Thermo-physical characterization of mortars made with uncontaminated marine sediments

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In a context of sustainable development, civil engineering must increasingly use recyclable materials to preserve natural resources. Sediments could be a solution in the context of their recovery in several areas. Uncontaminated marine sediments were used to partially substitute sand aggregate in mortars formulation. Physical, chemical, mineralogy and mechanical characterization were carried out to investigate their possible use and impact in cemented-based materials. Five mortars were studied with different percentage of sand substitution. The effect of sediments on the mechanical and thermo-physical properties were assessed.

This paper focus on the characterization of the thermo-physical properties. The mortars hydration kinetics were investigated at different temperatures. The acceleration of the chemical reactions was also assessed through the determination of the apparent activation energy of mortars. The thermal conductivity and the specific heat capacity were also evaluated. The measured heat released of mortars raise with the increase of sediment content. This result suggests an additional chemical activity linked to the presence of sediments within the matrix. The thermal conductivity of mortars decreased while the specific heat capacity increased with the percentage of sand replacement. This can be attributed to the high porosity and low density of the sediment mortars.

Keywords: Dredged sediments, mortars, sand substitution, thermo-physical properties.

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I. INTRODUCTION

The accumulation of sedimentary particles at the bottom and on the edges of watercourses and shipping lanes as well as in seaports leads to their clutter. In order to maintain and restore these accesses, it is necessary to dredge or clean up regularly from coast and estuarine lines around the world. Due to the shortages of natural resources and the environmental restrictions on the establishment of new quarries as well as the sustainable development approach adopted by several countries, sediment management is increasingly oriented towards valorization processes by respecting technical, environmental and economic criteria [1].

The main objective of this paper is the valorization of uncontaminated marine sediments, not subjected to any specific high cost pre-treatments and the preservation of natural resources.

Sediments are used to replace sand in the manufacture of mortars where five formulations were studied. This research was carried out to demonstrate the feasibility of substituting sediments by sand aggregate. Physical, chemical, mineralogy and mechanical characterization of the dredged sediments were assessed in order to ensure a sustainable management of sediments and investigate their possible use and impact in cemented-based materials. In order to understand the phenomena behind this substitution, a complete thermo-physical study was conducted. The hydration kinetic was studied by isothermal calorimetry at three different temperatures 20°, 30° and 40°C. The activation energy that describes the acceleration of the chemical reactions was determined in order to explain the reactivity issues in the presence of sediments. Therefore, the study was completed by the determination of the thermal conductivity and the specific heat capacity of mortars.

II. MATERIALS AND METHODS

Physical characterizations of sediments were performed and results are gathered in Table 1.

Table 1. Physical characterization of marine sediments.

Density NF EN 1097-7	**Surface area BET** NF EN ISO 18757	**Organic matter (450°C)** XP P94-047	**Liquid limit** NF P94-051	**Plastic limit** NF P94-051	**Fine fraction (D<63 µm)** ISO 13320	**Clay fraction (D<2 µm)** ISO 13320
2.45 g/cm^3	134472 cm^2/g	10.9%	107%	46%	72.06%	7.13%

Five formulations of sediment-mortars were prepared. The compressive strength was determined on prismatic samples 4×4×16cm^3 in accordance with the European standard EN 196-1. The total porosity of mortars was also measured using Mercury Intrusion Porosimetry technique (Standard NF P 94-410-3). Table 2 depicts the composition of these mortars for 1l of volume, the obtained compressive strengths with the corresponding standard deviation of six measurements and the total porosity at 28 days of curing in water. The water to cement ratio was kept constant (W/C=0.5). The compressive strength of mortars decreased with the proportion increase of sediment. This can be linked to the influence of sediments on the cement's hydration and the increase observed in the total porosity where the presence of sediments modifies the pore structure of mortars.

TABLE 2. Composition of the sediment-based mortars (in 1L)

Mortar	**MT**	**MT5**	**MT15**	**MT30**	**MT40**
Sand substitution (%)	**0**	**5**	**15**	**30**	**40**
Cement CEM I 52.5R (g)	507	507	507	507	507
Sand (g)	1526	1450	1298	1068	916
Sediment (g)	0	95	285	570	760
Density (g/cm^3)	2.11	2.09	2.07	2.04	1.98
Compressive Strength (MPa)	67.91±1.09	59.53±2.52	42.62±3.37	21.57±2.12	15.44±0.98
Total porosity (%)	9.92	9.85	11.95	13.45	16.56

III. EXPERIMENTS

In this paper, a study on the thermo-physical properties was conducted to deepen our understandings on the influence of sediments and the mechanisms that can occur when incorporated in mortars. The hydration reaction being thermo-active, an isothermal calorimeter was used at three imposed temperatures (20, 30 and 40 °C). The device is represented in Figure 1. It is based on the measurements of heat flux using specific flux meters. It is composed of a carry sample and a thermal regulation system made up of two exchangers plates connected to two thermostatic baths to maintain a constant imposed temperature. The flux sensors are integrated into the surface of the exchanger plates.

