New experimental approach of the use of sediments in a cement matrix.

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RÉSUMÉ. *Dans cette étude, des sédiments sont utilisés comme matière première secondaire en substitution du ciment moyennant un traitement préalable. Le traitement envisagé est un traitement physique par broyage et séparation afin d'obtenir différentes fractions, par voie sèche (1000µm, 250µm, 120µm) et par voie humide (250µm et 120µm). Ils sont par la suite traités thermiquement à des températures de 650°C, 750°C et 850°C pendant 1 heure et 3 heures, dans le but de les activer chimiquement par décarbonatation ou activation pouzzolanique du matériau.*

Différents essais de caractérisation ont été effectués. La détermination des caractéristiques physiques et chimiques principales est obtenue grâce à des essais de : granulométrie, masse volumique spécifique, la surface spécifique BET, estimation temps de début de prise ainsi que la chaleur d'hydratation par calorimétrie Langavant. Les essais chimiques menés sont entre autres : l'analyse ATG, la diffractométrie au rayon X (DRX) et la fluorescence X (FX), qui ont permis de quantifier les fractions, phases et éléments chimiques présents. Les essais à la compression ont été effectués conformément au NF EN 196-1 à des échéances de 7 jours – 14 jours - 28 jours and 60 jours sur l'ensemble des mortiers formulés : les mortiers à base de ciment CEM I 52.5N (OPC), sur ceux substitués à des taux de 8% et 15% par le sédiment traité. Ceux-ci ont permis de relever un apport dû à la l'activité confirmée par des essais de calorimétrie ou du point de vue physique à une possible nucléation hétérogène autour des grains de sédiment.

MOTS-CLÉS*: Sédiment, Caractérisation, Broyage, Traitement Thermique, Substitution.*

ABSTRACT*: In this study, a sediment was used as a secondary raw material in cement substitution with prior treatment. The treatment adopted is a physical treatment involving grinding and separation to obtain different fractions, using a dry method (1000µm, 250µm, 120µm) and washing method (250µm and 120µm). They were subsequently heat treated at temperatures of 650°C, 750°C and 850°C for 1 hour and 3 hours, in order to enable chemical activation by decarbonation or by pozzolanic activation of the material.*

Different characterization tests were performed. The determination of main physical and chemical characteristics was obtained through multiple techniques: particle size distribution, specific density, the BET surface area, the initial setting time and hydration heat calorimetry Langavant. The chemical tests include: ATG analysis, X-ray diffractometry (XRD) and X-ray fluorescence (XRF) which were used to quantify the fractions, phases and chemical elements present. Compression tests were performed conforming NF EN 196-1 French standard, over terms of 7 days - 14 days - 28 days and 60 days on all formulated mortars: reference mortar based on 100% CEM I 52.5N binder (OPC) and cement substituted mortars with 8% and 15% by treated sediment. This clearly evidenced contribution due to chemical activity which was confirmed by calorimetry monitoring and strength investigation.

KEY WORDS*: Sediment, Characterization, Grinding, heat treatment, Substitution.*

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1 Introduction

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 [ZAC 12], the recycling and the use of sediment as resource (USAR, SETARMS, SEDIBET project, etc.) is considered as a suitable solution for a sustainable development. 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. This is established as a solution to reduce the high rates of CO_2 emissions. Cement consumption in France has meanwhile reached almost 15.6 million tons in 2015. This represents a considerable financial wealth and environmental weight. Therefore, sediments can potentially be used as materials building sector [MIL 01]–[BEN 15]. The construction sector uses a huge volume of concrete amounting to over 20 billion tons a year. Also concrete possesses a high carbon footprint, being responsible for 7% of CO_2 emissions of industrial origin worldwide. Nowadays, much mineral addition are used in cement based material to reduce cost or involve performance (Metakaolin, Silica fume, Fly ash, etc)[GHR 07]–[KHO 10]

