Properties and hydration behavior of blended clinker and portland-sediment cement pastes

Ez-zaki H.[1], Diouri A. [1], Kamali-Bernard S. [2], Dang T.A.[2], Sassi O.[3] and Bernard F.[2]

[1]: Laboratoire de Chimie du Solide Appliquée, Faculté des Sciences, Université MohammedV-Agdal- Rabat-Maroc
[2] : Université Européenne de Bretagne, Laboratoire de Génie Civil et Génie Mécanique (LGCGM), Institut National des Sciences Appliquées, 20 Avenue des Buttes de Coësmes, 35043 Rennes Cedex, France
[3] : Laboratoire de Physico-Chimie des Matériaux, Ecole Normale Supérieure, Rabat-Maroc

Abstract. In recent years, an increase of the interest in the use of secondary raw materials (sediment, sludge…) in construction has been observed. This paper aims to contribute to the use of dredging sediments in the cement industry. Despite the literature on this subject, the available data on the aspects and phenomena related to the hydration process of such mixtures are incomplete. This paper aims to specify the calorimetric curves of hydration of mixtures made, from the sediment trapped at the site of Lyvet in the Brittany region of France. The mixtures are made using in one hand clinker and in the other hand Portland cement. Pastes with 8%, 16% and 33% of clinker or Portland cement substituted by sediment are used to determine the hydraulic properties of mixtures. The physico-chemical characterization of materials is made by different techniques to determine the chemical composition and physical properties. X-ray diffraction is used to determine the mineralogical compositions of samples before and after treatment. A Tian-Calvet microcalorimeter is used to explore hydration behavior of the blended Sediment-Portland cement pastes. The addition of untreated sediment to both clinker or Portland cement increase the dormant period duration. On the contrary, this period becomes shorter when the sediment is thermally treated. The results show that 8% of treated sediment improve hydration of blended Sediment-Portland cement pastes. Mechanical properties of blended sediment-cements are also investigated. After 28 days of curing in water, the mortar containing 8% of treated sediment exhibits a compressive strength equal to 93.7% of the one of the reference mortar, maintaining it in the same cement class (52.5).

1 Introduction

In recent years, environmentally sound solutions using dredged materials in construction are encouraged to be found. The dredged materials are usually soft soils with high natural water content. Many researchers have studied the mechanical properties of cement mixtures with dredged materials[1-8]. Most of these studies have focused on the influence of types of cementitious binders, binder content, water-to-binder ratio and curing conditions on mechanical properties of mixtures.
Different fields of valorization of dredged sediments as building materials were investigated in the literature. Agostini et al. have studied a possible valorization process for the treatment of contaminated dredged sediments and their use as aggregates [8]. The process is based on the stabilization of heavy metals and on the thermal elimination of organic matter. The treated sediment aggregate, composed by clay, silt and sand, is introduced in cement-based materials at different substitution ratios. An optimum substitution ratio has been observed around 33% with up to 20% of strength increase. The study proved the practical feasibility of the studied valorization process. Nevertheless, additional formulations and tests are required to improve the understanding of complex interactions mechanisms.
The use of sediments in the road engineering has been studied by several authors [2-4]. Kamali et al. [3] have proposed economical sediment-based mixtures fulfilling the criteria required for a use in foundation and base road layers. The robustness of the mixtures is furthermore checked performing sensitivity studies on water content. The use of sediments in cement industry has been investigated by a few researchers [5-7]. Properties, behavior and performance of cementitious materials based on sediment-cement depend mainly on the nature and structure of cement matrix that binds together all the components. Therefore, knowledge of the nature and the structure of the formed hydrates formed are essential to understand and control the properties of these new building materials..

This paper deals with the early hydration and structure development aspects of cement-sediment based systems.

2 Localisation and origin of sediment rocks

The used sediment comes from the Lyvet Rance trap located in Brittany region in France. The site was built in 2000; as a sediment trap to counter sedimentation downstream from power plant. Once the trap is full of sediment, the dredging operation is performed.

