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1 Recycling of dredged sediment as a raw material for the manufacture of Portland cement – Numerical modeling 2 of the hydration of synthesized cement using the CEMHYD3D code

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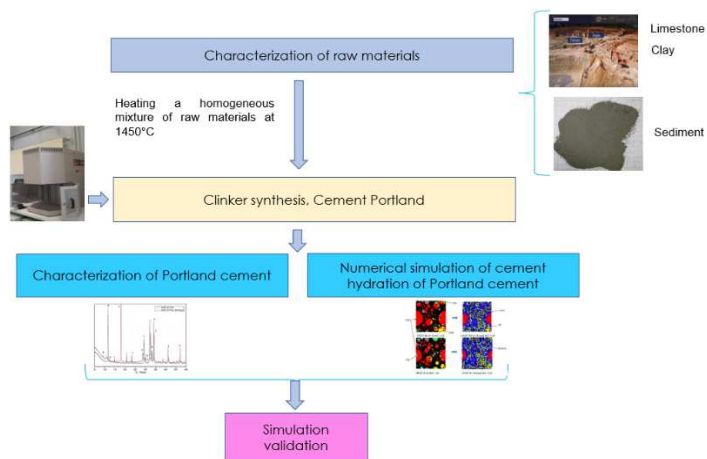
9 ABSTRACT

10 Around 56 million m³ of sediments are dredged in France per year to maintain the access to ports and waterways.
11 Sediments are considered as waste according regulations and cause environmental, ecological and economic
12 issues. This paper aims to use dredged sediments as raw material to replace traditional materials in Portland
13 cement production. Two cements were produced at the laboratory: a reference cement made from analytical
14 grade reagents of CaCO₃, SiO₂, Al₂O₃ and Fe₂O₃ and a second cement made from sediment as a partial substitution
15 for traditional materials. The components proportions in the raw meal were adjusted using the cementitious
16 modulus values (LSF, SR and AR). The produced clinkers/cements were characterized by X-ray diffraction; X-ray
17 fluorescence and scanning electron microscopy (SEM-EDS) in order to study their mineralogical and chemical
18 composition as well as their microstructure. The reactivity of the cements was measured by isothermal
19 calorimetry, and by the determination of the degree of hydration and the compressive strength. The CEMHYD3D
20 code was used to numerically model the hydration of cement paste in order to follow the evolution of all phases
21 and to predict the properties of hydrated cements.

22 The results demonstrate that sediments can be used as a raw material in the cement production at a high rate (31
23 wt%) without affecting the phase assemblage and the hydration behavior.

24 **Keywords:** Recycling, sediment, clinker, hydration, CEMHYD3D

25 Graphical abstract



26

27 1. INTRODUCTION

28 In 2016, the French cement industry produced around 17 million tons of cement and was the leader in Portland
29 cement production in the European Union [1]. However, the production of cement has a considerable impact on
30 the environment related to the extraction of natural resources and CO₂ emissions [2]. In 2012, around 800 million
31 tons of raw materials were extracted in France where 50% are allocated for the production of construction
32 materials [3]. Consequently, the recycling of industrial by-products and waste as raw materials in the manufacture
33 of cement has become a trend for reserving natural resources. Previous studies [4–9], have demonstrated the
34 effectiveness of wastes use for a partial replacement of raw materials in the manufacture of cement.

35 In France, around 56 million m³ of sediments (marine and river sediments) are dredged annually to restore
36 acceptable navigation thresholds, to avoid flooding and to improve the quality of the environment. The sediments
37 are either immersed in the sea, remained in the land (generally polluted sediment), or reused in various sectors
38 such as construction materials and agriculture. Several treatment methods for sediments have been studied and

39 applied in various fields of civil engineering. Among these, the reuse of sediments in road construction as a base
 40 layer or a form layer [10–14], the manufacture of artificial aggregates [15], and as a mineral addition in mortars
 41 [16, 17]. In most of these applications, sediments should be treated before recycling.

42 In addition to the applications listed above, some studies have shown that sediments can replace a part of the
 43 raw materials used in cement production due to their chemical composition, which contains the principal oxides
 44 (CaCO_3 , SiO_2 , Al_2O_3 , and Fe_2O_3) for clinker production. In fact, Portland cement contains approximately 95 wt% of
 45 clinker and 5 wt% of secondary constituents [18]. Portland clinker is made by burning at a high temperature (1450
 46 °C) of a raw meal generally containing 80% limestone as a source of calcium oxide and 20% clay as a source of
 47 silica, alumina, and iron oxide. At high temperature, the chemical elements recombine to form four principal
 48 mineral phases such as : Alite (C_3S : $3\text{CaO}\cdot\text{SiO}_2$), Belite (C_2S : $2\text{CaO}\cdot\text{SiO}_2$), Tricalcium aluminate (C_3A : $3\text{CaO}\cdot\text{Al}_2\text{O}_3$) and
 49 Alumino-tetracalcium ferrite (C_4AF : $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) (Table 1) [18].

50 **Table 1** Principal phases of clinker according to the cement nomenclature

Mineral phases	Cement nomenclature	Chemical formula	Minimum content (wt%)	Maximum content (wt%)
Alite	C_3S	Ca_3SiO_5	45.0	79.7
Belite	C_2S	Ca_2SiO_4	5.7	29.8
Tricalcium aluminate	C_3A	$\text{Ca}_3\text{Al}_2\text{O}_5$	1.1	14.9
Alumino-tetracalcium ferrite	C_4AF	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	2.0	16.5

51 Dalton et al. [19] have produced a clinker/cement on a laboratory and industrial scale, with raw materials
 52 extracted from quarries and contaminated sediment from the port of New Jersey (New York). Different
 53 formulations with variable substitution rates of sediment from 1 to 12 wt% were tested. The authors noted that
 54 the Alite/Belite ratio in the clinkers decreased when the sediment content in the clinker was greater than 6.5 wt%.
 55 The compressive strength of these cements was slightly lower than that of the reference Portland cement.
 56 Therefore, they conclude that cooling is necessary to prevent the decomposition of alite into belite and free lime.

57 Aouad et al [20] used the fraction of polluted sediment with particles size smaller than 2 mm from the Scarpe
 58 Canal, located in the industrial basin of the North of France, to produce clinker/cement in the laboratory with a
 59 39.1 wt% substitution rate of sediment. The authors showed that the four mineral phases of the cement were
 60 obtained without the appearance of secondary phases. The compressive strength of the cement paste made from
 61 sediment was 20% higher than that of the reference cement paste (CEM I 52.5 N) at 56 days.

62 The fine fraction of sediments with a particle size smaller than 200 μm from French hydroelectric reservoirs has
 63 been used by Faure et al. [21], [22] as a raw material for Portland cement production. The sediments replaced all
 64 or a part of the silico-aluminous raw materials in the raw mixes. Portland cements made from clinkers containing
 65 10 -15 wt% of sediments presented a high hydraulic reactivity and no constraints in terms of fresh state workability
 66 and shrinkage.

67 Therefore, the objectives of this study are, first to produce a clinker/cement at a laboratory with the maximal
 68 amount of sediment from the North of France. The cement made from substitution of sediment for the raw
 69 materials was characterized and compared to those produced from pure raw materials in order to study the
 70 substitution impacts of the sediment on the clinker/cement properties and the hydration behavior of cement
 71 paste. Second, the CEMHYD3D code was used to simulate numerically the hydration of the cement pastes over
 72 time. The experimental results were compared with the simulation results to validate the code. The simulation of
 73 cement hydration is interesting because it allows us to understand the hydration behavior and to follow the
 74 evolution of all phases over time.

75 2. MATERIALS AND RESEARCH METHOD

76 The raw materials used in this study for clinker/cement production are the analytical grade reagents of CaCO_3 ,
 77 SiO_2 , Al_2O_3 , Fe_2O_3 , and sediment. The sediment used is river sediment collected from different points on the site
 78 located in Noyelles-Sous-Lens (noted NSL sediment) of the North of France. The sediment was homogenized and

79 dried at 40 °C to reach a constant weight, then grounded to reach a particle size smaller than 200 µm with a
80 centrifugal ball mill.

81 **2.1. Results of the sediment characterization**

82 Different characterizations were conducted on the sediment before using it in the raw meal for clinker production.

83 The physical characterization consists of determining: the particle size distribution of the sediment measured
84 by the laser particle analyzer COULTER type LS 13 320 , the organic matter content (OM) measured according to
85 the XP P94-047 standard [23], the density determined using the helium pycnometer Accupyc 1330 type [24], the
86 specific surface area of sediment measured by the Brunauer-Emmett-Teller (BET) method, and the Blaine method
87 [25].

88 The chemical composition of the raw materials was identified using X-ray fluorescence analysis (XRF).

89 The mineralogy of the sediment was studied using the XRD analysis (XRD Bruker D2 Advance device equipped
90 with Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$) with the angle acquired 2θ from 5° to 80° and a step size of 0.02. In order to
91 complete the sediment's characterization, a thermogravimetric analysis TGA/DTA (Netzsch STA 409 device) was
92 performed on dried fine sediment (particle size smaller than 40 µm) with a rate of 10 °C/min and temperature
93 range from 40 °C to 1000 °C.

94 The mobility of the metallic trace elements (MTE) and the anionic elements of the sediment were measured
95 after the leaching of the sample using a liquid/solid ratio of 10 and an equilibrium time of 24h according to the
96 standard NF EN 12457-2 [26] using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES 5100
97 Agilent Technologies). The leaching limit values for inert waste (IW) and non-hazardous waste (NHW) specified in
98 Directive 1999/31/EC were used to verify material compliance.

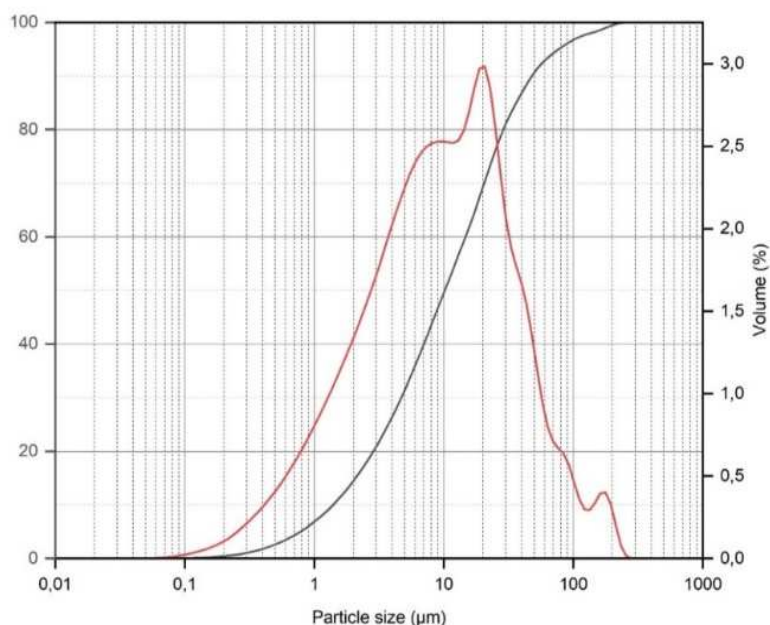
99 **2.1.1. The physical characteristics of the sediment**

100 The results of the physical characterization are shown in Table 2. The NSL sediment has an organic matter
101 content of 16.1 wt%. The Blaine surface of the sediment is two times larger than that of Portland cement (with a
102 value of 3800 cm²/g). The BET surface of the sediment is higher than that of Blaine because it is more influenced
103 by the roughness of the surface and the open porosity [18]. The value is five times larger than that of Portland
104 cement (with a value of 9000 cm²/g).

