ABOUT THE FORMULATION OF MORTARS BASED ON THERMALLY TREATED SEDIMENTS

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ABSTRACT

The transition to a more sustainable economy is directed by a reduction in the consumption of raw materials in equivalent production. Aggregates need account for nearly 55% of materials extracted for the French construction market. The recovery of by-products and especially the dredged sediment as mineral addition in cements matrix represents an alternative to reduce consumption of raw material and the construction sector's carbon footprint. However adequate and optimal treatment is required to use sediment efficiently.

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. This paper is about the effect of the optimized heat treatment of marine sediments in the physico-mechanical and environmental properties of mortars produced. A finding is that the optimal substitution of a portion of cement by the sediments treated 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 incorporation of calcined sediment up to 20% substitution of cement does not affect the durability of the matrix, besides 10% substitution of cement, improve the accelerated carbonation behaviour. 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).
KEY WORDS: Sediment - Characterization - Calcination - Pozzolanicity - Durability.

INTRODUCTION

In France, about 50 million m^3 of marine sediments are dredged annually. The large volumes of sediment dredged all over the world must be managed according to new environmental rules. Sediment can be considered dangerous because of their high content of heavy metals, organic matter (humic and fulvic acids) and soluble salts. Among the alternatives considered, one is their use as mineral addition to cement for the formulation of mortars and concretes. This is by the fact that industrial production of cement is particularly pollutant (1 T CO_2 / t clinker), costly in energy (8000 joules / 1 T clinker) and relatively expensive (200 € / 1 T clinker) [1].

The aim of this study is heat treatment of dredged sediments and their beneficial use in cement matrix. It has been established that for the substitution rate of 10% to 30%, cementitious matrix based on this calcined sediment compared to a standardized mortar (cement, sand, water), have mechanical, physical and chemical performances at least equal to those of standard reference mortar.

MATERIALS AND EXPERIMENTAL PROGRAM

Cement

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.

Sand

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

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 m^3 sediments each year. A sample of 500Kg 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.

Physical characterization

Concerning the physical characterization, the measurement of the density of the materials have 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: Wl and Wp 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.

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 device 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 ($CaCO_3$), Quartz (SiO_2), Anhydrite ($CaSO_4$), Pyrite (FeS_2). 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, for Rodríguez [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 2). It has revealed the presence of Oxygen (~50%), Silicon (~16.6%) and Calcium (~15%). These values are close to those found in previous studies [11][12] conducted on sediments GPMD. These results confirm the findings from the XRD analysis.

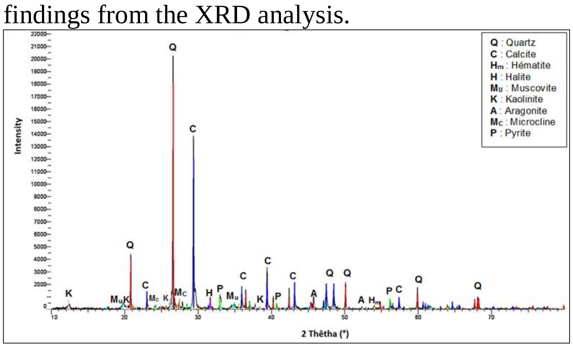

Fig.1 XRD mineralogical analysis

Characteristics	Raw sediment
Specific weight (g / cm3)	2.48
Water content %	80
VBS (g/100g MS)	2.8
Specific surface BET (m2/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

Table 1 Characterization of raw sediments

Chemical analysis

Leaching tests of the raw sediments have been made in accordance with the European standard EN 12457-2 (2002). These tests determine the proportions of heavy metals and pollutants leached from the sediments. The results are shown in Table 2. The values found are compared with the reference ISDI's thresholds (Decret of October 28, 2010 concerning inert waste storage facilities reference) and to estimate the degree of sediment's pollution. For all sediments used, note that the values found are below the threshold values. With the exception of Molybdenum (Mo) and Antimony (Sb) having concentrations above the threshold, all other pollutants are proportionately lower than the values ISDI facilities. This sediment is however considered as non-hazardous.

Elements	Concentration (%)
O	50.1
Na	1.1
Mg	1.5
Al	5.1
Si	16.6
P	0.2
S	1.8
Cl	0.9
K	1.5
Ca	15
Ti	0.3
Mn	0.1
Fe	5.5

Table 2 Concentrations of the major elements in the raw sediment (%)

Sediments treatment protocol

In order to determine the optimum temperature and the calcination time of sediments two steps has been carried out. They are described below:

The first phase concerns the thermogravimetric analysis (TAG) in order to have the most suitable calcination temperature. It is about the determination of the temperature allowing dehydroxylation OH, ie the loss of constitution water in the clay minerals and also the decarbonatation ($CaCO_3$, etc.).The TAG analysis consists in monitoring the mass loss as a function of changes in temperature. The result is shown in the Fig 2. This highlights a peak of weight loss corresponding to H_2O loss. This mass loss appears from 380°C to 600°C. This loss of H_2O is probably from the water content of clay minerals. The release of carbon monoxide (CO) between the temperatures of 350°C to 550°C could match with a partial combustion of organic matter in sediments. A CO_2 evolution peak appears between 600°C and 750°C, which corresponds mainly to the decarbonatation of calcite ($CaCO_3$) [13]. The calcite could have as origin the shells of marine species and the type of rock. According to this analysis the temperature which allows the optimum calcination of sediments must be greater than 730°C.