Samples of sediment from this trap were taken and studied in laboratory. The studied sediment was firstly washed by water in order to decrease its salinity and then dried at 20°C using air drying machine. The sediment is then ground and stored in closed bags before characterization. More details on the preparation of the sediment can be found in Tang et al [6].

3 Experimental

In the first part of the experimental work, the physical, chemical and mineralogical characterization was performed. In the second part, the hydration of mixtures of clinker, portland cement and different percentages of sediment was characterized using calorimetric technique. The heat generated by the hydration reactions is measured. In the last part, the compressive strength of the blended cements-sediments binders is investigated.

3.1 Materials

3.1.1 Raw sediment

The water content of the studied sediment was determined by drying three samples at 60°C until a constant weight. The water-to-solid content was estimated at 66%.
Particle size distribution test was carried out using a Cilas 1180 laser diffraction machine, one hand on the gross sediment after mechanical dispersion of the material in sodium hexametaphosphate, and in another hand on samples free of organic matter (MO) attacked by hydrogen peroxide and then dispersed in sodium hexametaphosphate. The granulometric curves of the sediment are given in Figure 1. It seems that the organic matter probably plays a role of glue that sticks the fine-grained sediments. The disappearance of organic matter release more small grains.
Chloride content measurements were performed using an ion meter machine. The measurements were performed on the raw sediment after a thermal treatment at 105 ° C during one hour. The chloride content is found to be equal to 2.84 g/l, this value is reduced to 0.58 g/l by simple washing with water.

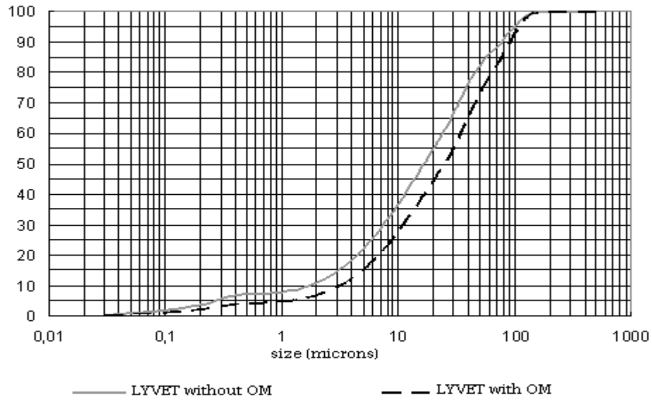

Fig. 1 Granulometric curves of Lyvet sediment with and without organic matter (OM)

The metal content of Lyvet sediment is determined in order to determine its potential pollution. The chemical analysis of the metallic elements was done. The results are presented in Table 1.

Table.1. Total concentrations of major and trace elements of the Lyvet sediment [5]

Element	**Dosage (g/Kg)**	**Trace elements**	**Dosage (mg/Kg)**
Silicium	188.68	Zinc	151
Calcium	67.05	Chromium	44
Iron	31.45	Lead	39
Aluminum	27.94	Copper	27
Sodium	10.74	Nickel	25
Magnesium	9.55	Arsenic	18.03
Potassium	6.35	Mercury	0.64
Sulfur	3.19	Cadmium	<0.42
Titanium	0.62		
Manganese	0.32		

3.1.2 Studied sediments and mineralogical characterization

Dang et al [6] have previously shown the benefic effect of a thermal treatment at 650°C during 5 hours of Lyvet sediment. Thus, thermally treated (LT) and untreated (L) Lyvet sediment material were considered in this paper.