However the beneficial use of dredged material is strongly controlled by some parameters: mineral composition, grain size distribution, physical and chemical characteristics [JUN 15]. Moreover, in this purpose of a beneficial use, a number of scientific challenges need to be solved. Among these, the possible content of sediment in inorganic contaminants such as heavy metals (lead, copper, chromium, etc), salts, cyanides, etc. But also as organic hydrocarbons: PAHs, PCBs, TBT [ROZ 15]. Studies in recent years on the beneficial use of sediments in the concrete showed that this material could be used as supplementary cementitious materials either in substitution or in addition to the cement as well as in the granular skeleton [BEN 09]–[GAS 15]. However their use can have an influence on the characteristics of the fresh concrete (the rheology) [ROZ 15], [BEN 09] and on hardened concrete (the mechanical strength, or the durability) [GAS 14], [TIR 13].

Sediments, because of their mineralogical and chemical constitution (silicious, 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. In this approach, the economical aspect is highly important particularly as regards the reduction of treatment cost. Adequate heat treatment at between 650 °C and 850 °C can provide multiple benefits for cementitious matrices from the economic, environmental and mechanical standpoints. The choice optimal fraction methodology is given in Figure 1. The sediments used in this study are extracted from the Grand Port Maritime de Dunkerque (GPMD).

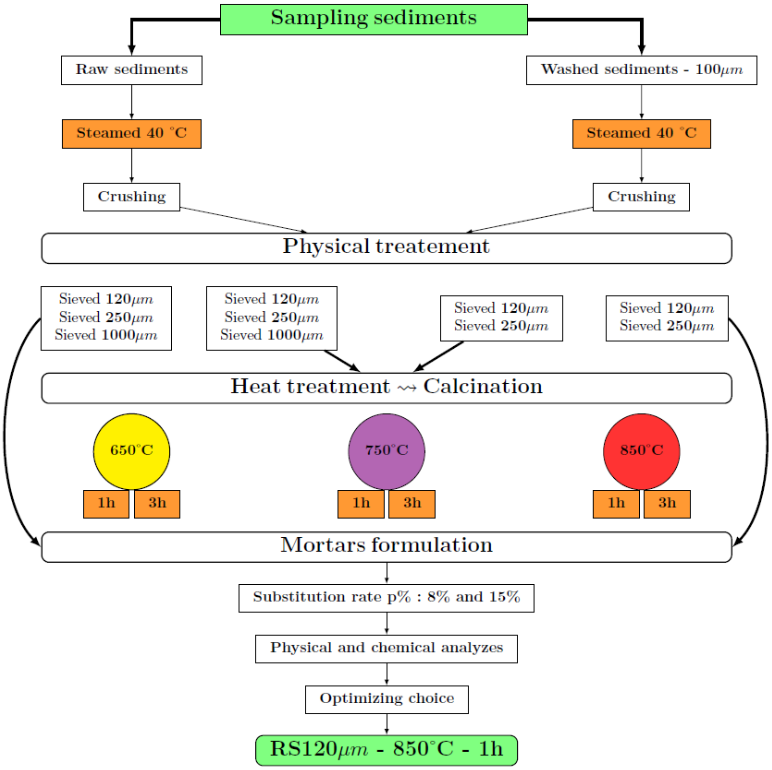

Figure 1.*Organization chart of the physico-thermal method applied as treatment*

2 Material and methods

2.1 Characterization techniques

All used materials were characterized using physical and chemical methods. The granulometry analysis was performed using a COULTER LS12330. This laser device allows determination of granular particle distribution under 1µm. Compressive strength were performed using three prismatic test sample 4x4x16 cm (NF EN 196-1 [AFN 06a]) in each test.

The heat release test using a semi-adiabatic CALORIMETER CERILH (method Langavant) according to the NF EN 196-9 [AFN 10] standard was also carried out during the first seven days. The apparatus is 400*160 mm with a dewar thermally sealed container.