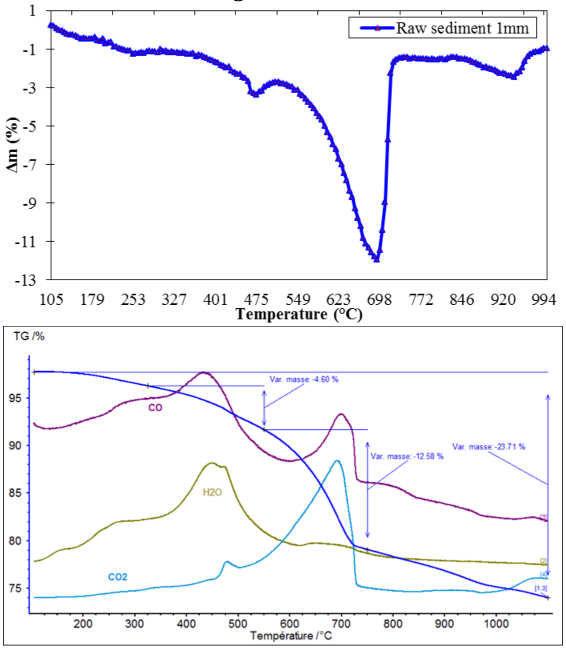

Fig. 2 TAG result analysis

The second phase is about the exact determination of the exact calcination time ensuring a efficient dehydroxylation of clays and almost completes the decarbonatation of carbonates. For this, several samples of raw sediments were calcined at a temperature set to 750°C at times from 0 to 4 hours. The monitor of the evolution of mass loss has been established. The Fig 2 shows the results of this analysis. It appears that after 2h calcination of the sediments, the mass loss begins to stabilize at a value between 10% and 12%. This can be by the fact that the organic matter decomposition, dehydroxylation of clay and calcite decarbonatation is almost complete. Similar consequences have been observed in a heat treatment applied to clays [8], [14]. Due to all this above reason and this analysis, the chosen treatment protocol for these sediments involves the calcination of at a temperature of 750 ° C for 2 h.

Formulation

The reference mortar (RM) is prepared in accordance with NF EN 196-1 French standard. For its formulation the following proportion are considered: one part cement, three parts of the CEN standard sand and a half part of water (water / cement ratio=W/C = 0.5) (Table 3).

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). The Table 3 presents the composition of the various formulations investigated. The water/binder =W/L ratio was kept constant for all formulations. This is done in order to not induce supplementary porosity.

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

Table 3 Composition of different formulations

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.

CHARACTERIZATION TESTS

Slump mini cone

In order to evaluate the variation of the consistency of the different mortars of formulations over time, a slump test was carried out. This will also allow seeing the effect of the addition of sediments at different proportion on the available water and the rheology of mortars. For this, a mini cone of height of 150 mm, with a base diameter of 100 mm and a top diameter of 50 mm, was used. The measurements were made at 0, 30, 60 and 90 minutes. Between each measurement, mixtures are isolated in plastic bags and kept at 20°C, out of contact with air to avoid water loss due to evaporation. The results are shown in Fig 3.

Mechanical strength

Simple compression and three points bending test. The strength measurements to simple compression and three points bending test were performed on samples 40*40*160mm. This tests were in accordance with the EN 196-1; curing (7; 14; 28; 60; 90 days). This test is completed by the dynamic modulus measure which allow to appreciate global elasticity, porosity and so the mechanical strength.

Mercury porosity measure

The measure of the pore size distribution was performed through a device such a Micromeritics Autopore IV. This test was performed on the reference mortar sample (RM) and sediment-based mortars (MSC10, MSC20, MSC30), which are stored by moist curing after 28 days.

Environmental acceptability

To evaluate the environmental impact of mortars formulated, leaching tests according to European standard EN 12457-2 (2002) were performed on crushed samples after 28 days. The Liquid/Solid = L/S ratio was set to 10. The leachate was analyzed to determine the concentrations of heavy metals and trace chemical elements.

RESULTS AND DISCUSSION

Evolution of the slump over the time

The 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 doesn't 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 ralated 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 (Ca^{2+}) and hydroxyl (OH^{-}). This may have significant effects on the workability of mortar and future chemical reactions.