105 **Table 2** Physical characteristics of the sediment

Physical characteristics	NSL
Density (g/cm ³)	2.43
BET (cm ² /g)	43 765
Blaine surface (cm ² /g)	6 562
OM content (wt%)	16.1
LOI 950°C (wt%)	27.63
d ₁₀ (µm)	1.39
d ₅₀ (µm)	10.16
d ₉₀ (µm)	47.90

106 The particle size distribution of the sediment presented in Fig. 1 shows that 99.7% of the particles are smaller
107 than 200 µm. This result is in accordance with the particle size required for the raw materials in the cement
108 industry [27].



109
 110 **Fig. 1** Particle size distribution of the NSL sediment

111 **2.1.2. Chemical and mineral characteristics**

112 Table 3 shows the chemical composition of the sediment as well as of the other raw materials. The four
 113 principal oxides of the sediment are SiO₂, CaO, Al₂O₃ and Fe₂O₃. In addition, minor oxides such as MgO, ZnO, Na₂O
 114 and K₂O are detected, and their presence could have an impact on the clinker properties. The chemical
 115 composition shows that the content of 4 principal oxides (CaO + SiO₂ + Al₂O₃ + Fe₂O₃) of the calcined sediment is
 116 equal to 89.75% which is in accordance with the agreement between French cement industry groups signed in
 117 2001 in order to define the limits of acceptability of the use of the mineral waste used as raw materials in the plant
 118 [28]. According to this agreement, calcined waste must comply with the following composition:

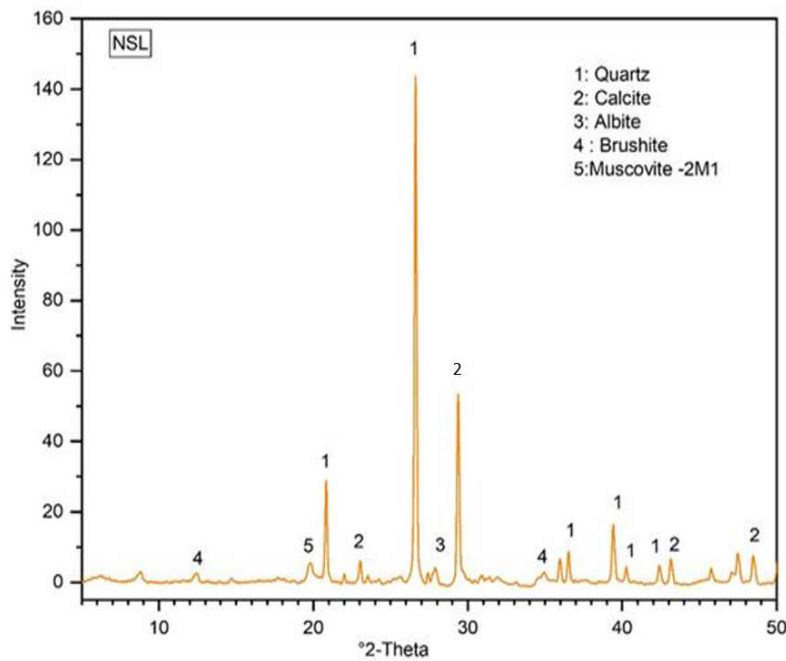
$$\text{CaO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 80\%$$

119
 120 **Table 3** Chemical compositions of raw materials measured by XRF analysis

Oxides (wt%)	NSL	CaCO ₃	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃
SiO ₂	39.62	0	0	98.5	0
Al ₂ O ₃	9.64	0	0	0.6	100
Fe ₂ O ₃	5.12	0	96	0.1	0
CaO	10.57	55	0	0	0
MgO	0.88	0	0	0	-
Na ₂ O	0.69	0	0	0	-
K ₂ O	1.84	0	0	0	-
SO ₃ total	0.22	0	0	0	-

TiO ₂	0.60	0	0	0	-
P ₂ O ₅	2.10	0	0	0	-
ZnO	0.27	0	0	0	-
L.O.I 950°C	27.63	45	0	0	-
Total (wt%)	99.17	100	96	99.2	100

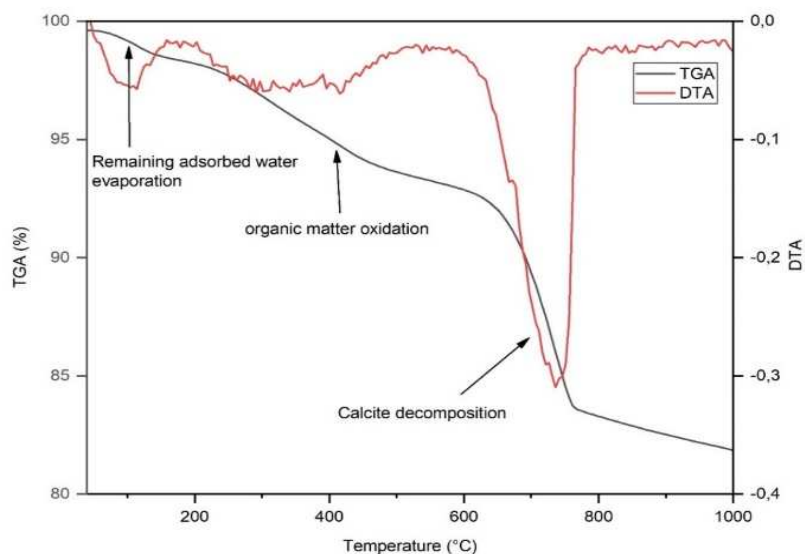
121 The results of the mineral analysis (Fig. 2) show that the principal phases of the sediment are quartz (SiO₂),
 122 calcite (CaCO₃), brushite (CaHPO₄·2H₂O) and muscovite (KAl₂(AlSi₃O₁₀)(OH,F)₂). These results are in accordance with
 123 previous studies conducted on the same sediment [10], [16], [21].



124
 125 **Fig. 2** X-ray diffraction (XRD) of the NSL sediment

126 The TGA - DTA analysis of NSL sediment (Fig. 3) shows three main peaks related to associated phenomena. The
 127 loss of mass between 212 °C and 550 °C is probably due to the combustion reactions of organic matter, organic
 128 pollutants (PAHs, PCBs, and TBT) [29], intergranular water, and constitution water from clay minerals [30] under
 129 the effect of temperature. A peak appears between 615 °C and 850 °C which corresponds mainly to the calcite
 130 decomposition. This result confirms that the presence of calcium oxide in the sediment is mainly in the form of
 131 calcite, corresponding to the result identified by XRD analysis. The results are summarized in Table 4.

132



133

134 Fig. 3 TGA/DTA analysis of the NSL sediment

135 **Table 4** Weight loss at different temperatures for NSL sediment

Temperature range (°C)	Weight loss (wt%)	Attributed reaction
105 °C – 150 °C	0.65	Remaining adsorbed water evaporation
212 °C – 550 °C	4.89	Organic matter, clay phase decomposition
615 °C – 850 °C	9.72	Calcite decomposition
40 °C – 1000 °C	17.74	Total weight loss

136 **2.1.3. Environmental characteristics**

137 The result of the leaching analysis shows the presence of metallic trace elements as well as anionic elements in
 138 the sediment (Table 5). The content of certain metallic trace elements in the NSL sediment exceeds the value
 139 specified for inert waste (IW), in particular, the Zn content. Nevertheless, these values are below the acceptable
 140 limits of heavy metals in the common agreement between the French cement industries [28].

141 **Table 5** Metallic trace elements and anionic element's content in sediment (mg/kg)

Elements	NSL	IW	NHW
As (mg/kg)	< 0.08	0.5	2
Ba (mg/kg)	1.4912	20	100
Cd (mg/kg)	< 0.008	0.04	1
Cr (mg/kg)	< 0.03	0.5	10
Cu (mg/kg)	2.0509	2	50
Mo (mg/kg)	0.5538	0.5	10
Ni (mg/kg)	0.4799	0.4	10

Pb (mg/kg)	0.0447	0.5	10
Sb (mg/kg)	-	0.06	0.7
Se (mg/kg)	0.1019	0.1	0.5
Zn (mg/kg)	7.8518	4	50
Fluoride (mg/kg)	< 1	10	150
Chloride (mg/kg)	265	800	15 000
Sulfates (mg/kg)	15 820	1000	20 000

142 **2.2. Clinker and cement synthesis method**

143 From the result of the material's chemical composition, the different formulations of the raw meal were set up
144 based on the following modulus usually used in the cement industry: the Lime Saturation Factor (LSF), the Silica
145 Ratio (SR) and the Alumina Ratio (AR) [18]. These are the main parameters to control the quality of the clinker [31].
146 The calculations of LSF, SR, and AR are presented by the following equations:

$$LSF = \frac{100 * \%CaO}{2.8 * \%SiO_2 + 1.18 * \%Al_2O_3 + 0.65 * \%Fe_2O_3} \quad Eq(1)$$

$$SR = \frac{\%SiO_2}{\%Al_2O_3 + \%Fe_2O_3} \quad Eq(2)$$

$$AR = \frac{\%Al_2O_3}{\%Fe_2O_3} \quad Eq(3)$$

148 The LSF ensures good stoichiometry between calcium oxide and the other three main oxides. A higher LSF
149 value corresponds to higher calcium silicate content, but the burning will be more difficult and may cause volume
150 instability of the hydrated cement (high content of free lime). In addition, the LSF helps to control the relationship
151 between the quantity of C₃S and C₂S [32]. The value of LSF is usually considered to be between 95 and 97 [33] but
152 technically the range of LSF can vary from 90 to 104 [34].

153 The SR allows the determination of the relative proportion between the silicate phases and the aluminate
154 phases. A high value of SR will cause difficulty in the clinkering process due to a lack of fluxing agents. This modulus
155 also affects the clinker properties including the setting and durability. The value of SR is between 2.0 and 3.0 [18],
156 but a more restrictive and optimized domain can be given between 2.4 and 2.6 [33].

157 Finally, the AR expresses the relative ratio in the interstitial phases between the C₃A and C₄AF phases. A high
158 value of AR will provoke the formation of a high content of C₃A in the clinker and this affects the resistance to
159 sulfates [35]. The appropriate AR value is between 1.5 and 1.8 [33].

160 From the chemical composition of each raw material, two different formulations of clinkers were formulated.
161 The first is a reference clinker referred by CP 97TM produced using analytical grade reagents of CaCO₃, SiO₂, Fe₂O₃
162 and Al₂O₃ (without sediment) only. The second referred by CP97, was produced with a partial replacement of the
163 raw material by the sediment. The modulus values applied to both clinkers are LSF = 97, SR = 2.6 and AR = 1.45.
164 The choice of value LSF = 97 is to avoid the significant presence of CaO_{free} and to have a significant content of C₃S in
165 the clinker. The solver option in Microsoft Excel was used to adjust and calculate the amount of the each raw
166 material in the formulation while respecting the values of the targeted modulus. Table 6 shows the mixes designs
167 of the two clinker raw meals.

168 **Table 6** Mixes designs for the two produced clinker raw meals

Constituents	NSL (wt%)	CaCO ₃ (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	SiO ₂ (wt%)
CP 97 TM	0	79.99	3.17	2.32	14.52

CP 97	31	67.61	0	0.5	0.89
-------	----	-------	---	-----	------

169 To prepare the raw mixes, all materials were first mixed by adding water with a water/material ratio = 0.6 to
170 better homogenize. After drying at 105 °C, the pellets (with a diameter = 40 mm and a height = 15 mm) were
171 produced using a press at 5 KN to obtain a more regular clinkering process. The pellets were burned at 200 °C for
172 20 minutes, then to 1450 °C with a rate of 7 °C/minute. After 15 min of burning at the clinkering temperature, the
173 clinker was slowly cooled in the furnace. The clinker was ground to a Blaine specific surface of 3500 cm²/g. Finally,
174 the cements were obtained by mixing pure gypsum (CaSO₄.2H₂O) with clinker. The addition of gypsum has a very
175 important role in controlling the setting of the cement. Indeed, the reaction of C₃A with water is very violent and
176 immediately stiffens the cement paste [36]. This phenomenon is due to the formation of hydrated calcium
177 aluminates according to Eq(4), which are distributed in the space filled with the mixing water and constitute
178 bridges between the particles of the cement causing a rapid setting.