In the laboratory scale, technical aspects are prioritized on the economic side. However we are currently conducting investigations for which the first results authorize to target a heat treatment cost less than 50 €/T with 16 €/T go to calcination only (about 1.2 MJ/kg to 2.3 MJ/kg) [INS 13], [EUR 09] and the electricity cost is 50 - 60 € TTC/MWh in France. This have to be added the cost of grinding, transport and storage. Also, the released gases during the heat treatment are studied in order to estimate the carbon footprint by infrared techniques. That guaranties that the efficient use will be more beneficial than using 100% cement binder. The choice of the firing temperature and duration was based on a 3-parameter optimization study were the stabilization of mass, grain size and time of calcination. This calcination technique does not target at this current research stage, a specific application but only the use of treated sediment as supplementary cementitious admixture such metakaolin, fly ash, etc. The notation showed in Table 1 will be used in the following of this paper.

Table 1. *Description of notation used.*

Raw sediment		***Washed sediment***		***Calcined sediment (D_{max} =120 µm)***
RS1000	D_{max} =1000 µm	---	---	SC650T1 → 650°C-1h SC650T3 → 650°C-3h
RS250	D_{max} =250 µm	WS250	D_{max} =250 µm	SC750T1 → 750°C-1h SC750T3 → 750°C-3h
RS120	D_{max} =120 µm	WS120	D_{max} =120 µm	SC850T1 → 850°C-1h SC850T3 → 850°C-3h

2.2 Granulometry analysis

In this study, the materials used were exclusively smaller than 2 mm in size and hence the logical and suitable option was to use laser granulometry. The granulometric analysis was carried out on all the studied fractions and was found to reveal differences between the raw and treated fractions.

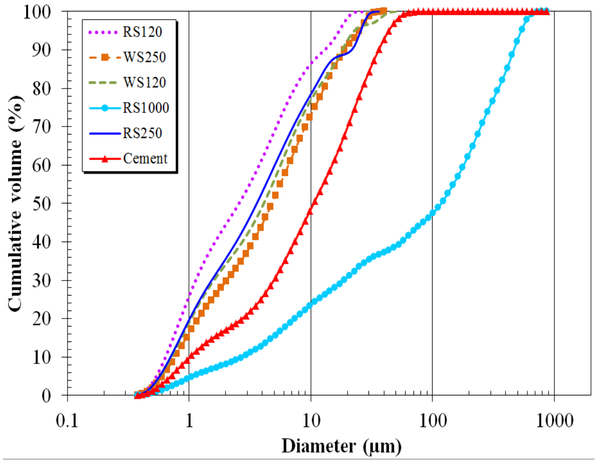

Figure 2. *Granulometric analysis on RS120, WS and OPC.*

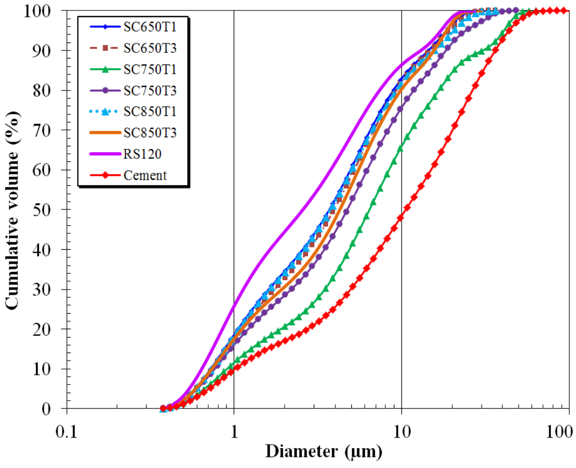

Figure 3. *Granulometric analysis on RS120, SC and OPC*

Except for the 1000µm fraction, the sharpness of the particles concentrates in a zone lower than 100µm (see Figure 2). In addition, the sediments prepared by the dry process were finer than the sediments prepared using a wet process as shown in Figure 3. This must be the fact of washing process that remove matter (organic for instance) around sediment grain patterns displays the granulometric analysis results performed on calcined sediments. These results indicate that the calcination has modified the sharpness and external form of particles. This infer to conclude that the coarser grains would sinter through a welding of grains or swelling phenomenon occurring under the effect of heat [RAM 08], [BER 14]. However these effects are non-linear because the higher the temperature, the lower the coarse grain (Figure 3).This leads to argue that that different physico chemical and relatively complex phenomenon occurs during calcination processes as assessed by Ramaroson et al.[RAM 12].

