the CEN standard sand, and a half part of water (water/cement ratio=W/C = 0.5) (Table II).

For the other formulations, a portion of cement is substituted by the calcined sediments following the proportions of 10% (MSC10), 20% (MSC20) and 30% (MSC30). Table II presents the composition of the various formulations investigated. The water/binder =W/L ratio was kept constant for all formulations. This is done not to induce supplementary porosity.

TABLE II
 COMPOSITION OF DIFFERENT FORMULATIONS

Mortar	Cement (g)	Sand (g)	Water (g)	Sediments (g)	W/B
MT	450	1350	225	0	0.5
MSC10	405	1350	225	45	0.5
MSC20	360	1350	225	90	0.5
MSC30	315	1350	225	135	0.5

Mixing mortar was done according to the mixing procedure described in the European standard EN 196-1, and 40*40*160 mm mortar bars were prepared.

III. RESULTS AND DISCUSSION

A. Evolution of the Slump over the Time

Fig. 3 shows the sprawling measurements for the different mortars in function of time. It appears that the sag of all formulations decreases over time. It also turns out that the mortars based on calcined sediments have less fluid behavior compared to the reference mortar, knowing that the W/B is constant for all the formulations. This decrease is proportional to the calcined sediments rates incorporated into the formulations. This shows that the water is potentially retained by the calcined sediments, and this water does not participate on the fluidity of mortars. Furthermore, the use of sediments in the granular structure can change some mortar properties (rheology, mechanical strength, durability, etc.) [15], [16]. This specific behavior can be related on its physicochemical nature. According to Cabane [17], in such structures, during the use of hydraulic binders, it may form some complexes in the lumps formed of interstitial fluids riches in the water and calcium ions (Ca²⁺) and hydroxyl (OH⁻). This may have significant effects on the workability of mortar and future chemical reactions.

B. Mechanical Characterization

Fig. 4 illustrates the results of the different mortar's strength. Mortars formulated with calcined sediments exhibit a good mechanical behavior at least comparable to the reference

mortar (RM). The series: MSC10 and MSC20 have substantially equal bending strengths to RM (Fig. 4). Regarding mortar series MSC30, a high resistance drop is observed in the order of 20% compared to the RM. Moreover, compression tests show that the MSC10 present resistance to compression greater than 10% to 15% at 7 days and 28 days, respectively, comparing to the RM. This trend was confirmed by the results of 60 days's tests.

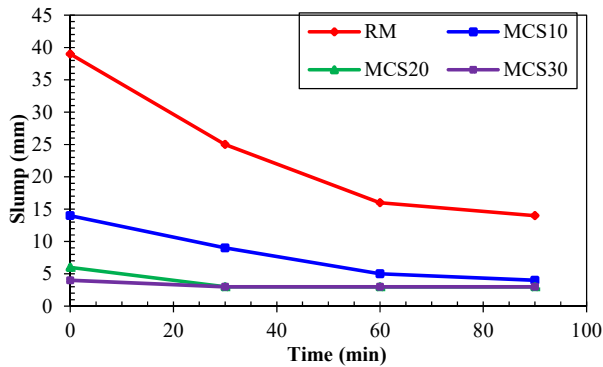


Fig. 3 Evolution of the mortars sprawling over time

The calcined sediments introduced into the formulation of mortars could have positive physical effects by being nucleation sites hydrates during the formation of the tobermorite gel (CSH) [19]. The activation of some mineral additions has been already investigated by previous studies [18], [19]. For this, a thermal treatment may be often necessary to improve the mechanical properties [16], [20], [21]. This suggests that the appropriate thermal treatment would have developed significant pozzolanic skills. Indeed, the fine sediments that contain a certain clay fraction, weakly crystallized could have a relatively high pozzolanic activity [9] during their use in cement matrix.

IV. MERCURY POROSIMETRY

The porosity measurement of a cement matrix is considered as the basis of all microstructural characterization or assessment of durability properties. It provides a global result ("total porosity"), indicator of the quality of the material, which is well correlated with the compressive strength. In fact, the decrease of the porosity, due to the addition of ultrafine for

example, corresponds to the best mechanical strength. Table III presents the measurement of the open porosity for the different samples after 28 days of treatment. These results show that porosity's mortars are between 14% and 17%. The porosity measured on samples MSC10 is almost equal to that of the reference mortar. The increase of the rate of calcined sediment in the formulations leads to an increase of the porosity. Indeed, the use of 20% and 30% of calcined sediments respectively increases the porosity of 11% and 18% compared to that measured on the reference mortar. This could be explained by the fact that over 20% of the sediment granular skeleton mortars is unstructured, with a loss of compactness. This compaction effect is resulted by the increase of voids in the cement matrix. According to Verbeck and Helmuth (cited in [22]), it seems that the variation of a 1% porosity or W/C can cause 10% elastic modulus loss. According to Maso [23], it is the porosity which mainly governs the resistance of mortars and concretes. This confirms our findings on strength results already shown. We should also remember that some pollutants (like zinc (Zn)) could adversely affect the mechanical strength by acting on the middle porosity and the correct germination of gel CSH [24], [25]. This could be a consequence of exchanges and transformation mechanisms [26].