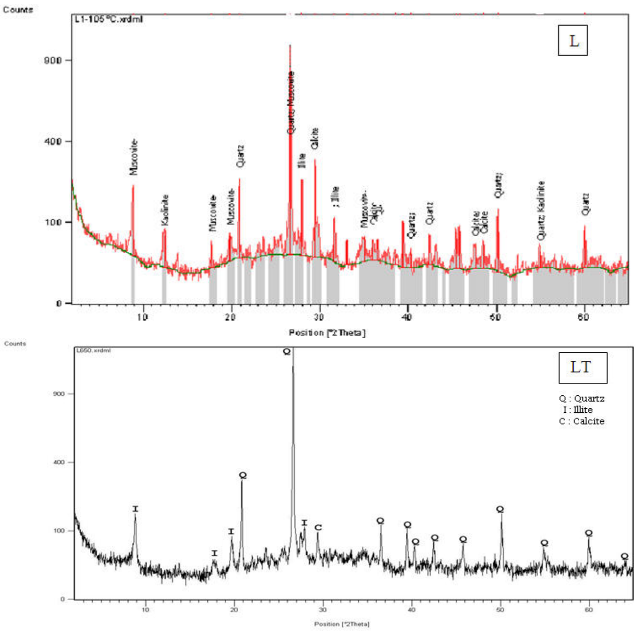

Fig. 2 Diffractograms of untreated sediment (L) and thermally treated sediment (LT).

The mineralogical characterization is performed using X-ray diffraction machine operating at 30 kV and 20 mA with Cu anode.. The sediments were dried at 105°C to remove free water and then ground before X-ray analysis. Figure 2 shows the diffractogram obtained for L and LT sediments.

Mineralogical analysis shows the presence of quartz, calcite, kaolinite and illite on L sample and illite, quartz and calcite on LT sample.

Above the temperature range of dehydroxylation, kaolinite transforms into metakaolin, a complex amorphous structure which retains some long-range order due to layer stacking [9,10].

3.1.3. Cementitious materials

Clinker, composite cement type CEM II (with a minimum of 65% of clinker and a maximum of 35% of additions like limestone, fly ash, pozzolans) are used for the hydration analysis. The mechanical tests were performed on standardized mortars using CEM I52.5 portland cement.

Chemical and mineralogical composition of the used clinker is listed in table 2.

Table. 2. Chemical analysis and characteristics of clinker

Chemical analysis	**%**
SiO_2	20.85
Al_2O_3	4.91
Fe_2O_3	3.37
CaO	66.26
MgO	1.11
SO_3	1.53
K_2O	0.85
TiO_2	0.34
MnO	0.07
P_2O_5	0.26
Na_2O	0.10
Mineralogical composition	
C_3S	61.79
C_2S	13,.25
C_3A	7.31
C_4AF	10.26
CaO_f	1.68

3.2. Blended mixtures

Different mixtures based on L and TL sediments, clinker and CEM II cement are performed. The composition and the notation of the different mixtures are given in Table 3. The hydration of these mixtures is then studied on pastes using Tian-Calvet microcalorimeter.

Table. 3.Composition of the mixtures in percentage and mixtures notation

Sample	**Clinker (K)**	**Cement (C)**	**Sediment (L)**	**Treated sediment (LT)**
K	100	-	-	-
KL8	92	-	8	-
KL16	84	-	16	-
KL33	67	-	33	-
KLT8	92	-	-	8
KLT16	84	-	-	16
KLT33	67	-	-	33
C	-	100	-	-
CL8	-	92	8	-
CL16	-	84	16	-
CL33	-	67	33	-
CLT8	-	92	-	8
CLT16	-	84	-	16
CLT33	-	67	-	33

4. Results and discussion

4.1. Hydration behavior

The isothermal test results of heat generation rates (mW) as a function of time, of all mixtures are illustrated in figures 3 and 4. The reacting components were firstly tempered until an “equilibrium state” (temperature equilibrium) was reached. Then, the liquid component (water) is added to the powder mixture. The heat of hydration reaction was then measured continuously for the specified time interval. The curves are divided into the three stages of hydration. The first period corresponds to the initiation by wetting the samples. The second period corresponds to the dormant period during which there is dissolution of the ions. The third period corresponds to the setting and hardening period.