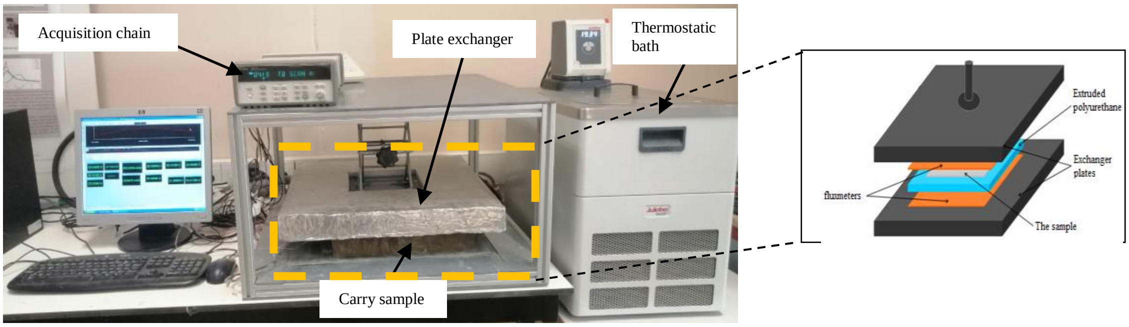

FIGURE 1. Isothermal calorimeter

For each formulation of mortar, the total flux, the hydration heat and the activation energy were determined. The activation energy of the formulated mortars was determined to understand the reactivity issues when substituting a given proportion of sand by sediment in cementitious matrix. In the case of concrete, previous studies have shown that the Arrhenius law was the most suitable to describe the chemical reactions acceleration, which is expressed as:

$$K(T) = A \exp\left(-\frac{Ea}{RT}\right) \tag{1}$$

where K(T) is the kinetic constant at temperature T, A is a proportionality constant (1/s), R is the perfect gaz constant (=8.314 J/(mol.K), E_a is the apparent activation energy (J/mol), T is the temperature (K).

In addition, the thermal conductivity (λ) of mortars was measured with the heat flux meter method, based on the EN 12664 standard. Same calorimeter device was used to determine λ. A temperature gradient is generated (ΔT = 10°C). Unidirectional flux is ensured in the central measurement area by means of the insulating boundary surrounding the sample. The thermal conductivity is calculated when the heat flux on both sample sides became equal and is expressed in Eq. 2 as:

$$\lambda = \frac{\sum \varphi \times e}{2 \times \Delta T} \tag{2}$$

with λ: thermal conductivity of the material (W. m^{-1}. K^{-1}), e: sample thickness (m), Σφ: sum of both recorded heat flux at the sample surface (W.m^{-2}) and ΔT: temperature gradient (°C).

The specific heat characterizes the ability of a material to store heat and represents the amount of heat per mass unit required to raise the temperature by one degree. It is determined based on the process of heat storage of the material. Between two different isothermal states (Tinit) and (Tfin), the sample stores an amount of energy (Q) that represents the system's internal energy variation. The material's specific heat (Cp) can then be calculated using Eq. (3).

$$Cp = \frac{Q}{\rho \times A \times e \times \Delta T} \tag{3}$$

with Cp: specific heat capacity (J. K^{-1}. kg^{-1}), e: sample thickness (m), ϱ: density (kg.m^{-3}), A: surface of the material in contact with the exchange plates, Q: stored energy (J) and ΔT: temperature gradient (°C).

IV. RESULTS AND DISCUSSION

The total flux of the mortars measured at 20, 30 and 40°C is presented in Figure 2. One can notice a delay of the hydration reactions when the percentage of sediments increase. This can be associated to the presence of some heavy metals such as Zinc (Zn) and to the presence of marine salts in sediments as shown by Minocha et al. [2]. In addition, it can be observed an increase in the maximum heat flux with the increase of sediment substitution. The physical characterization presented in table 1 show that 70% of the sediments have a diameter lower than 63 μm. The sediments have a certain chemical activity linked to their granulometry and mineralogical composition. At high temperature (40°C), there is an acceleration of the hydration reactions of cement. This effect can be highlighted by presenting the results of the activation energy in Table 3.

