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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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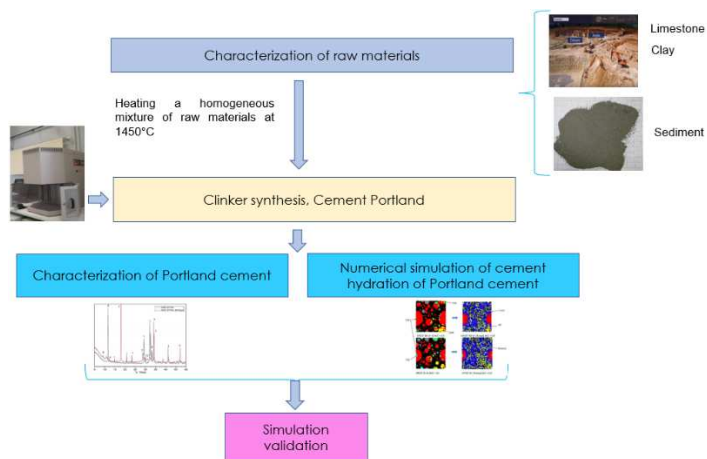
## 9 ABSTRACT

10 Around 56 million m<sup>3</sup> 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 CaCO<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub> 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 m<sup>3</sup> 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 ( $\text{CaCO}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ ) 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 ( $\text{C}_3\text{S}$ :  $3\text{CaO}\cdot\text{SiO}_2$ ), Belite ( $\text{C}_2\text{S}$ :  $2\text{CaO}\cdot\text{SiO}_2$ ), Tricalcium aluminate ( $\text{C}_3\text{A}$ :  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ) and  
 49 Alumino-tetracalcium ferrite ( $\text{C}_4\text{AF}$ :  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ ) (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	$\text{C}_3\text{S}$	$\text{Ca}_3\text{SiO}_5$	45.0	79.7
Belite	$\text{C}_2\text{S}$	$\text{Ca}_2\text{SiO}_4$	5.7	29.8
Tricalcium aluminate	$\text{C}_3\text{A}$	$\text{Ca}_3\text{Al}_2\text{O}_5$	1.1	14.9
Alumino-tetracalcium ferrite	$\text{C}_4\text{AF}$	$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$	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  $\mu\text{m}$  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  $\text{CaCO}_3$ ,  
 77  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , 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 $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ) with the angle acquired  $2\theta$  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.

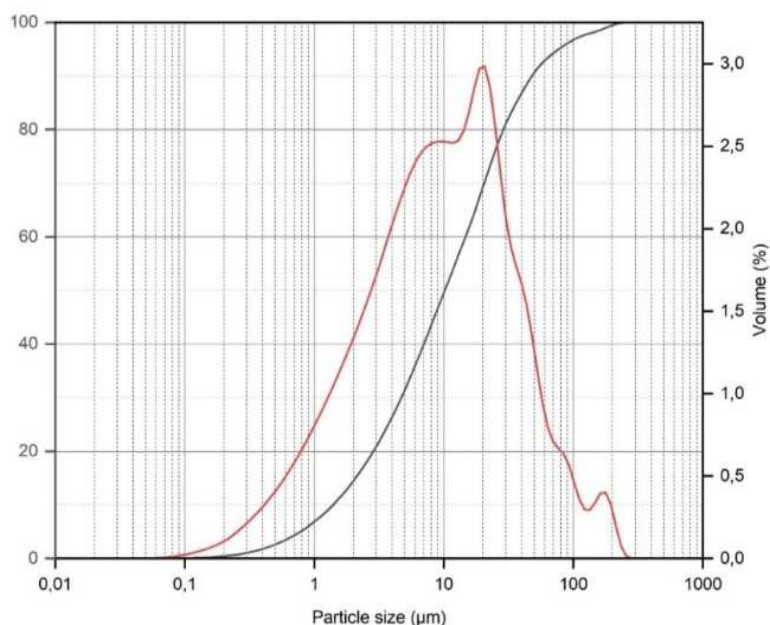
### 99 **2.1.1. The physical characteristics of the sediment**

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 cm<sup>2</sup>/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 cm<sup>2</sup>/g).