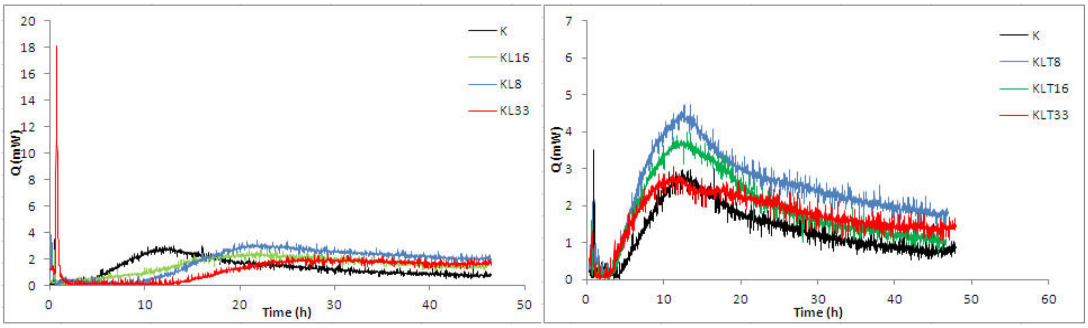

Fig. 3 Calorimetric curves of mixtures of clinker with untreated (L) and thermally treated sediments (LT).

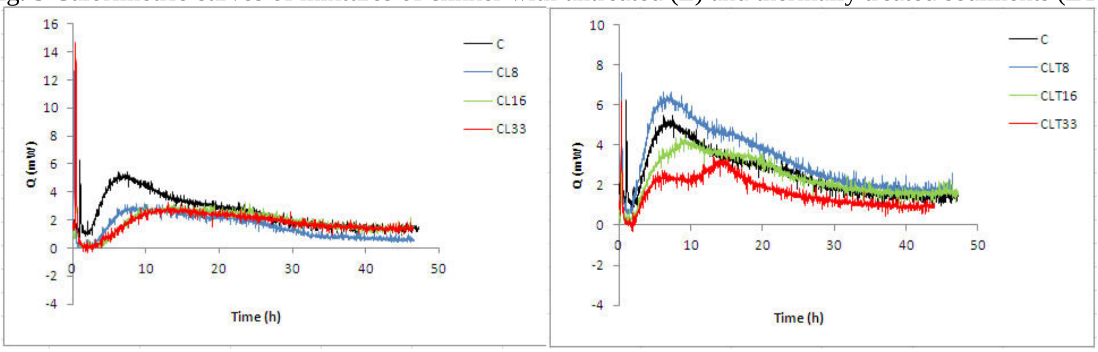

Fig. 4 Calorimetric curves of mixtures of CEM II cement with untreated (L) and thermally treated sediment (LT).

The calorimetric curve analysis allows identifying the characteristic values of the dormant period and setting times. These values are reported in Tables 4 and 5.
General observations from these results show that the addition of untreated sediment (L) to clinker increases the dormant period according to the percentage of the addition, from 232 min for single clinker (K) to 744 min for clinker with 33% of L sediment (KL33). An increase of the dormant period from119 min (KLT8) to 133 min (KLT33) was observed according to the percentage of treated sediment (LT). These periods are relatively reduced compared to the single clinker (K) (232 min) and the clinker with untreated sediment (296-744 min).
The observed heat effects show a large increase for KLT samples based on blended clinker with LT sediment.These heating effects can cause greater hydraulic reactivity which can be explained by the effect of co-grinding and surface area of blended clinker in the presence of metakaolin formed from the sediment after heat treatment at 650 ° C. Lagier et al. [11] have studied the influence of metakaolin on early age of Portland cement hydration, they conclude that the higher surface area of metakaolin had a great effect on enhance of dissolution of cementitious phases, well-dispersed sites for nucleation of hydration products. The delay observed in the dormant periods of KL mixtures is consistent with the results of Janotka et al. [12] who observed a similar effect on samples of cement mixed with sand metakaolin.