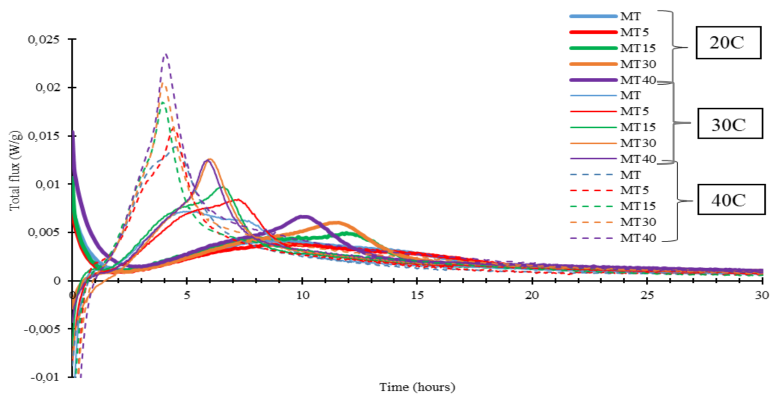

FIGURE 2. Total flux of the formulated mortars at imposed temperatures 20°, 30° and 40°C

It can be noticed that the apparent activation energy is higher when the substitution percentage of sediments is high for the two temperature pairs. This can be explained by the fact that higher energy is necessary to activate the hydration reaction of cement in the presence of the used sediments. This result confirms the decrease of the mechanical strengths shown in Table 1.

TABLE 3. Values of the apparent activation energy Ea (kJ/mol) determined by superposition method

Range of temperatures (°C)	MT	MT5	MT15	MT30	MT40
20-30	31.4	32.1	34.2	35.9	36.8
30-40	40.6	41.2	45.3	47.1	47.6

Figure 2 gives the evolution of the thermal conductivity and the specific heat capacity of the reference mortar (MT) and sediment-based mortars. The thermal conductivity of (MT) is 1.25

W.m^{-1}.K^{-1} which corroborates the values obtained in literature, then it linearly decreases to about 0.66 W.m^{-1}.K^{-1} for MT40. It ranges from 10% to 50% for MT5 and MT40 respectively. On the other hand, the specific heat capacity (C_P) linearly increases in the presence of sediments. It increases from 821 J/kg.K for MT to 1247 J/kg.K for MT40. It is observed that, for 40% of sand replacement, there is a 50% rise. These results can be linked to the high porosity observed in sediment-based mortars [3].

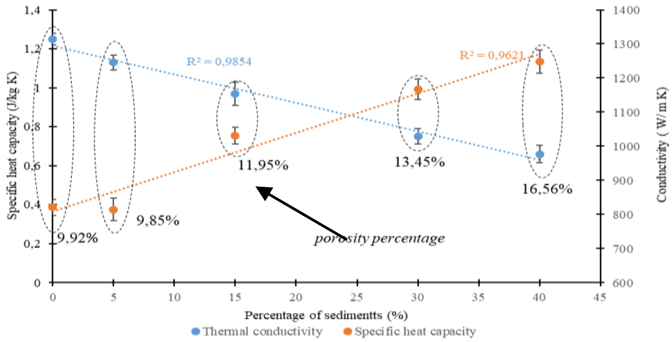

FIGURE 2. Evolution of the thermal conductivity and the specific heat capacity of mortars

V. CONCLUSIONS

From the mechanical and thermo-physical experimental results of this study, the uncontaminated marine sediments can be used as cementitious materials in mortars. The obtained properties confirm the possibility of sediments valorization depending on the intended applications. The total flux and heat released measured were higher in the presence of sediments. Sediments had a certain chemical activity linked to their granulometry and mineralogical compositions. A linear evolution of the apparent activation energy Ea was observed as function of sediments percentage. Higher energy was necessary to activate the hydration reactions in presence of sediments which confirm the decrease of the mechanical strengths. The thermal conductivity λ of mortars decreased while the specific heat capacity Cp increased with the percentage of sand replacement. This can be attributed to the high porosity and low density of the sediment-based mortars. MT is the mixture having the highest density correlated to the lowest value of Cp and highest value of λ. The higher the Cp value, the more the material retains stored heat and contributes to the insulation of the construction.

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