2.3 Chemical analysis

The chemical analysis consisted of determining the proportion of each chemical element by X-Ray Fluorescence (XRF). It has revealed the presence of main chemical elements: Oxygen (~50%), Silicon (~16.6%) and Calcium (~15%). These values are close to those found in previous studies [DUB 06][TRA 09] conducted on sediments from GPMD. There is some difference between calcined sediment and RS120 with for main oxide constituent: SiO_2, CaO, Al_2O_3, Fe_2O_3. These results tend to confirm that the calcination processes should have some impacts on chemical composition regarding changes between RS and SC material. Also, Table 2 and Table 3 summarize the chemical analysis results.

Table 2. *Major chemical elements RS120 and SC850T1 by XRF (%)*

Elements	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**Mn**	**Fe**	**Zn**
CEM I-52.5N	38.9	0.5	0.7	2.7	7.6	0.2	1.8	0.1	0.6	43.5	0.2	Traces	2.8	0.2
RS120	50.1	1.1	1.5	5.1	16.6	0.2	1.8	0.9	1.5	15.0	0.3	0.1	5.5	0.05
SC850T1	45.2	1.6	1.4	5.0	17.4	0.2	2.6	1.4	1.5	15.2	0.2	0.1	5.7	MTE$^{(*)}$

Table 3. *Oxide composition of RS120 and SC850T1 by XRF (%)*

	Na_2O	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**ZnO**
CEM I-52.5N	0.3	0.8	5.1	20	0.46	3.1	0.8	63.5	0.33	0.13	3.4	0.25
RS120	2.0	2.0	8.2	51.9	0.4	0.2	1.9	22.1	0.4	0.2	9.3	0.1
SC850T1	2.2	2.3	9.45	47.2	0.5	6.49	1.81	21.2	0.3	0.1	7.33	MTE$^{(*)}$

***MTE**= Metallic Trace Elements

3 Physico chemical impact of the presence of sediment in the cement matrix

In this study and for the following results, the reference mortar is named RM (100% cement binder) and mortar based on the treated sediment are designated MSC (MSC8 = 8% substitution rate and MSC15=15% substitution rate).

3.1 Measure of the heat of hydration

Because of their geomorphological origin, sediments have an impact on the cementitious matrix. This impact can be beneficial or disadvantageous. Indeed the presence of lime, which comes from the thermal transformation of Calcite, can enhance hydration reactions. However, the presence of constituents such as Zinc (Zn), Cadnium (Cd) or the Chromium (Cr) for instance, can modify the hydration processes and the setting of mortar. Some constituents can also disrupt the mechanisms which habitually lead to the formation of hydrates (CSH) or the pores network [MIN 03]–[MAL 06].

The aim of this test was to determine the heat of hydration of mortar with the sediments SC850T1. The method uses a semi-adiabatic calorimeter (Langavant method) according to the NF EN 196-9 standard. The principle of this test is to monitor the evolution of temperature and heat in the measuring cells. The composition of three mortars studied is given in Table 4.