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

Physical characteristics	NSL
Density (g/cm <sup>3</sup> )	2.43
BET (cm <sup>2</sup> /g)	43 765
Blaine surface (cm <sup>2</sup> /g)	6 562
OM content (wt%)	16.1
LOI 950°C (wt%)	27.63
d <sub>10</sub> (µm)	1.39
d <sub>50</sub> (µm)	10.16
d <sub>90</sub> (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 SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. In addition, minor oxides such as MgO, ZnO, Na<sub>2</sub>O  
 114 and K<sub>2</sub>O 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 + SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>) 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:

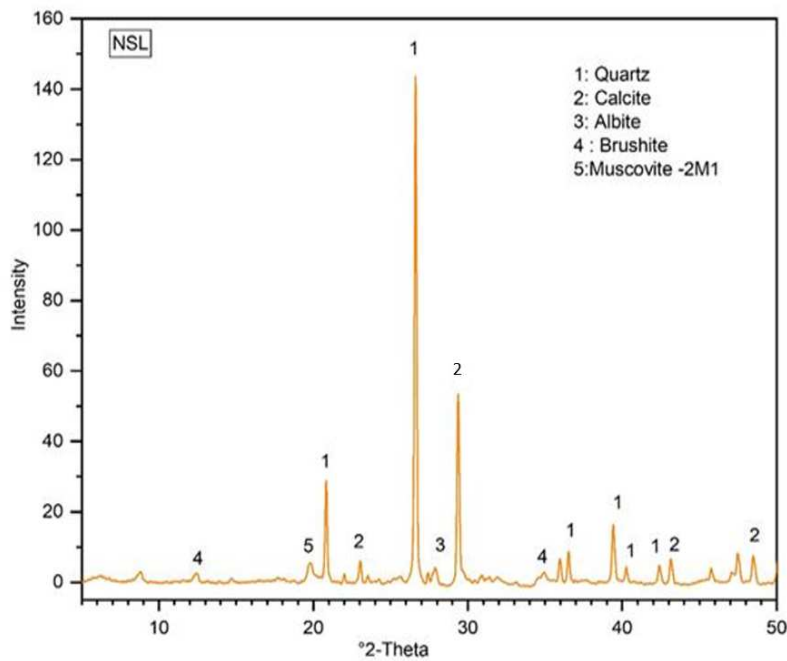
$$\text{CaO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 80\%$$

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

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

TiO <sub>2</sub>	0.60	0	0	0	-
P <sub>2</sub> O <sub>5</sub>	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

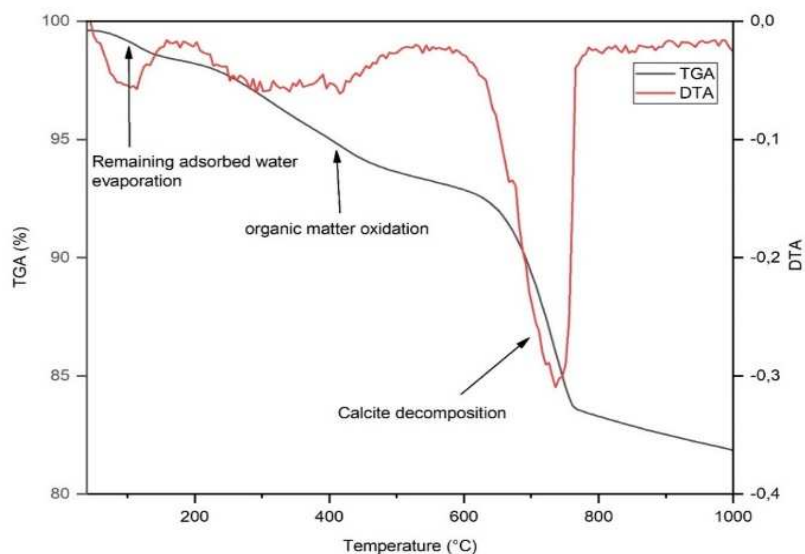
121 The results of the mineral analysis (Fig. 2) show that the principal phases of the sediment are quartz (SiO<sub>2</sub>),  
 122 calcite (CaCO<sub>3</sub>), brushite (CaHPO<sub>4</sub>·2H<sub>2</sub>O) and muscovite (KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH,F)<sub>2</sub>). These results 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	<b>0.5</b>	<b>2</b>
Ba (mg/kg)	1.4912	<b>20</b>	<b>100</b>
Cd (mg/kg)	< 0.008	<b>0.04</b>	<b>1</b>
Cr (mg/kg)	< 0.03	<b>0.5</b>	<b>10</b>
Cu (mg/kg)	2.0509	<b>2</b>	<b>50</b>
Mo (mg/kg)	0.5538	<b>0.5</b>	<b>10</b>
Ni (mg/kg)	0.4799	<b>0.4</b>	<b>10</b>

