Formulation of ternary binders based on flash-calcined sediments and ground granulated blast furnace slag

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ABSTRACT This study aims on the proposition of ternary binder formulation based on flash calcined sediment (FCS) and ground granulated blast-furnace slag (GGBS). In addition, it is allowing the valorization of dredged sediments. Physical and chemical characterization were done for the used materials –ordinary Portland cement (OPC), FCS and GGBS. Five formulations were investigated in fresh and hardened state. Results showed the incorporation of FCS decreases the workability and increases the density. Moreover, the reduction of the initial setting time and the heat of hydration peak increses compared to BSM were observed. At the hardened state, the mixture containing 10% FCS showed higher mechanical strengths than those of reference mortar at 90 days. The use of FCS in ternary binders could contribute to the concrete environmental impact reduction with enhancing its mechanical performance.

Keywords Dredged sediment, flash calcination method, ternary eco-binders, environmental impact

I. INTRODUCTION

The cement industry produces 7% of the global CO_2 emissions [1]. It is estimated that the production of one ton of ordinary Portland cement (OPC) releases the equivalent of one ton of CO_2 into the atmosphere. CPO is mainly composed of clinker (more than 95% by weight) which is obtained after the transformation of raw materials (limestone and clay) by high-temperature firing (≈ 1 450 °C). As this process highly impacts the environment, it is necessary to find mitigating alternative solutions to reduce the amount of clinker used. The development of binders based on cement substituted by additions such as dredged sediments seems convincing. Indeed, these additions have a doubly beneficial environmental impact: on one hand, they allow the reduction of the amount of CO_2 released into the atmosphere by decreasing the amount of clinker used. On another, they allow the valorization of these products. In this context, this study was aimed at the formulation of ternary eco-binders composed of CEM I 52.5 N cement, ground-granulated blast-furnace slag (GGBS), and flash calcined sediment (FCS).

II. MATERIALS AND METHODS

A. Materials

The cement used is a CEM I 52.5 N (95% clinker and 5% mineral additions) compliant with European standard NF EN 197-1, 2012. A slag used was from Ecocem company compliant with NF EN 15167-1, 2006 standard where the vitrification rate was superior to 90%. Dredged sediments used as mineral addition are marine sediments dredged at Grand Port Maritime de Dunkerque (GPMD) harbour. Sediments were ground and sieved at 120 µm, then flash calcined at 820°C.

The physicochemical characteristics of the used powders are summarized in Table 1. FCS shows a finer granulometry with D_{50} = 5.75 µm, which is about two times less than OPC. This modification of fineness can be attributed to the grain densification of the sediment during the heat treatment process. The BET specific surface area of FCS is more significant than those of OPC and GGBS while the density of FCS is inferior to those of OPC and GGBS. According to the results of the X-ray fluorescence analysis, the major elements composing these materials are silica, alumina and calcium.

TABLE 1. **Physicochemical characteristics of the powders.**

	Characteristics	**OPC**	**GGBS**	**FCS**
Physical properties	Density (g/cm³)	3.21	2.91	2.64
	Surface area BET (cm²/g)	9 194	16 102	59 930
	D_{10} (µm)	1.01	1.04	0.95
	D_{50} (µm)	10.7	9.82	5.75
Major oxides (wt %)	Al_2O_3	5.10	10.8	8.00
	CaO	60.9	40.7	21.6
	Fe_2O_3	4.00	0.53	9.00
	MgO	1.16	6.23	2.00
	SiO_2	16.3	31.7	52.8
	ZnO	0.25	-	0.12

B. Methods

For the ternary structure (OPC + GGBS + FCS), 5 mortar formulations including three ternary formulations based on GGBS and FCS (TSM), one binary formulation (BSM), and one reference formulation (RM) were made according to NF EN 196-1 standard (see Table 2). For characterization study, different equipment's were used: Fluorescence X (FX) analysis S4 from Bruker, the BET specific surface area (NF EN ISO 18757) from Micrometritics, the laser granulometry (LS 13320 particle size analyser, Beckman Coulter).

To assess the effect of the presence of flash calcined sediments on the fresh mortar properties, the density (NF EN 1015-6, 1999), the air content (NF EN 1015-7), the flow table test, the heat of hydration by the Langavant adiabatic method (NF EN 196-9, 2010) were investigated. At the hardened state, compression tests and mercury porosimetry were carried out.

TABLE 2. **Composition of the blended cement (%).**

Index	**OPC**	**GGBS**	**FCS**
RM	100	–	–
BSM 50-0	50	50	–
TSM 40-10	50	40	10
TSM 35-15	50	35	15
TSM 30-20	50	30	20

III. RESULTS AND DISCUSSION

The fresh state properties are shown in Table 3. The flow table test results show that the use of FCS leads to a loss of workability, proportional to the rate of FCS. This can be explained by the specific surface area of FCS. An improvement in density was also noted with FCS. It is attributed to the fineness of FCS. Results show that the use of a ternary system comes with a reduction of the air content. Both BSM and TSM present a delay in the initial setting time compared to RM, attributed to the cement dilution effect as 50% of OPC is substituted. In fact, the amounts of cement components (especially C_3S) which are quickly hydrated in contact with water, are reduced [2]. Furthermore, the incorporation of FCS into the ternary system allows the reduction of this delay.