Table 4. *Composition of the RM and MSC (8% and 15%) in evaluation of the heat of hydration (NF IN 196-3)*

Constituent	*RM*	*MSC8*	*MSC15*
Cement CEM I 52,5 N (g)	360.0	331.2	306.0
SC850T1 (g)	---	28.8	54.0
Normalized quartz sand (g)	1080.0	1080.0	1080.0
Water (g)	180.0	180.0	180.0
Total mass (g)		1620,0	

The tests results expressed in terms of heat of hydration are plotted in patterns Figure 4. The expression of heat can be deduced from the expression in Eq [1] :

$$Q = \frac{C}{m_c}\theta_t \qquad (1)$$

Where:
C= Total heat capacity (J/ K)
θ_t=Temperature difference between the reference cell and measuring cell (K);
m_c=Mass of cement (g)

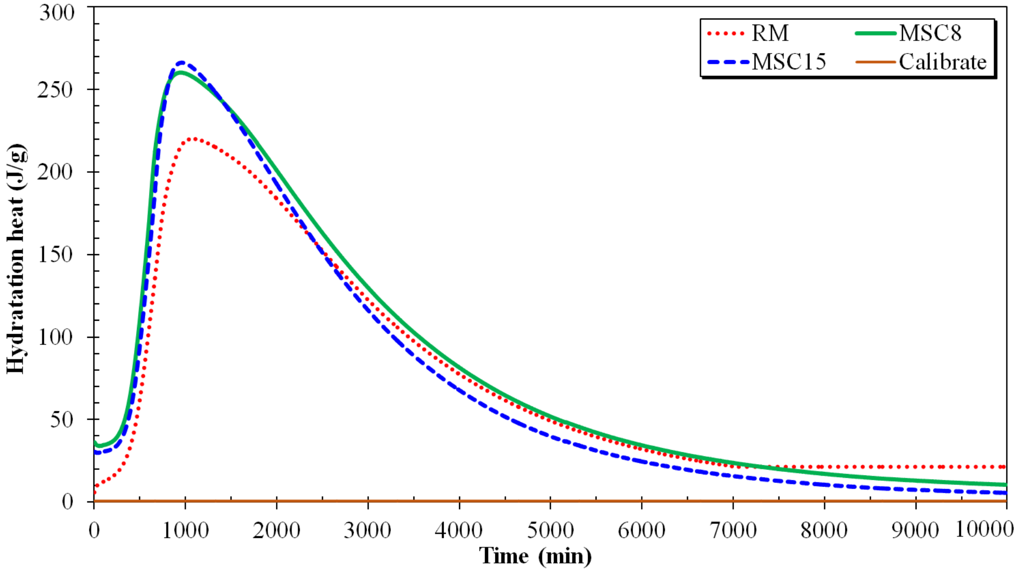

Figure 4. *Relationship between heat of hydration and time for RM and MSC.*

The RM reached a maximal temperature of 51.9 ° C after 17.80 hours which corresponds to 220.08 J/g of heat generated. The mortars substituted for 8% and for 15%, the heat released at the end of 15.60 and 15.90 hours corresponded to 262.45 J/g and 265.47 J/g respectively. The cumulative heat patterns clearly demonstrate that the MSC mortars show higher heat that the RM and appears to react faster. This allows considering that there was additional chemical activity because of the presence of sediment. This can be attributed to a filler effect relatively to the fineness of sediment according to De Weerdt et al. [WEE 11]. However, this contribution of heat can be considered to be both negative and beneficial depending on the targeted application. One option to lower it would be to use a pure clinker or cement with a low heat of hydration. It should also be noted that graphs corresponding to the substituted mortars have the same overall appearance (8% and 15%).

The finding is that an additional heat release should be generated by sediment particles due to physical or chemical activity. It can also be related to the lime phase which reacts with water following Eq [2] [MIL 01] or the hydration of hemihydrate ($CaSO_4$ | $0.5H_2O$) in Eq [3] that produces additional heat output [MOS 05].

$$CaO + H_2O \rightarrow Ca(OH)_2 + Heat \qquad (2)$$

$$\langle CaSO_4 \mid 0.5H_2O\rangle + 1.5\,H_2O \rightarrow \langle CaSO_4 \mid 2H_2O\rangle + Heat \qquad (3)$$

3.2 Mechanical strength investigation

The optimized choice of calcination process depends on multiple parameters. The main parameters identified were the time of calcination, the temperature and the substitution rate. In the light of this, mortars based on calcined sediments were prepared and treated at 650 °C ; 750 °C ; 850 °C with calcination times of 1h and 3h, substitution rates of 8% and 15% and strength is also investigated.