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

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 C<sub>3</sub>S and C<sub>2</sub>S [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 C<sub>3</sub>A and C<sub>4</sub>AF phases. A high  
 158 value of AR will provoke the formation of a high content of C<sub>3</sub>A 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 CaCO<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>  
 162 and Al<sub>2</sub>O<sub>3</sub> (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<sub>free</sub> and to have a significant content of C<sub>3</sub>S 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 <sub>3</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	SiO <sub>2</sub> (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 cm<sup>2</sup>/g. Finally,  
174 the cements were obtained by mixing pure gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) with clinker. The addition of gypsum has a very  
175 important role in controlling the setting of the cement. Indeed, the reaction of C<sub>3</sub>A 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 C<sub>3</sub>S, 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 SO<sub>3</sub> 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 SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>  
184 ratio greater than 0.7. In this study, gypsum was added to reach an SO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 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 $\alpha$  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  $\mu\text{m}$  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  $^{\circ}\text{C}$ . Based on a previous study [42], 8 g of cement and 4 g of water previously stored at 20  $^{\circ}\text{C}$  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  $^{\circ}\text{C}$ . The  
223 sample was demoulded after 24h and stored in saturated lime solution at 20  $^{\circ}\text{C}$  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  $^{\circ}\text{C}$

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

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  $^{\circ}\text{C}$  to  
246 105  $^{\circ}\text{C}$  with a rate of 2  $^{\circ}\text{C}/\text{min}$ , then maintained at 105  $^{\circ}\text{C}$  for 1h before increasing to the 1100  $^{\circ}\text{C}$  with a rate of 3  
247  $^{\circ}\text{C}/\text{min}$ .

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 cm<sup>3</sup> 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 C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF respectively at time t.

269  $[\%C3S]$ ,  $[\%C2S]$ ,  $[\%C3A]$ ,  $[\%C4AF]$ : Initial mass proportion of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF 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 μm<sup>3</sup>, called voxels, each  
 280 representing a phase for example: solid (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF, 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 μm<sup>3</sup> 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  $\sigma_0$ : 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 ( $\beta$ ) 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  $\beta$ : Conversion factor cycles/time in hour/(cycles)<sup>2</sup>.

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<sup>°</sup>: Temperature of the system in °C.

312 To determine the  $\beta$  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 <sub>2</sub>	14.30	13.8	13.19	12.9
Al <sub>2</sub> O <sub>3</sub>	3.26	2.8	3.00	3.05
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.00	0.00	0.21	Traces
K <sub>2</sub> O	0.00	0.00	0.57	0.59
SO <sub>3</sub> total	0.00	0.00	0.07	0.12
TiO <sub>2</sub>	0.00	0.00	0.19	0.17
P <sub>2</sub> O <sub>5</sub>	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 <sub>2</sub>	3.08	3.17	3.08	3.12

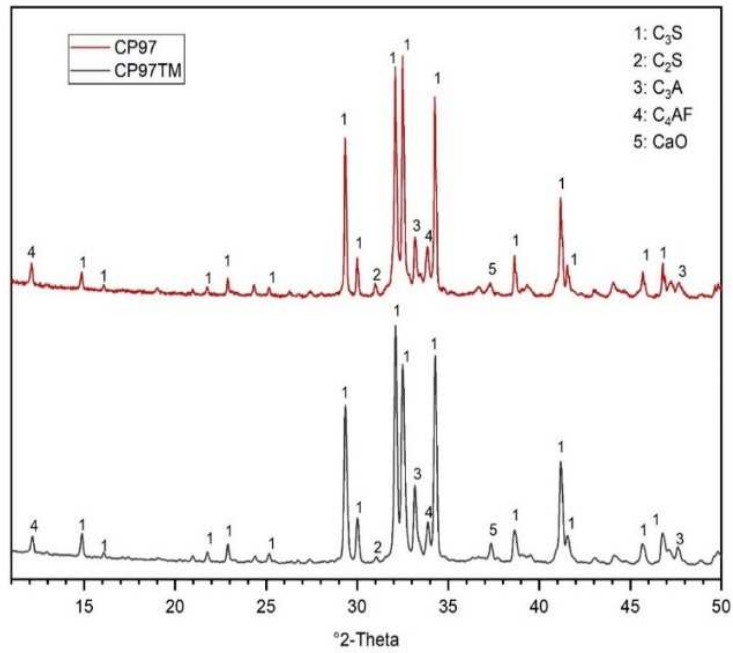
323 The experimental result was compared to the theoretical value in order to check the values of the modules  
324 used. A good compatibility was observed in particular in the case of the CP 97 formulation between the  
325 experimental and theoretical composition. However, an increase of LSF value in the case of the CP 97 TM  
326 formulation was noted. The result shows the presence of minor elements such as ZnO, SO<sub>3</sub>, 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 C<sub>3</sub>S in the M1 polymorph. In contrast, the presence of SO<sub>3</sub> promotes the  
329 formation of C<sub>3</sub>S 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 C<sub>3</sub>A. A decrease in C<sub>3</sub>A 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 <sub>3</sub> S	76.83	66.99
C <sub>2</sub> S	4.96	10.69
C <sub>3</sub> A	6.16	7.59
C <sub>4</sub> 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 C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF 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