179 In addition, the presence of sulfate increases the hydration of C₃S, which requires an improvement in the
180 development of compressive strength [37] and stability control of the volume of the paste [18]. However, an
181 excess of sulfate can cause swelling by the late reaction with tricalcium aluminate [38], which increases the rate of
182 degradation and deterioration of concrete [39]. The limit content of SO₃ is set at 3.5 wt% by the standard EN 197-1
183 [40]. Based on Day's hypothesis which assumed that the ettringite's formation would be delayed for a SO₃/Al₂O₃
184 ratio greater than 0.7. In this study, gypsum was added to reach an SO₃/Al₂O₃ ratio of 0.6. Table 7 shows the
185 proportions of the constituents of the two cements.

186 **Table 7** Mixes design of the OPC 97 TM and OPC 97 cement

Component	OPC 97 TM	OPC 97
Clinker (wt%)	95.67	95.16
Gypsum (wt%)	4.33	4.84

187 2.3. Clinkers/Cements characterization method

188 The chemical composition of raw meals, clinkers and cements measured by XRF analysis allows us to verify the
189 values of the modulus used.

190 The mineralogy of the clinkers, cements and cement pastes was studied by XRD analysis using XRD Bruker D2
191 Advance device equipped with Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$. The polymorphs of crystalline phases of clinkers were
192 studied in detail to understand the influence of the substitution of sediment on the formation of crystalline
193 phases. The Bogue's formula [7] was used to quantify the crystalline phases of the clinker according to the
194 following equations (Eq(5) -> Eq(8)) :

$$C_3S = 4.07 * (CaO_{Total} - CaO_{free\ lime}) - 6.72 * Al_2O_3 - 1.43 * Fe_2O_3 \quad \text{Eq(5)}$$

$$C_2S = 8.60 * SiO_2 + 1.08 * Fe_2O_3 + 5.07 * Al_2O_3 - 3.07 * (CaO_{Total} - CaO_{free\ lime}) \quad \text{Eq(6)}$$

$$C_3A = 2.65 * Al_2O_3 - 1.69 * Fe_2O_3 \quad \text{Eq(7)}$$

$$C_4AF = 3.04 * Fe_2O_3 \quad \text{Eq(8)}$$

195 The free lime content of the clinker is an important parameter to evaluate the quality of the clinkering process.
196 In general, a free lime content less than 2 wt% is acceptable in the cement industry [41]. In this study, the free lime
197 content of the clinker was determined according to the Schlafer-Bukokowski method.

198 To observe the effect of the substitution of sediment on the form of crystalline phases, the optical microscope
199 was used to study the microstructure of clinker.

200 The chemical composition of the clinker phases was studied on polished sections with a Hitachi S-4300 SE/N
201 scanning electron microscope operating in backscattered electron mode (20 keV) and equipped with an energy

202 dispersive X-ray spectrometer (EDS). To make the polished section, the clinker sample was vacuum impregnated in
203 epoxy resin and polished down to 1 μm with ethanol to avoid reaction with water. Finally, the sample was coated
204 with carbon before observation. About 50 points were measured for each crystalline phases of clinker on several
205 zones.

206 The hydration reactions of the cement paste are exothermic and can be followed by measuring the rate of heat
207 release. Therefore, the reactivity of the cements was followed using the isothermal calorimetry measurements
208 performed at 20 °C. Based on a previous study [42], 8 g of cement and 4 g of water previously stored at 20 °C were
209 mixed manually for two minutes before introduction in cells that were placed inside the calorimeter. The
210 calorimeter was a home-made calorimeter using fluxmeters the allowed the calorimeter to equilibrate in less than
211 5 min.

212 The reactivity of the cements was also investigated by the measurement of the degree of cement paste
213 hydration. In the literature, several methods were used to determine the degree of hydration of cement such as:

- 214 • Scanning electron microscopy (SEM-BSE) [43]
- 215 • Thermogravimetric analysis (TGA) [43]
- 216 • X-ray diffraction (XRD)
- 217 • Compressive strength

218 In a previous study, CHU et al [43] determined the degree of hydration of Portland cement by three different
219 methods. The result shows that the bound water quantification method gave the most reasonable result. In this
220 study, the degree of hydration of cement paste was determined by the bound water quantification method using
221 TGA analysis. To prepare the cement paste, cement and water were manually mixed for 3 minutes with a W/C
222 ration equal to 0.5. The paste was introduced into moulds and kept for 24h at 100% relative humidity at 20 °C. The
223 sample was demoulded after 24h and stored in saturated lime solution at 20 °C to avoid the carbonation
224 phenomenon before measurement at 2 and 28 days. The relative humidity of conservation considerably modifies
225 the kinetics of hydration of the cementitious material. In fact, the hydration of CEM I cement is greatly reduced
226 when the internal relative humidity passes below 80% [44]. Snyder et al. [45] showed that internal humidity was
227 influenced by external relative humidity and the degree of hydration of the sample stored in the endogenous
228 condition was lower than that of the sample stored in a saturated environment. For this reason, in this study, the
229 curing was performed at 100% relative humidity.

230 The degree of hydration of the cement paste was determined according to the following equation:

$$\alpha(t) = \frac{W_n(t)}{W_n(\infty)} \quad \text{Eq(9)}$$

231 With:

232 $\alpha(t)$: Degree of hydration of the sample at time t.

233 $W_n(t)$: Amount of bound water at time t (in gram of water per 100 g of anhydrous cement).

234 $W_n(\infty)$: Amount of bound water for a complete hydration of the cement paste (in gram of water per 100 g of
235 anhydrous cement).

236 The value of $W_n(t)$ can be determined experimentally using the equation Eq(10) if the two following conditions are
237 met:

- 238 • No carbonation in the cement paste.
- 239 • Low weight loss of anhydrous cement before 1000 °C

$$W_n(t) = \frac{\Delta m_{\text{sample}}(105^\circ\text{C}-1000^\circ\text{C})(t)}{m_{\text{sample}}(1000^\circ\text{C})(t)} * 100 \quad \text{Eq(10)}$$

240 To determine the value of $W_n(\infty)$, NIST (National Institute of Standards and Technology) provides an
241 approximate theoretical estimation of the amount of bound water produced for the five principal mineral phases
242 of cement when the hydration is complete [46] (Table 12). In addition, in this study, no method for arresting for
243 hydration of cement was used to avoid the carbonation phenomenon in the cement paste. The cement paste for
244 the TGA analysis was immediately analyzed after reaching the desired hydration time (2 and 28 days) using the
245 NETZSCH STA 409 type device according to the following condition: the temperature was increased from 30 °C to
246 105 °C with a rate of 2 °C/min, then maintained at 105 °C for 1h before increasing to the 1100 °C with a rate of 3
247 °C/min.

248 The compressive strength is measured to evaluate the quality and the mechanical performance of the
 249 produced cement. Due to limited quantities of the produced cement at laboratory (about 150 g), the compressive
 250 strength was determined on small cubes of dimension 1 x 1 x 1 cm³ made from the cement paste with a W/C ratio
 251 equal to 0.5. The preparation process of the cement paste in this part is similar to that in the analysis of the degree
 252 of hydration. Based on previous studies [20, 43, 47], the compressive strength was measured on 6 samples after 2,
 253 15 and 28 days performing at a constant stress of 0.3 MPa/s.

254 2.4. Numerical modeling of cement hydration using the CEMHYD3D code

255 2.4.1. CEMHYD3D code

256 The hydration of cementitious materials is a complex physicochemical process. Consequently, a numerical
 257 simulation of this process is very useful to know the state of the material as well as to follow the evolution of the
 258 phases in the hydration time. There are four main models for modeling cementitious materials hydration in the
 259 literature:

- 260 • Analytical models [48]
- 261 • Semi – analytical models [49]
- 262 • Thermodynamic models [50]
- 263 • Models associated with the development of microstructure (CEMHYD3D, HYMOSTRUC [51])

264 The semi-analytical model gives the degree of hydration of the cement from the degree of hydration of each
 265 phase of the clinker according to the following equation:

$$\alpha(t) = \alpha_{C3S}(t) * [\%C3S] + \alpha_{C2S}(t) * [\%C2S] + \alpha_{C3A}(t) * [\%C3A] + \alpha_{C4AF}(t) * [\%C4AF] \quad \text{Eq(11)}$$

266 With:

267 $\alpha(t)$: Degree of hydration of the cement at time t.

268 $\alpha_{C3S}(t)$, $\alpha_{C2S}(t)$, $\alpha_{C3A}(t)$, $\alpha_{C4AF}(t)$: Degree of hydration of C₃S, C₂S, C₃A and C₄AF respectively at time t.

269 $[\%C3S]$, $[\%C2S]$, $[\%C3A]$, $[\%C4AF]$: Initial mass proportion of C₃S, C₂S, C₃A and C₄AF respectively in the cement.

270 However, it is difficult to determine the degree of hydration of each phase in this case. Therefore, this model is not
 271 suitable to simulate the hydration of cement in this study.

272 The CEMHYD3D code developed by P.Bentz at NIST has been used successfully in several previous studies
 273 [52],[53],[54]. It allows the user to numerically generate and hydrate a 3D - microstructure of the cement paste
 274 made from the data input such as : the mineral composition, the particle size distribution and W/C volume ratio,
 275 under controlled hydration conditions [55]. The code does not use a classical chemical equations with the
 276 equilibrium of species in solution and the resolution of the associated equations systems, but instead uses a
 277 completely original mechanism of reaction between species using cellular automata [56]. A list of the chemical
 278 equations taken into account to perform the hydration of the numerical cement is detailed by P.Bentz in the
 279 CEMHYD3D user guide [57]. A 3D microstructure consists of micro cubes of dimension of 1 μm³, called voxels, each
 280 representing a phase for example: solid (C₃S, C₂S, C₃A, C₄AF, gypsum, hydrates etc.), liquid (water). The advantage
 281 of the CEMHYD3D code is to allow the user to access to all the information such as the amount and the evolution
 282 of all phases, the porosity and the mechanical resistance of the hydrated cement paste over time. The
 283 microstructure generated from CEMHYD3D code could be used to study the leaching, the interfacial transition
 284 zone (ITZ) properties of the cementitious material [58, 59]. However, the porosity of the microstructure measured
 285 in the CEMHYD3D code is limited to the capillary porosity due to the size of the voxels equal to 1 μm³ which is
 286 larger than the pore size in the hydrated cement paste.

287 The compressive strength in the model is estimated using Powers's empirical relation [57] according to the
 288 following equation :

$$\sigma_c(t) = \sigma_0(X(t))^n \quad \text{Eq(12)}$$

289 With:

290 $\sigma_c(t)$: Compressive strength of sample at time t.

291 σ_0 : Compressive strength of sample when capillary porosity is equal to 0. It is calibrated from the experimental
 292 resistance measured at 28 days.

293 n: Value is between 2.6 and 3.0. In general, a value equal to 2.6 is applied for CEM I.