Curves in Figure 5 illustrates the results of the compression test. These results clearly demonstrated that sediments calcined at 1h seem more efficient than those calcined 3h. In addition, 3 h calcination method should have higher cost compared to 1h.

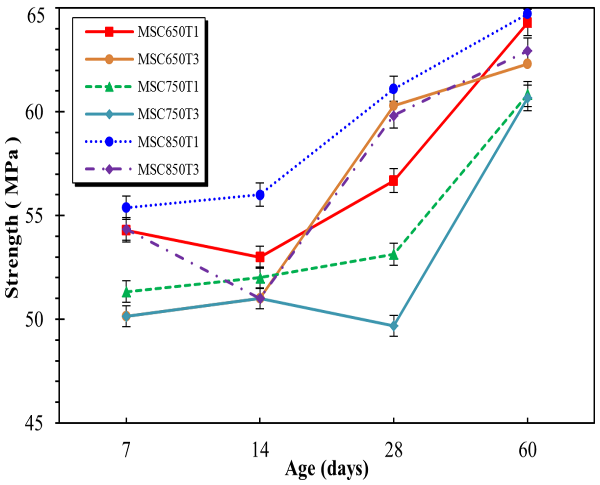

Figure 5. *Relationship between compressive strength and time for 1h and 3h calcined sediment.*

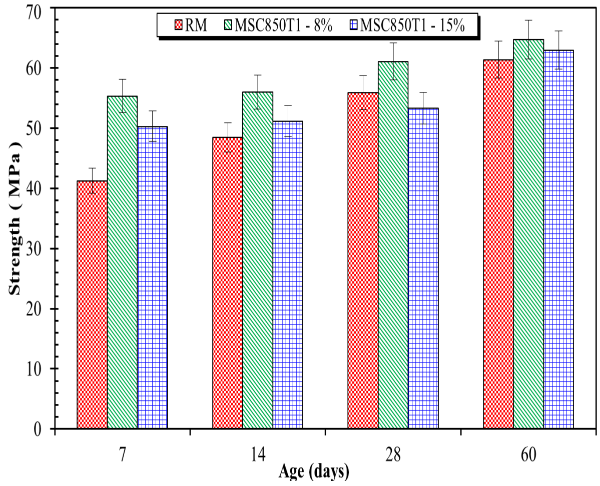

Figure 6. *Compressive strength of RM, MSC850T1*

The results in Figure 6 evidenced that the compression strength is better for a substitution rate of 8% than for 15% at any calcination temperature for a calcination time of 1h. The beneficial effect of the fine crushed calcined admixture cannot be solely attributed to a physical effect by heterogeneous nucleation as assessed by De Weerdt [WEE 11]. But also a chemical effect due to chemical activity or pozzolanic activity must occur [DAN 13].

A previous study conducted by Roziére et al. [ROZ 15] established the heterogeneous nucleation effect using SEM analysis and nanoindentation measurements on sediment based mortars. The main findings are (i) the elastic modulus of cement paste where increased, (ii) the presence of sediment particles generates nucleation sites for hydrates leading to an enhancement of the hydration process.

Finally, regardless the time of calcination, the sediment treated at SC850°C-1h sieved at 120µm (SC850T1) presented the best performances regarding all other formulations including the RM. In fact these results highlighted that MSC8 was found to have a higher compressive strength than the RM for all maturities (7 days to 60 days) whereas the MSC15 presented equivalent strength to the RM.

For this reason, the fraction used for the rest of this study is the SC850T1. Also, its mechanical performance when used in cementitious matrix and the limited calcination time make it economically interesting.