The heat of hydration results are presented in Fig 1. They show that the substitution of 50% of OPC by FCS and GGBS reduces the heat of hydration, from 231.07 J/g for RM to 146.29 J/g on average for TSM, and 112.25 J/g for BSM. This is due to the slow hydration of GGBS. Moreover, the presence of FCS in the ternary system increases the heat of hydration compared to BSM. Considering the fineness of calcined sediments (D_{50} = 5.75 μm) and their significant specific surface area, the pozzolanic reaction is sped up and particularly by the nucleation effect [3].

Also, the compressive strength increases with the curing age for all formulations (Fig. 1). At 14 days, the strength of RM is superior to that of BSM and TMS. The latter contains 50% OPC less and thus less C_3S which forms a resistant C-S-H gel upon its quick hydration in the short term. In addition, BSM and TSM long-term strengths increase significantly. TSM 40-10 formulation shows a strength that exceeds that of RM from 60 days of curing, which is evidence of the high level of reactivity of FCS. This activity is linked to the physical and chemical aspects of those sediments: their granulometry is very fine, and the flash calcination treatment allows obtaining spherical particles, thus constituting nucleation zones favourable to the formation of hydrates. On the other hand, the activation of certain clayey phases of sediments (including kaolinite) by flash calcination contributes to an increased pozzolanic reaction.

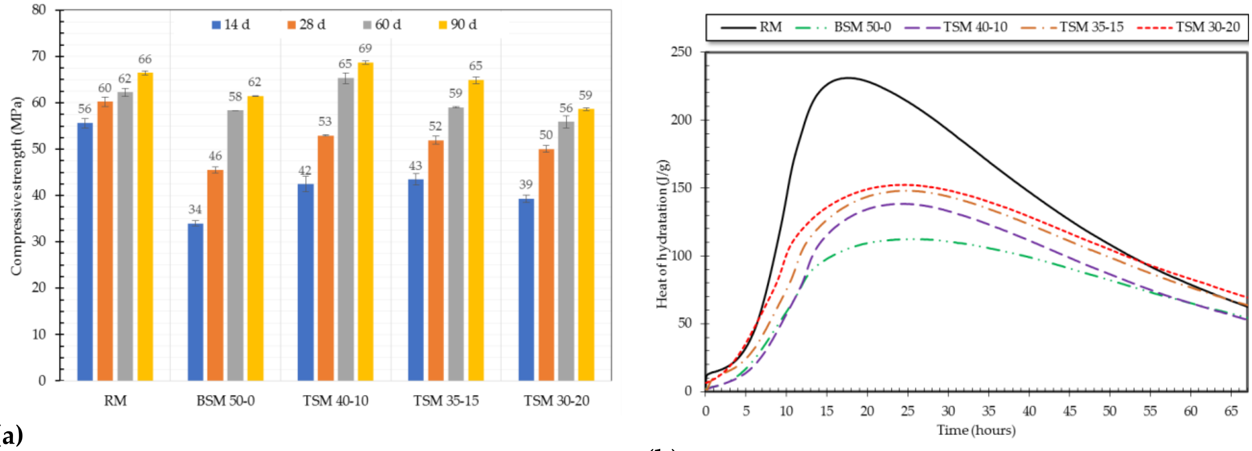
The results of porosity measurements are shown in Table 4. We note that all formulations have a total porosity between 7.12 and 12.55% and that porosities decrease for all studied materials with age. At 14 days, the porosities of TSM are similar to those of RM (12% on average). However, at 90 days, the porosities of mortars containing FCS are lower than those of the control mortar. This suggests that the pozzolanic activity of flash calcined sediments and slag generates new hydrates, which allows filling in the total porosity and improves the density of the structure.

TABLE 3. Properties of the mortars based on blended cement.

	RM	BSM 50-0	TSM 40-10	TSM 35-15	TSM 30-20
Fresh density (kg/m^3)	2 188	2 151	2 207	2 212	2 215
Air content (%)	7.2	6.6	4.0	4.1	4.5
Flow (cm)	22.4	22.0	21.5	21.0	18.7
Initial setting time (min)	256	338	318	311	308

TABLE 4. Total porosity of studied samples at 14, 28 and 90 days.

	RM	BSM 50-0	TSM 40-10	TSM 35-15	TSM 30-20
At 14 days (%)	12.46	16.44	12.37	11.84	12.10
At 28 days (%)	11.87	12.55	8.81	10.85	10.45
At 90 days (%)	11.10	8.25	7.89	7.12	8.81



(a)

(b)

FIGURE 1. **(a) Evolution of the compressive strength; (b) Evolution of the heat of hydration**

VI. CONCLUSIONS

This study focuses on the development of a ternary eco-binder composed of dredged sediment and slag as partial replacements for cement (up to 50%). The results of this study highlighted the positive impact of using ternary binders in a cement matrix on the mechanical properties of mortars. The characterization of mortars at the fresh state showed that using FCS reduces the workability of mortars, increases the density and decreases the air content proportionally to the rate of sediment. The substitution of 50% OPC by FCS and GGBS results in a lower hydration heat peak and a delay in the initial setting time. The characterization at the hardened state (compressive strength) showed that the use of 10% FCS combined with 40% GGBS and 50% OPC (TSM 40-10) results in mechanical properties at 90 days superior to those of the control mortar RM composed of 100% OPC. The study of porosity comforts this result, it showed that using FCS reduces the total porosity of the matrix.

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