294 X(t): Ratio of hydrate gel-space. In the CEMHYD3D code, X(t) is determined according to the following equation:

$$X(t) = \frac{\text{Number of hydrate pixels}}{\text{Number of hydrate pixels} + \text{Number of porosity pixels}} \quad \text{Eq(13)}$$

295 We also have:

$$X(t) = \frac{0.68 \alpha(t)}{0.32\alpha(t) + \frac{W}{C}} \quad \text{Eq(14)}$$

296 With:

297 $\alpha(t)$: Degree of hydration of sample at time t.

298 W/C: water/cement ratio

299 2.4.2. Determination of time constant

300 The time constant (β) is used to convert times/cycles in the CEMHYD3D code. The value should be determined
301 experimentally by the user depending on the type of cement used. The relationship between time and the number
302 of cycles is according to the following equation:

$$t = \frac{\beta}{K} * c^2 \quad \text{Eq(15)}$$

303 With:

304 t: Time of hydration in hours.

305 c: Number of hydration cycles performed by the program in the CEMHYD3D

306 β : Conversion factor cycles/time in hour/(cycles)².

307 K: Speed coefficient for the cycle.

308 The value of K is determined according to the following equation:

$$K = e^{\frac{E}{8.314} \left(\frac{1}{298.15} - \frac{1}{T^{\circ} + 273.15} \right)} \quad \text{Eq(16)}$$

309 With:

310 E: Activation energy of the cement in KJ/mol.

311 T[°]: Temperature of the system in °C.

312 To determine the β value, the degree of hydration of the cement paste should be used. The value of the
313 coefficient K is calculated according to Eq(16) equation with the activation energy of the cement E = 40 (KJ/mol)
314 and gives a result of K = 0.9997. Knowing the experimental value of the degree of hydration of the cement paste at
315 a given time, the user determines the number of hydration cycles for which the program reaches the same value
316 as the experimental $\alpha(t)$ [56].

317 3. RESULTS AND DISCUSSIONS

318 3.1. Clinker characterization

319 3.1.1. Mineral and chemical composition of CP 97 TM and CP 97 clinker

320 The chemical composition (before sintering) of the two formulations (CP 97TM and CP 97) was analyzed by XRF
321 analysis in order to verify experimental content of principal oxides (Table 8).

322 **Table 8** Chemical composition of CP 97TM and CP 97 raw meals measured by XRF analysis

Oxide (wt%)	CP 97 TM		CP 97	
	Theoretical	Experimental	Theoretical	Experimental
SiO ₂	14.30	13.8	13.19	12.9
Al ₂ O ₃	3.26	2.8	3.00	3.05
Fe ₂ O ₃	2.25	2.1	2.07	2.07
CaO	43.99	43.8	40.58	40.26
MgO	0.00	0.00	0.27	0.33

Na ₂ O	0.00	0.00	0.21	Traces
K ₂ O	0.00	0.00	0.57	0.59
SO ₃ total	0.00	0.00	0.07	0.12
TiO ₂	0.00	0.00	0.19	0.17
P ₂ O ₅	0.00	0.00	0.65	0.56
ZnO	0.00	0.00	0.08	0.1
LOI 950°C (wt%)	35.99	36.88	39.10	39.4
Total (%)	99.79	99.38	100.00	99.55
LSF	97.00	101.1	97.00	98.04
SR	2.60	2.81	2.60	2.52
AR	1.45	1.33	1.45	1.47
CaO/SiO ₂	3.08	3.17	3.08	3.12

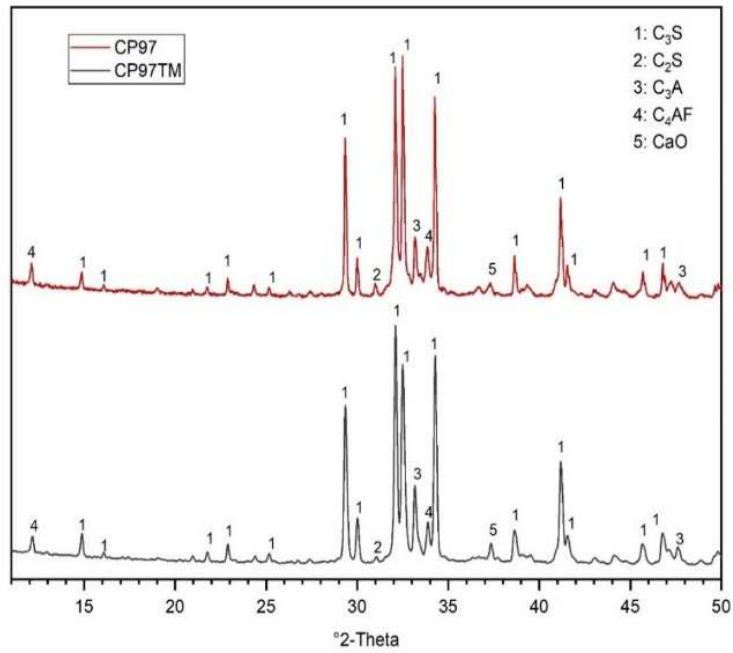
323 The experimental result was compared to the theoretical value in order to check the values of the modules
324 used. A good compatibility was observed in particular in the case of the CP 97 formulation between the
325 experimental and theoretical composition. However, an increase of LSF value in the case of the CP 97 TM
326 formulation was noted. The result shows the presence of minor elements such as ZnO, SO₃, and MgO in the CP 97
327 formulation. These elements could have an effect on the formation of the clinker phases. Indeed, the presence of
328 MgO promotes the formation of C₃S in the M1 polymorph. In contrast, the presence of SO₃ promotes the
329 formation of C₃S in the M3 polymorph which is less reactive than the M1 polymorph [60]. In a previous study,
330 Gineys et al. [61] showed that Zn affected the formation of C₃A. A decrease in C₃A content was observed when the
331 Zn content was higher than 0.7 wt%.

332 The free lime content of two clinkers CP 97 TM and CP 97 corresponds to 1.287 wt% and 0.786 wt%
333 respectively. The values are obviously below the acceptable threshold for free lime content in the cement industry
334 (2 wt%). The result confirms that the clinkering was complete. Table 9 shows the mineralogical compositions
335 according to the Bogue formula of two clinkers after sintering.

336 **Table 9** Mineral composition of two clinkers CP 97TM and CP 97 measured by the Bogue's formula

Mineral phases (wt%)	CP 97TM	CP 97
C ₃ S	76.83	66.99
C ₂ S	4.96	10.69
C ₃ A	6.16	7.59
C ₄ AF	10.15	10.41
CaO free	1.287	0.786

337 To study the mineralogical assemblage of the two clinkers, XRD analysis was performed on the clinker powders.
338 The XRD pattern represented in the Fig. 4 shows the presence of the four principal crystalline phases of clinker
339 such as C₃S, C₂S, C₃A and C₄AF as well as the presence of free lime which was also determined according to the
340 Schläfer-Bukokowski method. In addition, the result also indicates that no secondary mineral phase are identified
341 in the CP 97 clinker and the major crystalline phases in the CP 97TM clinker are all present in the CP 97 clinker.



342

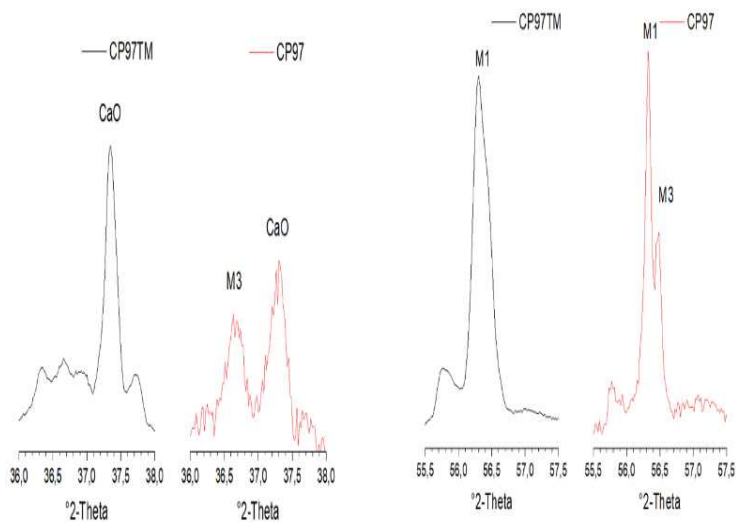
343 **Fig. 4** X-ray diffraction (XRD) of the CP 97 TM and CP 97 clinker

344 The XRD pattern was examined at various ranges to study the effects of the substitution rate of the sediment in
 345 the raw materials on the polymorph of the crystalline phases formed in the clinker (Table 10).

346 **Table 10** The angular range 2θ for the different mineral phases of clinker

Mineral phases	C ₃ S	C ₂ S	C ₃ A
2θ	[36°-38°] [55.5°-57.5°]	[30.5°-32°] [32.7°-33.7°]	[47°-48°]

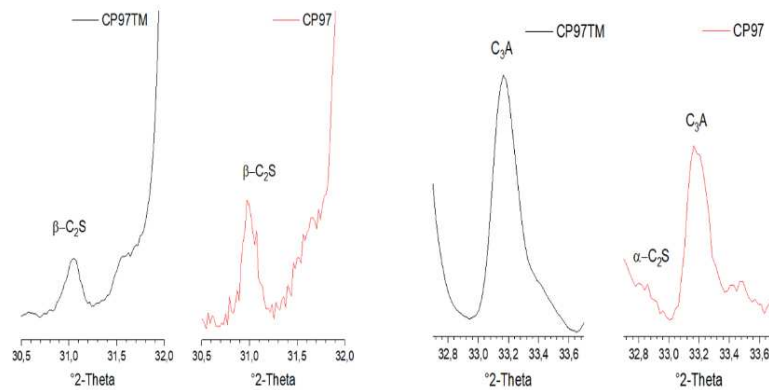
347 We note that the XRD pattern curve of the CP 97TM clinker is more "smooth" than that of the CP 97 clinker.
 348 This may be due to the purity of the raw mix of CP 97 TM formulation which does not contain minor oxides.
 349 Concerning the polymorph of C₃S in the clinker, the XRD pattern presented in the Fig. 5 indicated the formation of
 350 the M1 and M3 polymorph in the CP 97 clinker whilst the M3 polymorph was not identified in the CP 97TM clinker.