Table. 4. Characteristic values of dormant period and setting times of mixtures of clinker with L and LT sediments

	First pic		Dormant period			Second pic		Third pic	
Sample	$Q_{1(mW)}$	$t_{1(s)}$	$t_{i\,(min)}$	$t_{f\,(min)}$	Duration = $t_f - t_{i\,(min)}$	$Q_{2(mW)}$	$t_{2\,(h)}$	$Q_{3(mW)}$	$t_{3(h)}$
K	3.70	108	14	246	232	2.78	11.45	-	-
KL8	3.89	144	7	303	296	3.08	21.2	-	-
KL16	2.60	72	24	555	531	2.39	20.18	-	-
KL33	18.43	216	36	780	744	1.94	25.42	-	-
KLT8	2.25	72	9	128	119	4.54	11.88	-	-
KLT16	1.67	72	12	140	128	3.75	11.55	-	-
KLT33	1.37	252	29	162	133	2.78	11.49	2.46	16.81

Table. 5. Characteristic values of dormant period and setting times of mixtures of cement with L and LT sediments

	First pic		Dormants period			Second pic		Third pic	
Sample	$Q_{1(mW)}$	$t_{1(s)}$	$t_{i\,(min)}$	$t_{f\,(min)}$	Duration= $t_f - t_{i\,(min)}$	$Q_{2(mW)}$	$t_{2\,(h)}$	$Q_{3(mW)}$	$t_{3(h)}$
C	6.48	180	74	144	70	5.30	6.74	2.94	24.34
CL8	12.89	180	33	187	154	3.53	7.33	2.26	22.76
CL16	8.65	360	30	240	210	3.01	10.5	2.82	15.07
CL33	15.01	180	28	243	215	3.11	13.4	-	-
CLT8	7.67	216	42	90	48	6.53	6.16	4.66	14.81
CLT16	5.86	180	24	120	96	4.23	8.97	3.52	17.87
CLT33	6.19	216	20	150	130	2.39	5.26	3.17	14.30

According to the obtained results, the dormant period of cement paste is shorter than the one of clinker paste. The addition of untreated Lyvet sediment (L) to CEM II cement increases the dormant period according to the percentage of the addition, 70 min for single cement (C) to 215 min for cement with 33% of L sediment (CL33). When treated sediment (LT) is added, the dormant period increases with the percentage of the addition, 48 min for cement with 8% of treated Lyvet (CLT8) to 130 min for cement with 33% (CLT33). The dormant periods of cements with LT sediment are shorter compared to those of untreated sediment (L).

The CLT mixtures (cement-treated sediment) show a high calorific effect for only one sample CLT8 at 8% of treated sediment, this highlights an optimal composition with good hydraulic reactivity which weakened progressively by increasing the amont of sediment addition (16% and 33%). Another important effect is observed on the samples CLT16 and CLT33 by an exothermic effect which appears to occur between the cements and treated sediment, particularly observed at approximately 17 h. These reactions seem to be most closely associated to the "third peak" observed in calorimetry, that which is most often related to the reaction of calcium aluminate phases and metakaolin [11].

In conclusion to this calorimetric study, the addition of L sediment, both to clinker and cement acts by increasing the dormant period. Except for 8% of LT sediment, this remark is also valuable for the addition of thermally treated sediment (LT) to CEM II cement. In contrary, the addition of thermally treated sediment to clinker decreases the duration of this period. An important calorimetric effect is observed on cement-treated sediment with 8% of LT sediment (CLT8).

4.2. Compressive strength of blended binders

Compressive strength of different binders based on CEM I 52.5 portland cement and the studied sediments was investigated. Thre three substitution rates (8%,16% and 33%) of portland cement by L and TL sediments were considered. The strength class of the different sediment based binders was determined according to EN 196-1 standard [13]. Thus, standardized mortars were performed and then tested in compression after 28 days of curing in water. The mechanical tests were performed using an Instron® machine. The tests are monitored with a speed of 0.5 mm / minute. Figure 5 shows the evolution of the compressive strength at 28 days.