4 Conclusion

In this paper a new method for the reuse of sediment and formulation of sediment based mortar is studied. The results demonstrated that the use of sediments in cementitious matrix as substitute or supplementary product is a potential way to efficiently reuse these materials. The important conclusions which can be drawn trough this work are the following:

This study highlighted certain parameters which can be considered dominant in the treatment, formulation and hydration processes. These include the fineness, the substitution rate, the temperature, the time of calcination, etc. This study evidenced that optimum was heat treatment and stands for the raw sediment, crushed and sieved at 120 µm at 850°C for 1 hour (SC850T1). Mortars based on this sediment presented interesting mechanical performances which exceeded those of the RM. This paper brought out also the following facts which have real potential for use in concretes or mortars:

- Raw sediments (RS), due to their moderate transport and treatment costs and relatively important mechanical performances can be possible additions to cementitious matrix.
- SC650T1, seem to combine economic and mechanical performances which are positive for their effective use as mineral addition.

Washed sediments (WS) were also found to a possible solution for use because they present similar performances to those of the MRS series albeit slightly lower.

An extended study of durability and pozzolanic activity on this sediment has already been conducted and will be the main subject of a forthcoming study.

5 Bibliography

[ZAC 12] A. Zacco, A. Gianoncelli, R. Ardesi, S. Sacrato, L. Guerini, E. Bontempi, G. Tomasoni, M. Alberti, and L. E. Depero, “Use of colloidal silica to obtain a new inert from municipal solid waste incinerator (MSWI) fly ash: first results about reuse,” Clean Technol. Environ. Policy, vol. 14, no. 2, pp. 291–297, Apr. 2012.

[MIL 01] K. Millrath, S. Kozlova, S. Shimanovich, and C. Meyer, “Beneficial Use of Dredge Material,” 2001.

[YXY 14] Y. Xu, C. Yan, B. Xu, X. Ruan, and Z. Wei, “The use of urban river sediments as a primary raw material in the production of highly insulating brick,” Ceram. Int., vol. 40, no. 6, pp. 8833–8840, 2014.

[BEN 15] F. K. A.- Benslafa, D. Kerdal, M. Ameur, B. Mekerta, and A. Semcha, “Durability of Mortars Made with Dredged Sediments,” Procedia Eng., vol. 118, pp. 240–250, 2015.

[JUN 15] N. Junakova, J. Junak, and M. Balintova, “Reservoir sediment as a secondary raw material in concrete production,” Clean Technol. Environ. Policy, vol. 17, no. 5, pp. 1161–1169, Jun. 2015.

[ROZ 15] E. Rozière, M. Samara, A. Loukili, and D. Damidot, “Valorisation of sediments in self-consolidating concrete: Mix-design and microstructure,” Constr. Build. Mater., vol. 81, pp. 1–10, 2015.

[BEN 09] M. Benkaddour, F. Kazi Aoual, and A. Semcha, “Durabilité des mortiers à base de pouzzolane naturelle et de pouzzolane artificielle,” Rev. Nat. Tecnol., no. 1, pp. 63–73, 2009.

[DAN 13] T. A. Dang, S. Kamali-Bernard, and W. A. Prince, “Design of new blended cement based on marine dredged sediment,” Constr. Build. Mater., vol. 41, pp. 602–611, 2013.

[GAS 15] A. L. G. Gastaldini, M. F. Hengen, M. C. C. Gastaldini, F. D. do Amaral, M. B. Antolini, and T. Coletto, “The use of water treatment plant sludge ash as a mineral addition,” Constr. Build. Mater., vol. 94, pp. 513–520, 2015.

[GAS 14] A. L. G. Gastaldini, M. P. da Silva, F. B. Zamberlan, and C. Z. Mostardeiro Neto, “Total shrinkage, chloride penetration, and compressive strength of concretes that contain clear-colored rice husk ash,” Constr. Build. Mater., vol. 54, pp. 369–377, Mar. 2014.

[TIR 13] A. Tironi, M. A. Trezza, A. N. Scian, and E. F. Irassar, “Assessment of pozzolanic activity of different calcined clays,” Cem. Concr. Compos., vol. 37, pp. 319–327, Mar. 2013.