351

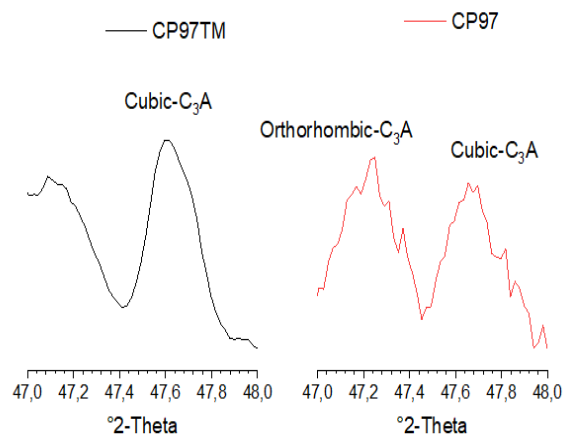
352 **Fig. 5** M1 and M3 polymorph of C₃S of the clinker CP 97 TM and CP 97

353 To study the C₂S polymorph, the result presented in Fig. 6 shows that the incorporation of sediment in the raw
 354 meal did not affect the formation of C₂S. The result also shows that the β-C₂S polymorph is the principal polymorph
 355 of C₂S in the two clinkers. In addition, the result confirms that the cooling process in this study does not cause the
 356 decomposition of C₃S into γ-C₂S polymorph and CaO_{free} in the clinker. The decomposition of C₃S directly influences
 357 the quality of the cement because the γ-C₂S polymorph is much less reactive than C₃S, and this causes a decrease
 358 in C-S-H content which is the principal hydrate and contributes significantly to the macro – properties of concrete
 359 such as strength and durability [62, 63].
 360



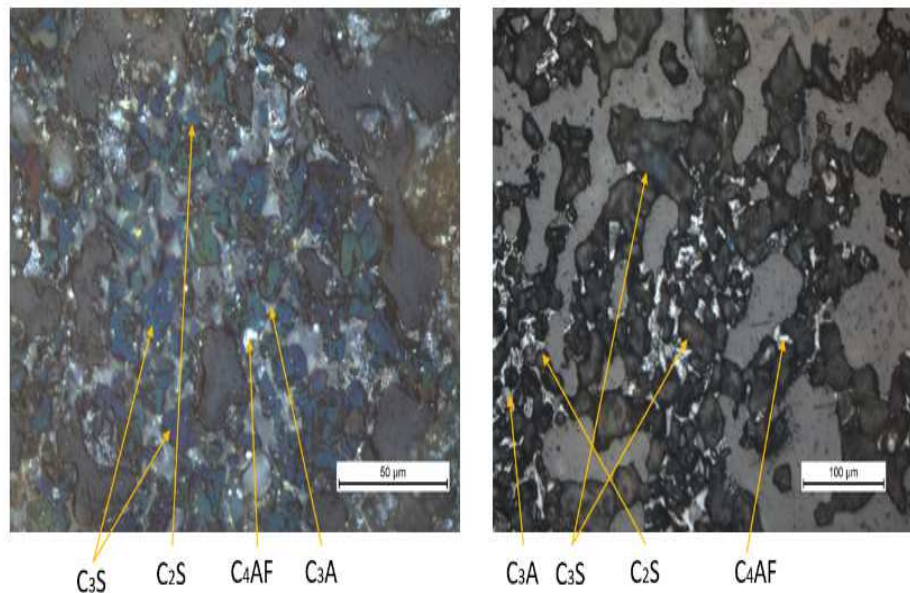
361
 362 **Fig. 6** β-C₂S and α-C₂S polymorph of the CP 97 TM and CP 97 clinker

363 The formation of orthorhombic polymorph of C₃A (Fig. 7) was observed in the CP 97 clinker. This could be due
 364 to the presence of Na⁺ ions which replaced Ca²⁺ ions and led to the change from the cubic system to the
 365 orthorhombic system [64].



366
 367 **Fig. 7** Polymorph of C₃A phase of the CP 97 TM and CP 97 clinker

368 Fig.8 shows the polished sections of CP 97 TM and CP 97 clinkers observed by optical microscopy.

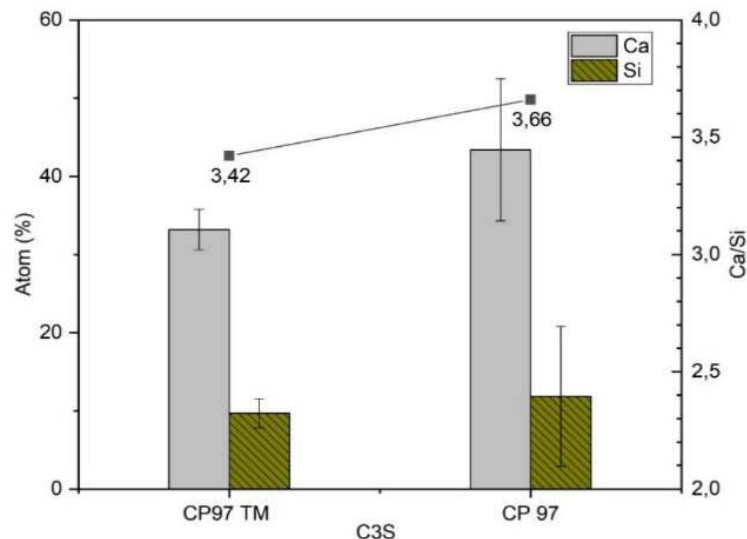


369
 370 **Fig. 8** Observation by optical microscope on the polished section of CP 97 TM (left) and CP 97 (right) clinker

371 A good distribution of silicate phases (C_3S and C_2S) and interstitial phases (C_3A and C_4AF) in the two clinkers was
 372 observed. The alite grains appeared to be angular whereas the belite is round. In addition, the presence of sulfate
 373 (SO_3) in the CP 97 clinker reduces the viscosity and surface tension of the interstitial liquid phase, and promotes
 374 the formation of alite crystals larger than those of reference clinker [65]. The result confirms that the substitution
 375 of sediment for traditional raw materials did not show any modification of distribution and form of the principal
 376 crystalline phases.

377 **3.1.2. Chemical composition of mineral phases of clinkers (SEM-EDS analysis)**

378 Fig. 9 and Fig. 10 show the result of the SEM – EDS analysis performed on the silicate phases of the CP 97 TM
 379 and CP 97 clinker.

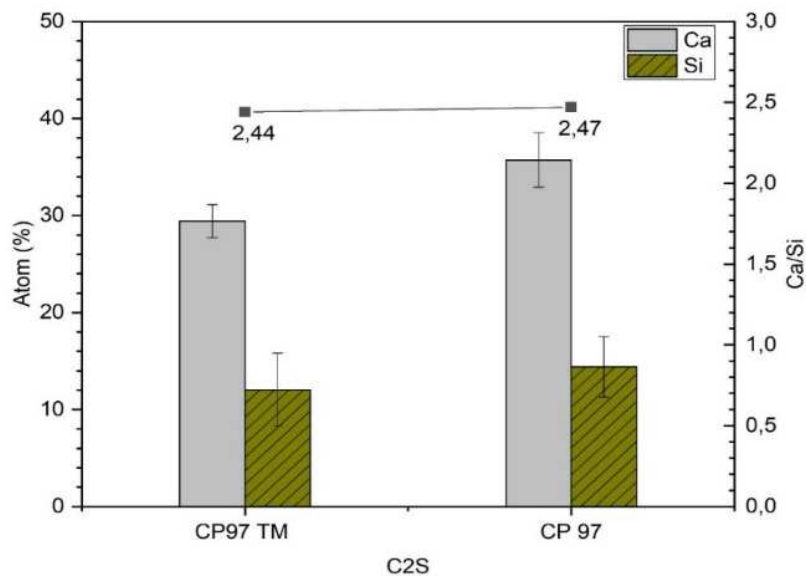


380
 381 **Fig. 9** Chemical composition and the ratio of major elements of C_3S phase

382 The result of the measurement of the C_3S phase shows that:

- 383 • The major elements of this phase identified are Ca, Si and O. The C/S (CaO/SiO_2) ratio measured by SEM –
 384 EDS analysis is higher than the theoretical value ($C/S = 3$) in the two clinkers This difference can be due to
 385 the points measured and to the size of the diffusion bulb which analyzes an area and not a point [66]. In
 386 addition, this ratio of CP 97 clinker is higher than that of CP 97 TM clinker.

- 387
- 388
- 389
- 390
- 391
- 392
- 393
- The minor elements incorporated in this phase are Al, Fe for CP 97 TM clinker and Al, Fe, Mg, alkali (Na, K) for CP 97 clinker. The Al/Si ratio is equal to 0.07 for the two clinkers. This value is higher than that in the Taylor's study which gave a Al/Si ratio equal to 0.04. The presence of Mg identified in this phase of the CP 97 clinker is in accordance with than previously observed by XRD analysis which shows the incorporation of Mg promotes the formation of M3 polymorph of the C₃S phase (Fig. 5).
 - This phase of the CP 97 TM and CP 97 clinkers contains 1.14 wt% and 2 wt% of the minor elements respectively.



- 394
- 395 **Fig. 10** Chemical composition and the ratio of major elements of C₂S phase
- 396 The result of the SEM - EDS analysis of the C₂S phase shows the following:
- 397
- 398
- 399
- 400
- 401
- 402
- 403
- 404
- The major elements of this phase also are Ca, Si and O. In addition, the C/S ratio of the two clinkers is higher than the theoretical value of the C₂S phase (C/S = 2). However, this ration is similar for the two clinkers.
 - Same as the C₃S phase, the C₂S phase contains the minor elements such as Al, Fe in the CP 97 TM clinker and Al, Fe, Mg, alkali (Na, K) in the CP 97 clinker. The Al/Si ratio is equal to 0.07 for the two clinkers and this value is relatively similar to that in the Taylor's study (Al/Si = 0.077).
 - The C₂S phase of the CP 97TM and CP 97 clinkers incorporates 1.42 wt% and 3.03 wt% of the minor elements respectively.

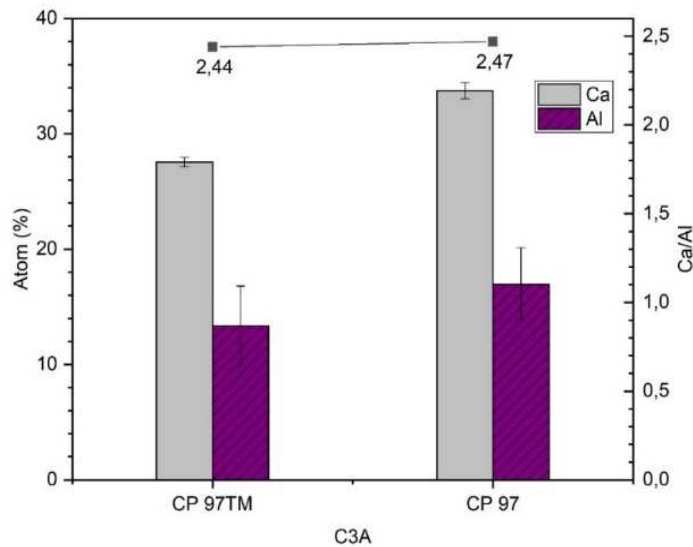
405 The result of the SEM - EDS analysis performed on the C₃S and C₂S phases shows that the substitution of

406 sediment for the raw materials does not affect the ratio of major elements of the C₂S phase whilst it considerably

407 affects the ratio of major elements of the phase C₃S. This is interesting because the C₃S phase contributes

408 considerably to the hydration behavior and the mechanical performance of Portland cement.

409 Fig. 11 and Fig. 12 show the results of the SEM - EDS analysis at the interstitial crystalline phases.

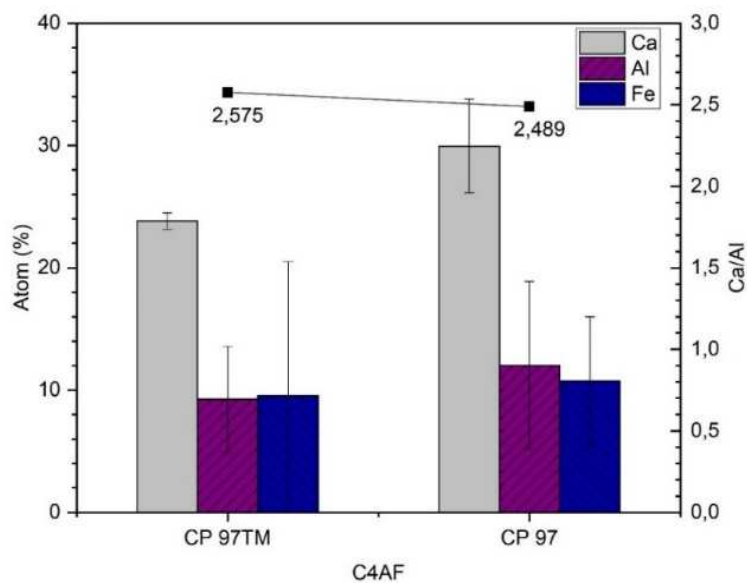


410

411 **Fig. 11** Chemical composition and the ratio of the major elements of C₃A phase

412 From the result illustrated in Fig. 11, some conclusions can be made:

- 413
- 414 • The major elements identified in the C₃A phase are Ca, Al and O. The C/A (CaO/Al₂O₃) ratio in the two
415 clinkers is higher than the theoretical value (Ca/Al = 1.5) of this phase. However, this ratio is relatively
416 similar for the two clinkers.
 - 417 • The C₃A phase contains the minor elements such as Fe, Si in the CP 97 TM clinker and Si, Fe, Mg, alkali
418 (Na, K) in the CP 97 clinker. However, the amount of Mg incorporated into this phase is 10 times less than
419 that in the C₃S phase.
 - 420 • The presence of alkali (Na, K) identified in this phase of the CP 97 clinker is in accordance with than
421 previously observed by XRD analysis which shows the incorporation of alkali promotes the formation of
422 orthorhombic polymorph of C₃A phase (Fig. 7). The amount of alkali in this phase of the CP 97 clinker is
423 five higher than that of the C₃S phase.
 - 424 • The C₃A phase of the CP 97 TM and CP 97 clinkers incorporates 3.42 wt% and 4.55 wt% of the minor
elements respectively.