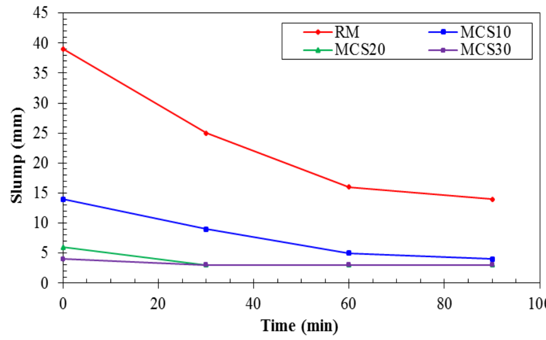

Fig. 3 Evolution of the mortars sprawling over time

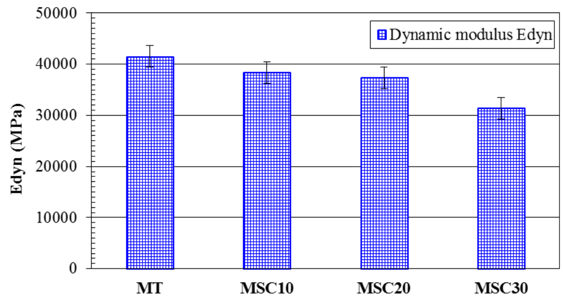

Fig. 4 Evolution of the dynamic modulus for the different mortars

Mechanical characterization

The Figure 5 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 (Figure 5 ; Figure 6). 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.

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]). 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.

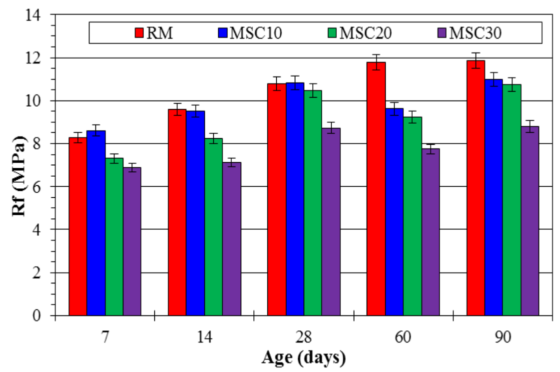

Fig. 5 Mechanical strength: 3 points bending test.

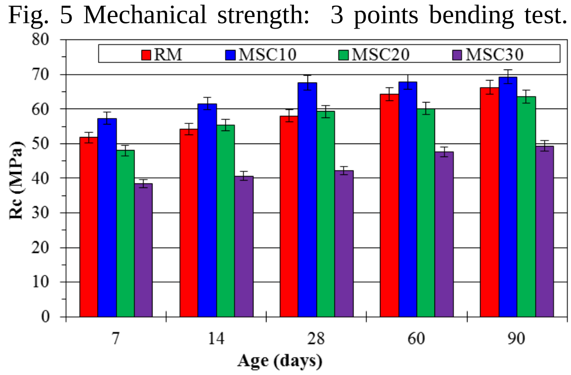

Fig. 6 Mechanical strength: compression test.

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. The Table 4 presents the measurement of the open porosity for the different samples after 28 days of treatment. These results show that porositie'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 increase 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. For J.C. 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 the 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].

	MT	MSC10	MSC20	MSC30
Total Intrusion Volume (mL/g)	0.0659	0.0662	0.0752	0.0800
Total Pore Area (m²/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

Table 4 Results for the measure of the porosity by mercury intrusion for all the formulations

ENVIRONMENTAL ACCEPTABILITY

From environmental impact point of view, it is suitable to estimate the presence in proportion of polluting components such as heavy metals which are mineral contaminants. The concentrations found are compared to those from the ISDI and to estimate the degree of sediment pollution. In the table below, is taken comparative results. The analysis of the results of Table 5 shows that the concentrations of the various formulated mortars (based on calcined sediment) remain below the threshold limits of the reference ISDI. The Molybdenum (Mo) and the Antimony (Sb) which are present in proportion exceeding the thresholds in the raw sediments are now located below the limits when treated. So, we could argue that the process of treatment and hydration had a stabilizing role for heavy metals.

Element (mg/kg)	RM	MSC10	MSC20	MSC30	ISDI
As	< 0.03	<0.03	< 0.03	< 0.03	0.5
Cd	0.01	< 0.001	< 0.001	< 0.001	0.04
Cr	0.35	0.13	0.08	0.08	0.5
Cu	< 0.06	< 0.01	< 0.01	< 0.01	2
Mo	0.04	0.04	0.05	0.06	0.5
Ni	< 0.02	< 0.02	< 0.02	< 0.02	0.4
Pb	< 0.07	< 0.05	< 0.05	< 0.05	0.5
Sb	0.06	< 0.04	< 0.04	< 0.04	0.06
Se	< 0.05	< 0.06	< 0.06	< 0.06	0.1
Zn	0.02	0.09	<0.004	<0.004	4

Table 5 Analysis of chemical elements in the leachate (L / S = 10)

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 this 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 to 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 exhaustive study of durability is not performed in this article. It may be the object of another detailed study.

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