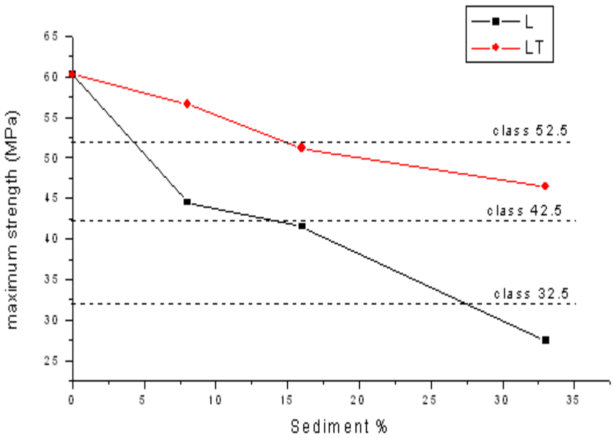

Fig. 5 Compressive strength at 28 days in function of the percentage of L and LT sediments in the blended binders

Replacing a portion of the CEM I cement by L or LT sediment, results in a decrease of the compression strength. These results are normal since the added sediments have less performance than portland cement. The results show that the compressive strength of the control mortar is 60.3 MPa after 28 days curing in water. For the mortar containing 8% of treated sediment, a value of 56.6 MPa was obtained. This value is higher than 52.5 MPa. This result is consistent with the high hydraulic reactivity of the same proportion of sediment in the sample CLT8 observed in calorimetric measurements.

One can conclude that the CLT8 binder remains in the 52.5 strength class, while the mortars containing 8% of untreated sediment (L) provide lower resistance and can be considered in 42.5 strength class. Samples with 16% and 33% of untreated sediment can be considered in 32.5 strength class.

5. Conclusions

The environmental challenges should involve the use of recycled materials instead of natural resources. This paper has studied the possibility to reuse of sediment as an addition material to conventional portland cement

From the discussed results presented above, the following preliminary conclusions can be made:

• The calorimetric study shows that the addition of untreated sediment, both to clinker and cement acts by increasing the dormant period. Except for blended binders with 8% of thermally treated sediment, this remark is also valuable for the addition of thermally treated sediment to CEM II cement. In contrary, the addition of thermally treated sediment to clinker decreases the duration of this period.

• A large increase of calorimetric effect for KLT samples based on blended clinker with thermally treated sediment. These heating effects can cause greater hydraulic reactivity which can be explained by the effect of co-grinding and surface area of blended clinker in the presence of metakaolin formed from the sediment after a thermal treatment at 650°C.
• An important calorimetric effect is observed on blended cement-treated sediment binder for only one sample CLT8 with 8% of thermally treated sediment. This highlights an optimal composition with good hydraulic reactivity which weakened progressively to adding sediment (16% and 33%).
• The exothermic effect associated with the “third peak” observed on the samples CLT16 and CLT33, particularly observed at approximately 17 h, is most often related to the reaction of calcium aluminates phases and Metakaolin.
• Replacing a portion of portland cement (CEM I) by sediment, results in a decrease, more or less important, of the compression strength. These results are normal since the added sediments have less performance than portland cement. The binder containing 8% of thermally treated sediment remains in the same strength class of the control portalnd cement (here 52.5 class). This result is consistent with the high hydraulic reactivity observed in calorimetric measurements for the same proportion of sediment. Blended binders with untreated sediment (L) provide lower resistances. Binders with 16% and 33% of untreated sediment can be considered in 32.5 strength class.
As a general conclusion, the use of sediment in substitution of conventional cement is possible and mainly in applications that do not require high mechanical strength. This can have a significant impact on the environment, on one hand by the recovery of the waste sediment and in the second hand by the gain in energy as well as in CO2 emissions related to the manufacture of clinker.

Acknowledgement

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