425

426 **Fig. 12** Chemical composition and the ratio of the major elements of the C₄AF phase

427 The result of the SEM-EDS analysis of the phase C_4AF (Fig. 12) shows that:
 428 • The major elements of this phase are Ca, Al, Fe and O. The Ca/Al (CaO/Al_2O_3) ratio in the two clinkers is
 429 higher than the theoretical value of this phase ($Ca/Al = 2$). However, this ration is similar in the two
 430 clinkers.
 431 • In addition, the Al/Fe ratio is equal to 0.99 for CP 97TM clinker and equal to 1.12 for CP 97 clinker, which
 432 is relatively close to the theoretical value ($Al/Fe = 1$) of this phase.

433 The zinc is well known to have a retardation effect on the cement paste hydration [67]. Therefore, the
 434 determination of the location of zinc in the clinker phases is important in order to understand the effect of this
 435 element on the hydration behavior of cement. The result of the SEM – EDS analysis performed on the CP 97 clinker
 436 shows that Zn is present in all the clinker phases except in the C_2S phase (0.16 wt% in C_3S phase, 0.33 wt% in C_3A
 437 phase and 0.83 wt% in C_4AF phase). This result is in accordance with that previously observed [67]. In a previous
 438 study, Hornain also indicated that it is difficult for zinc to enter into C_2S phase [68].

439 3.2. CEMENT CHARACTERIZATION

440 3.2.1. Chemical composition of cements

441 The chemical composition of the two cements measured by XRF analysis is presented in Table 11. The result
 442 shows that the chemical composition of the principal oxides of OPC 97 cement is comparable to that of OPC 97 TM
 443 cement. However, it is important to note that the amount of zinc in OPC 97 is 10 times higher than that in Ordinary
 444 Portland Cement [20].

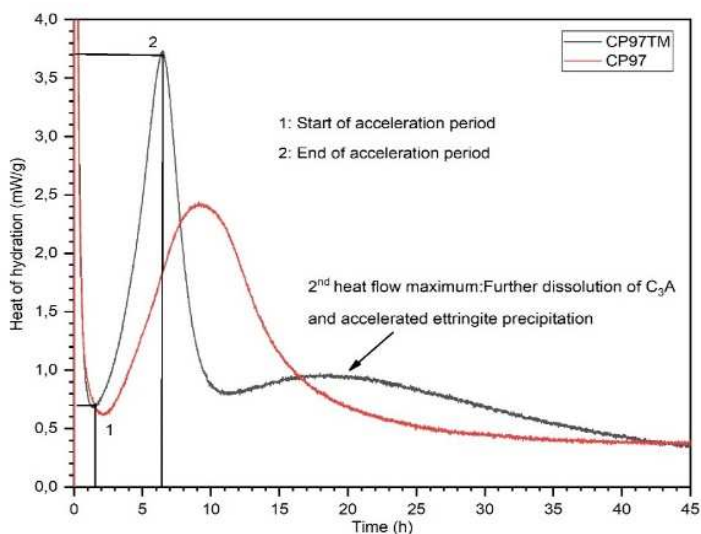
445 **Table 11** Chemical composition of the OPC 97 TM, OPC97 cements measured by XRF analysis

Oxides (wt%)	OPC 97 TM	OPC 97
SiO ₂	20.5	19.7
Al ₂ O ₃	4.7	5
Fe ₂ O ₃	3.1	3.1
CaO	65.5	62.4
MgO	ND	0.6
Na ₂ O	ND	ND
K ₂ O	ND	0.5
SO ₃	1.9	2.5
TiO ₂	ND	0.3
P ₂ O ₅	ND	0.9
ZnO	ND	0.2
L.O.I	3.6	4.0
Total (%)	99.2	99.0

446 3.2.2. Heat of cement hydration

447 The rates of heat evolution of the hydrated cement pastes are shown in Fig. 13. The result indicates that the
 448 OPC 97 cement presents hydration behavior similar to the OPC 97 TM because the curve shapes are similar. By
 449 comparing the two curves, we also note that the setting of OPC 97 TM begins before OPC 97 cement (point 1). This
 450 could be due to the higher reactivity of the M1 polymorph compared to the M3 polymorph in C_3S phase. Indeed,
 451 OPC 97 TM cement mainly contains M1 polymorph whilst OPC 97 cements contain the M1 and M3 polymorph (Fig.
 452 5). In addition, a high amount of C_2S phase of the CP 97 clinker (10.69 wt% - Table 9) is a cause de delay because
 453 the C_2S phase is less reactive than the C_3S phase. Previous studies [20, 67] show that the presence of zinc during

454 clinkerisation had no effect on cement hydration. This is particularly interesting for sediment which often contains
 455 the elements such as zinc.



456
 457 **Fig. 13** Heat of hydration of cement pastes (W/C = 0.5)

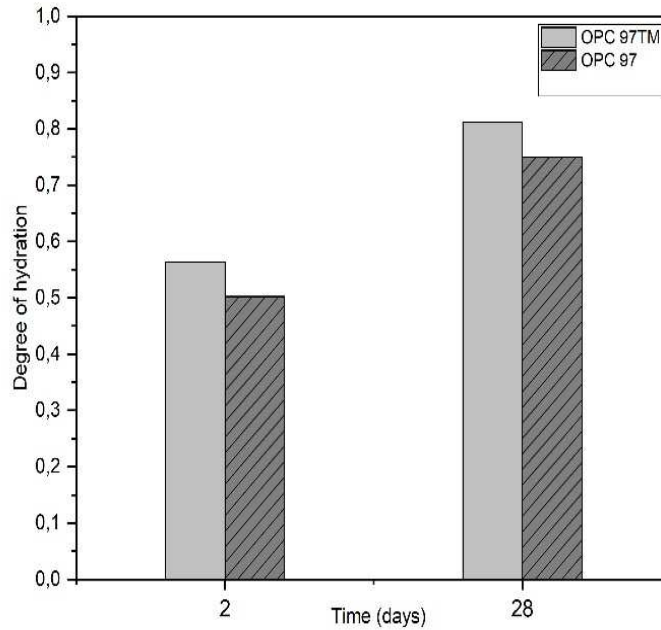
458 **3.2.3. Degree of hydration of cements**

459 Table 12 shows the theoretical amount of bound water for the two cements for complete hydration. These
 460 values depend on the contents of the mineral phases of each cement.

461 **Table 12** Determination of $W_n(\infty)$ from the mineral composition of the cement and the theoretical values of bound
 462 water produced for the major phases of the cement for complete hydration

Phase	Coefficient proposed by NIST	Mineral composition of cements (wt%)		Mass of bound water for complete hydration (g/100 g of anhydrous cement)	
		OPC 97 TM	OPC 97	OPC 97 TM	OPC 97
C ₃ S	0.24	73.96	66.33	17.75	15.92
C ₂ S	0.21	4.77	10.58	1.00	2.22
C ₃ A	0.4	5.93	7.51	2.37	3.00
C ₄ AF	0.37	9.77	10.31	3.62	3.814
Lime	0.33	1.24	0.78	0.408	0.257
Total (%)		95.67	95.51	25.148	25.22

463 The degree of hydration of the cement pastes after 2 and 28 days of curing using the result from the TGA
 464 analysis is shown in Fig. 14.



465
466 **Fig. 14** Degree of hydration of cement pastes (W/C = 0.5)

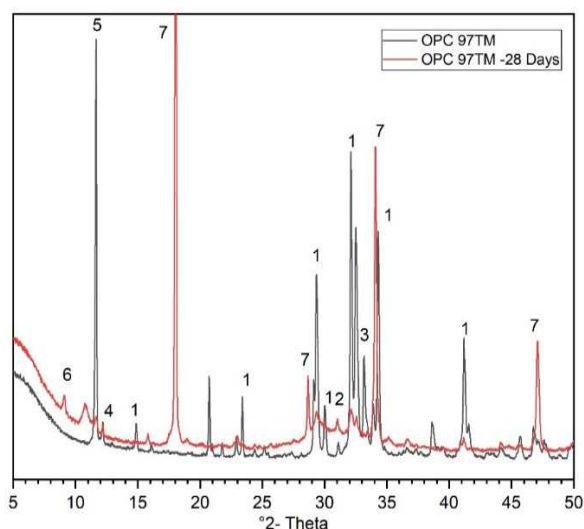
467 The measurement result shows that the OPC 97 possesses hydration behavior similar to the OPC 97 TM cement
468 because the degree of hydration of the two cement pastes increases over time of hydration. The degree of
469 hydration of OPC 97 cement reaches 0.51 after 2 days and 0.76 after 28 days. These values are comparable to
470 those of the commercial cement [56]. However, OPC 97 TM cement has the higher degree of hydration than the
471 OPC 97 cement at early ages as well as long term. This is in accordance with that of the calorimetry measurement.
472 In addition, the Ca(OH)_2 content formed during cement paste hydration was also measured by TGA analysis. Table
473 13 presents the Ca(OH)_2 /initial cement mass ratio of the two cement pastes over time of hydration.

474 **Table 13** Ca(OH)_2 /initial cement mass ratio over time of hydration

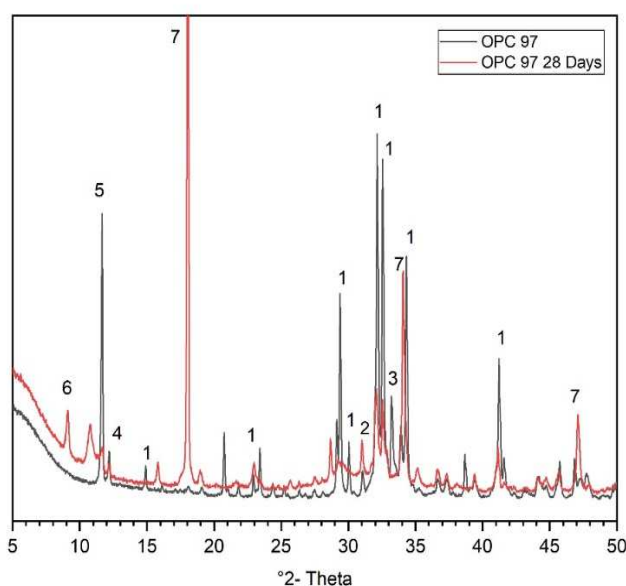
Time (days)	OPC 97 TM	OPC 97
2 days	20.15%	16.31%
28 days	29.04%	25.33%

475 The result shows that the Ca(OH)₂ content formed by the OPC 97 cement paste is lower than that formed by
 476 the OPC 97 TM cement paste. The difference is due to the lower content of the C₃S phase of OPC 97 cement
 477 compared to OPC 97 TM cement. It should be noted that for Portland cement, a low content of Ca(OH)₂
 478 corresponds to a low content of C-S-H phase.