TABLE III
 RESULTS OF MEASURING THE POROSITY BY MERCURY INTRUSION FOR ALL THE FORMULATIONS

	MT	MSC10	MSC20	MSC30
Total Intrusion Volume (mL/g)	0.0659	0.0662	0.0752	0.0800
Total Pore Area (m ² /g)	4.571	5.919	6.786	7.888
Median Pore Diameter (Volume) (μm)	0.1145	0.0651	0.0664	0.0618
Median Pore Diameter (Area) (μm)	0.0266	0.0274	0.0255	0.0231
Average Pore Diameter (4V/A) (μm)	0.0577	0.0447	0.0444	0.0408
Bulk Density at 0.10 psia (g/mL)	2.1401	2.1744	2.0847	2.0937
Apparent (skeletal) Density (g/mL)	2.4915	2.5397	2.4725	2.5144
Porosity (%)	14.103	14.383	15.685	16.736

Due to this test, we got Fig. 5, respectively for mortars containing sediments. We see that the carbonation is accentuated in proportion of cement substitution rates by sediments, but they remain close to or below the reference as to MSC10 mortars.

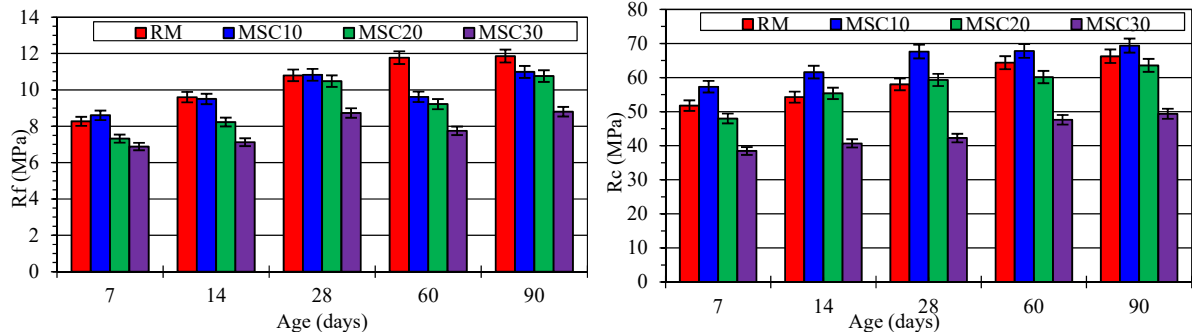


Fig. I Mechanical strength: 3 points bending test and compression test

The substitution of 10% of cement by calcined sediments has reduced the effects of carbonation about 70% to 30% compared to the RM, in 14 and 28 days, respectively. The decrease of the amount of cement due to its replacement by calcined sediments, leads to consider that the amount of calcium which can react in case of carbonation is reduced. This may explain the resistance to carbonation reactions observed for MSC10 mortars.

After 14 days of exposure, the MSC20 has a carbonation thickness of 62.5% lower compared to RM samples. At 28 days, we observed totally the opposite, the carbonation thickness for the samples containing sediments exceed those of RM by 11%. This can be explained by the fact that between 14 days and 28 days, penetration of carbon in samples of mortars based on sediments is more important. This effect is enhanced by the porosity of the MSC20 which is higher than 11% compared to the RM. Similar observation is observed for MSC30.

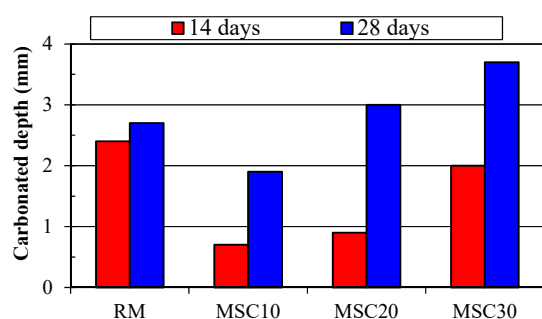


Fig. 5 Carbonated thickness of different samples of mortars

V.CONCLUSION

A study on suitable treatment of dredged sediments for recovery in cement matrix was conducted. The proposed treatment consisted of direct calcination of the raw materials at the temperature of 750 °C for 2 hours. This allowed improving some physicochemical properties such as chemical activation, pozzolanicity or total elimination of organic waste.

Mortars based on these calcined sediments shows really interesting mechanical performance compared to the RM. A mortar with 10% replacement of cement by the treated sediments has a compressive strength at 28 days greater in the order of 10% to that of the standard reference mortar (EN 196-1). This improvement can be attributed to a certain pozzolanic activity of this addition or it can be related by a physical effect due to a heterogeneous nucleation as found on previous studies [16], [27].

It would be appropriate to develop chemical methods for assessing entirely this activity. In terms of environmental impact, it should be noted that all the contaminants are proportionately lower than the values of ISDI. It would be interesting to assess their specific impact on physicochemical reactions.

The accelerated carbonation is evaluated and shows a 40% drop in the carbonation front for MSC10 comparing to the RM. The exhaustive study of durability is not performed in

this article. It may be the object of another detailed study.

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