[GHR 07] M. Ghrici, S. Kenai, and M. Said-Mansour, “Mechanical properties and durability of mortar and concrete containing natural pozzolana and limestone blended cements,” Cem. Concr. Compos., vol. 29, no. 7, pp. 542–549, 2007.

[SNE 16] R. Snellings, Ö. Cizer, L. Horckmans, P. T. Durdziński, P. Dierckx, P. Nielsen, K. Van Balen, and L. Vandewalle, “Properties and pozzolanic reactivity of flash calcined dredging sediments,” Appl. Clay Sci., vol. 129, pp. 35–39, Aug. 2016.

[CLA 15] M. Claverie, F. Martin, J. P. P. Tardy, M. Cyr, P. De Parseval, O. Grauby, and C. Le Roux, “Structural and chemical changes in kaolinite caused by flash calcination: Formation of spherical particles,” Appl. Clay Sci., vol. 114, pp. 247–255, 2015.

[KHO 10] M. I. A. Khokhar, E. Roziere, P. Turcry, F. Grondin, and A. Loukili, “Mix design of concrete with high content of mineral additions: Optimisation to improve early age strength,” Cem. Concr. Compos., vol. 32, no. 5, pp. 377–385, 2010.

[AFN 06a] AFNOR, “NF EN 196-1 - Methods of testing cement - Part 1: determination of strength,” 2006.

[AFN 10] AFNOR, “NF EN 196-9 - Methods of testing cement - Part 9: heat of hydration - Semi-adiabatic method,” 2010.

[INS 13] Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau, “Production of Cement , Lime and Magnesium Oxide,” Eur. Comm., pp. 35–45, 2013.

[EUR 09] (EC) European Commission, “Report. Reference document on the best available techniques. Management of tailings and waste-rock in mining activities,” Ref. Doc. Best Available Tech., no. January, p. 511, 2009.

[RAM 08] J. Ramaroson, “Calcination des sédiments de dragage contaminés. Etudes des propriétés physico-chimiques,” INSA Lyon, 2008.

[BER 14] D. Bernache-assollant, “Spectrométrie de masse; Principe Frittage : Frittage, aspects physico-chimiques, frittage en phase solide,” Tech. l’Ingénieur, 2014.

[RAM 12] J. Ramaroson, M. Dia, J. L. Dirion, A. Nzihou, and G. Depelsenaire, “Thermal treatment of dredged sediment in a rotary kiln: Investigation of structural changes,” Ind. Eng. Chem. Res., vol. 51, no. 21, pp. 7146–7152, 2012.

[DUB 06] V. Dubois, “Etude du comportement physico-mécanique et caractérisation environnementale des sédiments marins – Valorisation en technique routière.,” Thesis, University of Artois, 2006.

[TRA 09] N. T. Tran, “Valorisation de sédiments marins et fluviaux en technique routière,” Thesis, University of Artois, 2009.

[MIN 03] A. K. Minocha, N. Jain, and C. L. Verma, “Effect of inorganic materials on the solidification of heavy metal sludge.,” Cem. Concr. Res., vol. 33, no. 10, pp. 1695–1701, Oct. 2003.

[PAR 00] C.-K. Park, “Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials,” Cem. Concr. Res., vol. 30, no. 3, pp. 429–435, Mar. 2000.

[MAL 06] R. Malviya and R. Chaudhary, “Factors affecting hazardous waste solidification/stabilization: A review,” J. Hazard. Mater., vol. 137, no. 1, pp. 267–276, 2006.

[WEE 11] K. De Weerdt, M. Ben Haha, G. Le Saout, K. O. Kjellsen, H. Justnes, and B. Lothenbach, “Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash,” Cem. Concr. Res., vol. 41, no. 3, pp. 279–291, 2011.

[MOS 05] N. Y. Mostafa and P. W. Brown, “Heat of hydration of high reactive pozzolans in blended cements: Isothermal conduction calorimetry,” Thermochim. Acta, vol. 435, no. 2, pp. 162–167, 2005.