479 The evolution of the mineral phases of hydrated cement paste over time of hydration is presented in Fig. 15
 480 and Fig. 16. The result clearly shows a decrease of anhydrous phases as well as the formation of hydrate phases
 481 such as portlandite and ettringite (Aft). However, the presence of C-S-H phase is not identified in the XRD pattern
 482 due to its amorphous nature. In conclusion, the substitution rate of the sediment in the raw meal does not modify
 483 the mineralogical assemblage of the hydrated cement pastes.



484
 485 **Fig. 15** X-ray diffraction (XRD) of OPC 97 TM cement paste over time of hydration (1: C₃S, 2: C₂S, 3: C₃A, 4: C₄AF, 5:
 486 Gypsum, 6: Ettringite (Aft), 7: Portlandite)

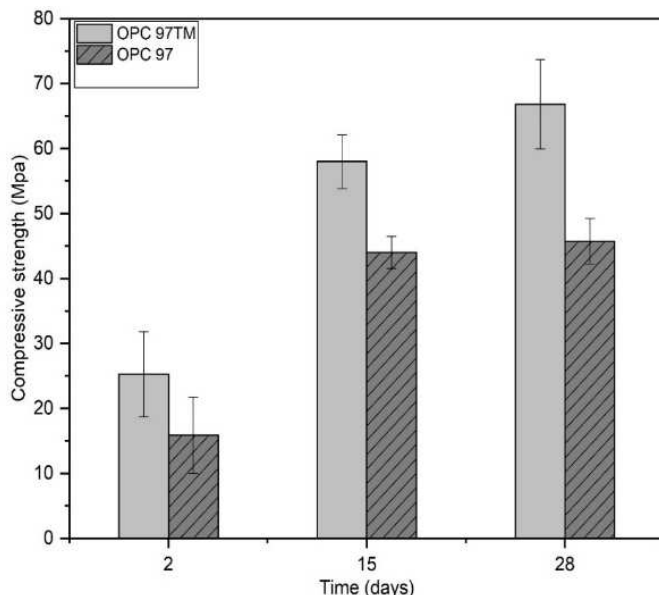


487
 488 **Fig. 16** X-ray diffraction (XRD) of OPC 97 cement paste over time of hydration (1: C₃S, 2: C₂S, 3: C₃A, 4: C₄AF, 5:
 489 Gypsum, 6: Ettringite (Aft), 7: Portlandite)

3.2.4. Mechanical performances

Fig. 17 represents the compressive strength of cement pastes after 2, 15 and 28 days of hydration. This choice allows us to study the behavior of resistance development of hydrate cement paste between early ages (2 days) and long term. The development of compressive strength over time was observed in both cement pastes. This is due to the anhydrous cement hydration reaction to form hydrates such as C-S-H phase, which is the origin of the mechanical resistance in the cementitious material. This result also in accordance with XRD result and degree of hydration result. However, OPC 97 TM cement shows higher compressive strength than the OPC 97 cements at an early ages (2 days) and long term (15 and 28 days). This difference in the compressive strength of the cement pastes could be explained by:

- The retardation effect of the hydration of C₃S observed by the isothermal calorimetry of OPC 97 cement compared to OPC 97 TM cement (Fig. 13) at an early age.
- The C₃S/C₂S ratio of OPC 97 TM cement is higher than that of OPC 97 cement (15.5 and 6.25 for OPC 97 TM, OPC 97 respectively). Knowing that the C₃S reactivity is much higher than that of C₂S phase, this allows to quickly forming the C-S-H phase in the cement paste during hydration.
- The presence of alkali in OPC 97 cement could also have a retardation effect on the hydration and influencing the compressive strength [69].
- After 15 days of hydration, the development of mechanical resistance in the two cement pastes slowed down, in particular in the case of OPC 97 cement which has a high content of C₂S showing slow hydration behavior.



509

510 **Fig. 17** Compressive strength of cement pastes (W/C = 0.5) after 2, 15 and 28 days of hydration

511 3.3. NUMERICAL MODELING OF CEMENT HYDRATION

512 The hydration of the OPC 97 TM and OPC 97 cement was numerically modeled using the CEMHYD3D code. The
513 characteristics of the two cements such as the particle size distribution, the mineral composition were used as the
514 input data to build a numerical cement into the CEMHYD3D code before numerical modeling.

515 3.3.1. Particle size distribution of cements

516 The particle size distribution of the OPC 97 TM and OPC 97 cement was measured using the laser particle
517 analyzer COULTER LS 13 320 type. Tables 14 - 15 present the experimental and numerical measurement result of
518 the OPC 97 TM and OPC 97 cements respectively. The result shows that the particle size distribution of the
519 cements used in the CEMHYD3D code is comparable to that of experimental result. This is very important to
520 assume the hydration behavior of cement modeled in the CEMHYD3D code. Indeed, a finer granularity of the
521 cement leads to an acceleration of the hydration kinetics [70].

522 **Table 14** Particle size distribution of OPC 97 TM cement (Experimental and numerical result)

Diameter of particles (μm)	Mass fraction (%) (Exp)	Mass fraction (%) (CEMHYD3D)
1	12.805	12.236
3	4.056	3.874
5	6.023	5.756
7	6.443	6.176
9	6.163	5.909
11	5.662	5.328
13	5.127	4.898
15	4.644	4.611
17	4.259	3.944
19	3.982	3.805
21	3.736	3.820
23	3.490	3.297
25	3.241	2.116
29	5.808	6.639
33	7.257	4.854
37	4.199	6.886
49	10.860	12.851
73	2.250	3.000
Total (%)	100.00	100

523

524 **Table 15** Particle size distribution of OPC 97 cement (Experimental and numerical result)

Diameter of particles (μm)	Mass fraction (%) (Exp)	Mass fraction (%) (CEMHYD3D)
1	11.3487	10.9460
3	3.8930	3.7573
5	5.9458	5.7252
7	7.0075	6.7446
9	7.2094	6.9749
11	6.9718	6.7212
13	6.4481	6.1794
15	5.8153	5.5849

17	5.1927	5.3073
19	4.6175	4.8009
21	4.0419	3.8550
23	3.5097	3.3277
25	3.0766	2.1353
29	5.2911	6.7007
33	6.7252	4.8991
37	3.9203	6.9499
41	6.5334	6.3905
53	1.6881	3.01
57	0.7630	-
Total (%)	99.9993	100.0000

525 **3.3.2. Mineral composition of OPC 97 TM and OPC 97 cement**

526 The CEMHYD3D code uses the volume fraction of mineral phases as input data to build a 3D – microstructure of
527 cement. Therefore, the mineral composition of the cement presented in the Table 12 must be converted into the
528 volume proportion using the densities values of the mineral phases proposed by NIST [71]. Table 16 shows the
529 experimental and numerical result of the mineral composition (volume fraction) of two cements OPC 97 TM and
530 OPC 97 as well as the W/C ratio used. The result demonstrated a good coherence between the experimental and
531 numerical result on the proportion of the phases as well as the W/C ratio. This is very important to assume the
532 precision of the numerical result.

533 **Table 16** Volume fraction of cements OPC 97 TM and OPC 97 (Experimental and numerical result)

Phases	OPC 97 TM cement			OPC 97 cement		
	Exp (%)	CEMHYD3D code		Exp (%)	CEMHYD3D code	
		Pixels	%Volume		Pixels	%Volume
C ₃ S	74.693	289811	74.617209	66.64	257381	66.267505
C ₂ S	4.719	18378	4.7317564	10.41	39609	10.198071
C ₃ A	6.344	24902	6.411481	8	30572	7.8713275
C ₄ AF	8.492	32944	8.4820429	8.91	34026	8.7606238
Gypsum	5.75	22362	5.757511	6.04	23235	5.982281
Total (%)	99.998	388397	100	100	384823	99.0798
W/C	0.5	0.4999		0.5	0.5	

534 **3.3.3. Determination of the β value in the CEMHYD3D code**

535 In order to determine the β value in the CEMHYD3D code, the values of the degree of hydration of OPC 97 TM
536 and OPC 97 cement pastes at 2 days of hydration measured by TGA analysis were used as the calibration values. In
537 fact, we run a simulation of 1000 cycles with any β value, then we look for the value of the number of cycles that

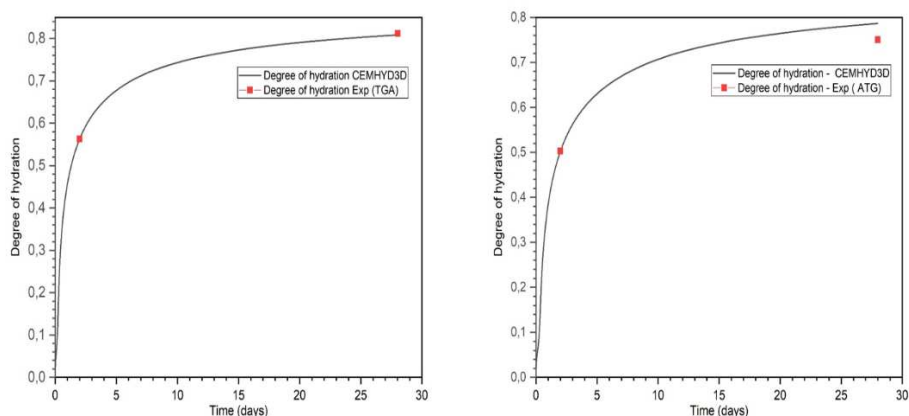
538 allows to reach a degree of hydration corresponding to the experimental value of the degree of hydration at 2
 539 days.
 540 The β value is determined according to Eq(15) and Eq(16) equations with the cycle number values previously
 541 found. In our case, the β values are equal to 0.00008742 for OPC 97 TM cement and equal to 0.00011186 for OPC
 542 97 cement.

543 3.3.4. Results of the numerical modeling of cement hydration in the CEMHYD3D code

544 The hydration of the two cements (OPC 97 TM and OPC 97) was numerically modeled in the code CEMHYD3D
 545 at a constant temperature of 20 °C and in the 100% relative humidity, which are similar with the experimental
 546 hydration conditions. The modeling results are presented in the following figures and compared with the
 547 experimental results to assess the reliability of the CEMHYD3D code in this study.

548 a) Degree of hydration of cement pastes

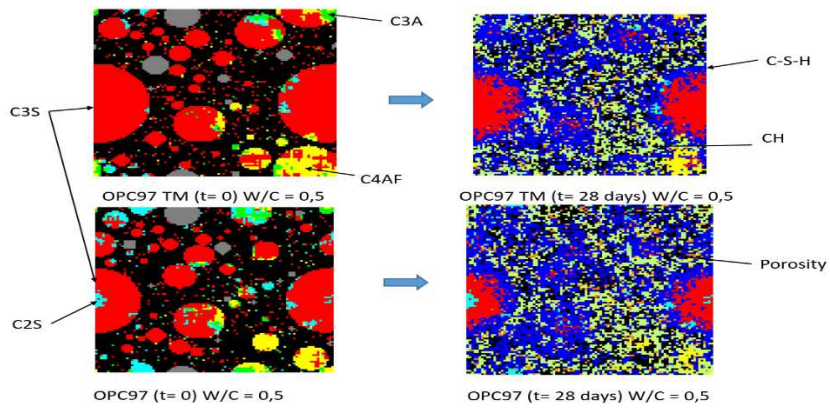
549 Fig. 18 shows the degree of hydration estimated by the CEMHYD3D code comparing with the experimental
 550 values measured by the TGA analysis at 2 and 28 days of hydration. A good consistency between the numerical
 551 and experimental values was observed. The result in the CEMHYD3D code also showed a higher degree of
 552 hydration of OPC 97 TM cement compared to OPC 97 cement at early ages and long term. This is in accordance
 553 with previous experimental results.



554
 555 **Fig. 18** Degree of hydration of OPC 97 TM (left) and OPC 97 (right) cements (Experimental and numerical result)

556 Fig. 19 shows the microstructure of cement paste generated from the CEMHYD3D code at the initial state ($t =$
 557 0) and after 28 days of hydration. This result is very interesting because:

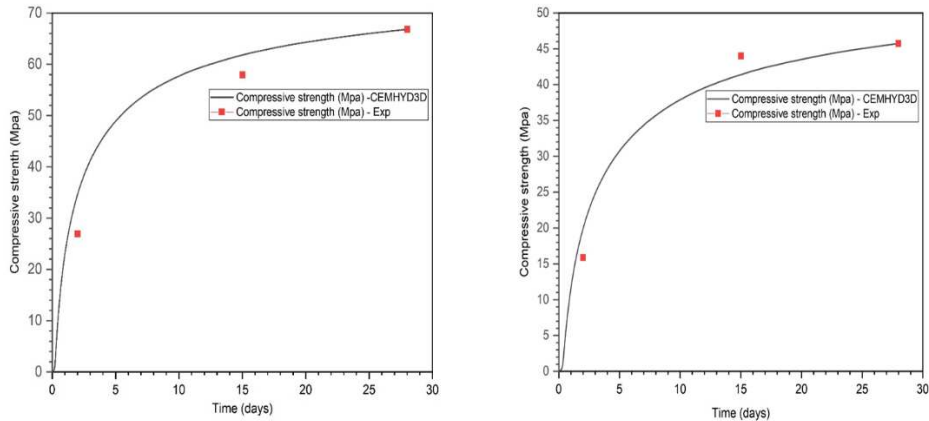
- 558 • At the initial state, all the mineral phases of the two cements are present. The size of the anhydrous
 559 cement grains is in accordance with the experimental result.
- 560 • After 28 days of hydration, the hydrate formation such as C-S-H phase, Ca(OH)_2 and the consumption of
 561 anhydrous cement grains were also observed. The result shows the influence of anhydrous cement grains
 562 size on reactivity during hydration.
- 563 • The microstructure generated from the CEMHYD3D code is comparable to that observed by SEM analysis
 564 in previous studies [20, 43].



565
 566 **Fig. 19** Microstructure generated in the CEMHYD3D code of OPC 97 TM and OPC 97 cements in the initial state
 567 (left) and after 28 days of hydration

568 **b) Compressive strength of cement pastes**

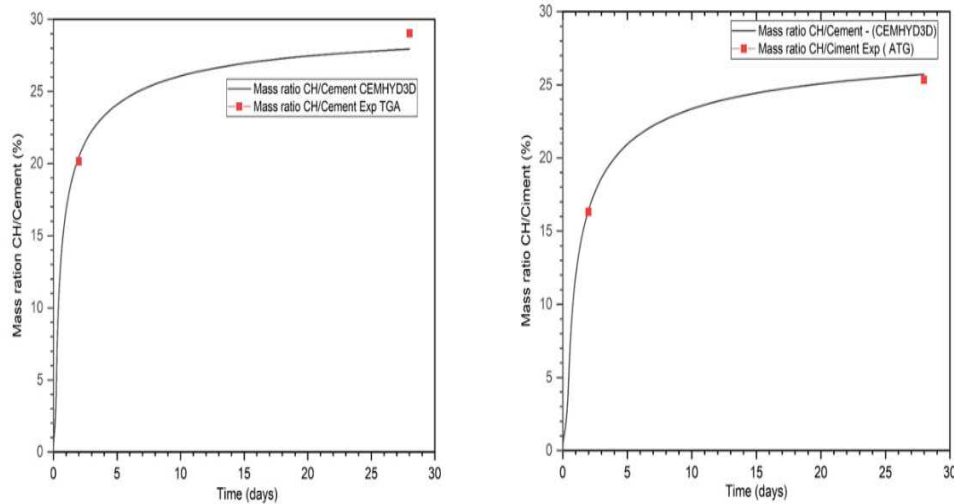
569 The CEMHYD3D code uses Eq(12) equation to estimate the compressive strength of cement paste over time of
 570 hydration. The numerical and experimental result of the compressive strength is presented in Fig. 20. The
 571 compressive strength estimated by the CEMHYD3D code is in accordance with the experimental results for the two
 572 cement pastes. This result confirms that the development behavior of mechanical resistance of the two cement is
 573 similar.



574
 575 **Fig. 20** Numerical and experimental result of the compressive strength of OPC 97 TM (left) and OPC 97 (right)
 576 cements

577 **c) Ca(OH)₂ quantification in the CEMHYD3D code**

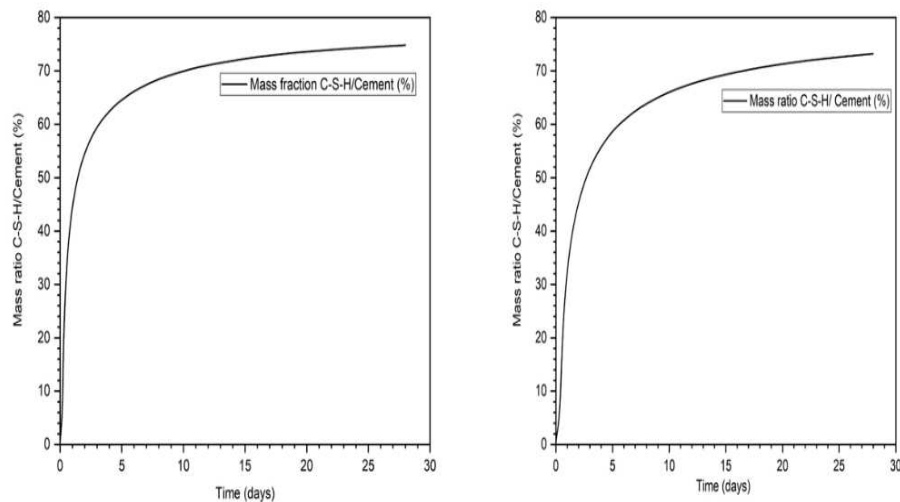
578 Because the Ca(OH)₂ phase is a data which can be determined using the TGA analysis, we chose to compare the
 579 numerical and experimental quantity of this hydrate to evaluate the reliability of the CEMHYD3D code in our study.
 580 CEMHYD3D code presented the evolution of Ca(OH)₂ volume over time of hydration, a Ca(OH)₂ density value equal
 581 of 2.24 (g/cm³) is used to convert from volume fraction to mass fraction. Fig. 21 shows the Ca(OH)₂/ initial cement
 582 mass ratio of two cement pastes over the time of hydration.



583

584 **Fig. 21** CH/initial cement mass ratio of OPC 97 TM (left) and OPC 97 (right) cement paste

585 From the result in Fig. 21, we note that the CEHDYD3D code shows a good consistency with the experimental
 586 results for the two cement pastes. In addition, the CEMHYD3D code also makes it possible to monitor the
 587 evolution of the anhydrous phases as well as the hydrates over time of hydration. This is interesting because it is
 588 difficult to follow the evolution of phases by experimental analysis, for example C-S-H phase. This phase is
 589 responsible for the development of mechanical resistance in the cementitious materials. Following the evolution
 590 of C-S-H could help understand the development of mechanical strength. In this study, we present the numerical
 591 result of the evolution of C-S-H over time of hydration in the CEMHYD3D code (Fig. 22).



592

593 **Fig. 22** C-S-H/initial cement mass ratio measured by CEMHYD3D code for OPC 97 TM (left) and OPC 97 (right)
 594 cement pastes over time of hydration

595 From the result of the C-S-H/initial cement mass ration, we can extract the following conclusions:

- 596 • OPC 97TM has a higher C-S-H/ initial cement mass ratio than OPC 97 cement at early ages (2 days). This
 597 may explain the higher mechanical resistance development of OPC 97TM compared to OPC 97.
- 598 • At 28 days of hydration, this ratio is relatively similar for the two cements, however the compressive
 599 strength of the OPC 97TM cement is higher than that of the OPC 97 cement. This may be due to the
 600 presence of the minor elements integrated into C-S-H phase which influence mechanical performance.

601 4. CONCLUSION

602 The objective of this study is to recycle the maximum amount of the NSL sediment as a raw material in the
 603 cement production at laboratory. The following principal results are obtained:

- 604 - The NSL sediment contains the 4 principal oxides such as CaO SiO₂, Al₂O₃ and Fe₂O₃ which needs to
 605 produce the Portland cement.

606 - A substitution rate of 31 wt% of NSL sediment can be recycle in the raw meal to produce Portland cement.
607 - In all produced clinkers (the reference clinker and the clinker made from the substitution of sediment), the
608 4 principal crystalline phases of an ordinary Portland cement such as C₃S, C₂S, C₃A and C₄AF are identified. The XRD
609 pattern and SEM – EDS analysis indicate that the substitution of the sediment promotes the formation of M3
610 polymorph in C₃S phase and an orthorhombic polymorph in C₃A phase due to the presence of minor oxides such as
611 MgO, Na₂O.

612 - The result of free lime content quantification and the identification of the crystalline phases of the clinkers
613 show that the cooling process used in this study did not cause a negative effect such as the decomposition of alite.

614 - The typical form of alite and belite was also identified. The presence of SO₃ in CP97 clinkers promotes the
615 formation of larger crystals of alite than those in the reference clinker CP 97 TM.

616 - The atomic ratio of the major elements in the main phases of the two clinkers measured from the SEM-
617 EDS analysis is higher than the theoretical values. However, the ratio of C₂S, C₃A, C₄AF phases are relatively similar,
618 while the ratio in C₃S phase of clinker made from the substitution of the sediment is higher than that of reference
619 clinker. The substitution of sediment seems to have more effect on the C₃S formation than other phases in the
620 clinker.

621 - The two cements show similar hydration behavior similar. However, the mechanical performance of
622 cement decreases with the substitution rate of sediment. This can be explained by the formation of the M3
623 polymorph of C₃S in the clinker-based sediment which is less reactive than the M1 polymorph.

624 - The zinc presence in the sediment does not modify the C₃A formation in the clinker. The zinc is present in
625 all phases except in the C₂S phase. In addition, the presence of zinc in clinker phases does not influence on the
626 hydration behavior of cement. This is very interesting because the sediment often contains elements such as zinc.

627 - The CEMHYD3D code was used to simulate the hydration of OPC 97 TM and OPC 97 cement paste. The
628 numerical and experimental results are quite consistent. The modeling result confirms the hydration behavior of
629 cement produced at laboratory. This code also allows us to visually follow the evolution of all phases over time of
630 hydration. This is interesting because the hydration of the cement is a complex process and difficult to follow all
631 the evolutions by the experimental analysis. In addition, based on the numerical modeling result generated from
632 the CEMHYD3D code, several studies of the microstructure can be investigated as leaching coupling with other
633 computer code.

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636 **Declarations of Competing Interest**

637 The authors declare that they have no known competing financial interests or personal relationships that could
638 have appeared to influence the work reported in this paper.

639 **Availability of data and material:**

640 We confirm that all results are available in the database. If necessary, please contact us at the address:
641 duc.chinh.chu@imt-lille-douai.fr

642 **Code availability:** CEMHYD3D: A Three-Dimensional Cement Hydration and Microstructure Development
643 Modelling Package. Version 2.0 | NIST

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