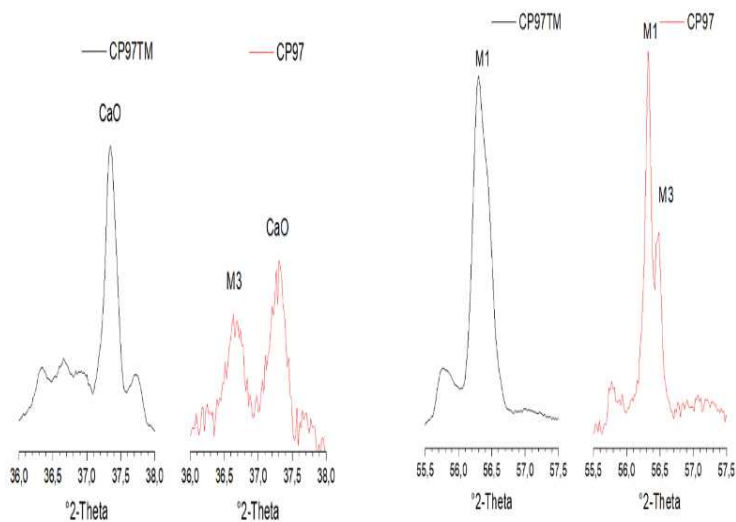
343 **Fig. 4** X-ray diffraction (XRD) of the CP 97 TM and CP 97 clinker

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 <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A
2θ	[36°-38°] [55.5°-57.5°]	[30.5°-32°] [32.7°-33.7°]	[47°-48°]

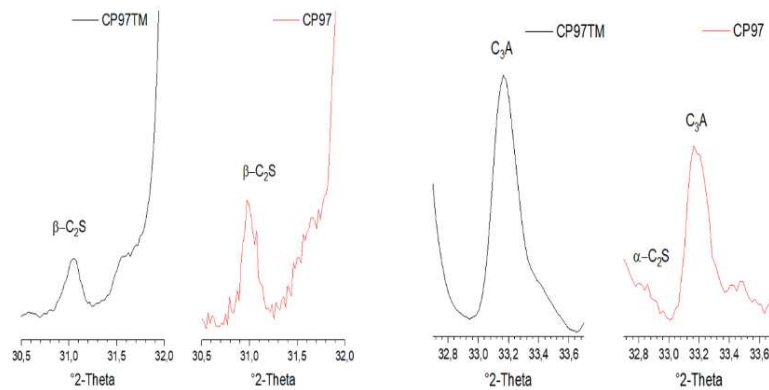
347 We note that the XRD pattern curve of the CP 97TM clinker is more "smooth" than that of the CP 97 clinker.  
 348 This may be due to the purity of the raw mix of CP 97 TM formulation which does not contain minor oxides.  
 349 Concerning the polymorph of C<sub>3</sub>S in the clinker, the XRD pattern 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

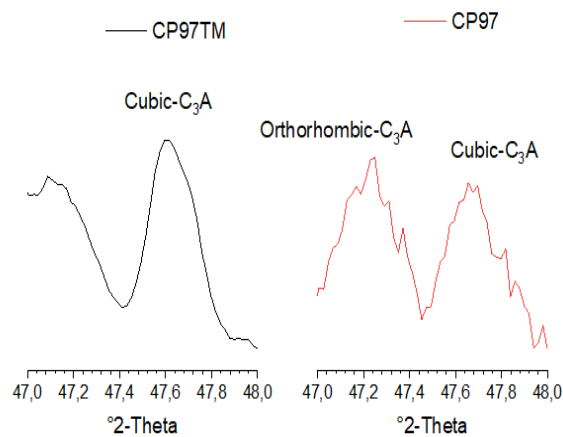
352 **Fig. 5** M1 and M3 polymorph of C<sub>3</sub>S of the clinker CP 97 TM and CP 97

353 To study the C<sub>2</sub>S polymorph, the result presented in Fig. 6 shows that the incorporation of sediment in the raw  
 354 meal did not affect the formation of C<sub>2</sub>S. The result also shows that the β-C<sub>2</sub>S polymorph is the principal polymorph  
 355 of C<sub>2</sub>S in the two clinkers. In addition, the result confirms that the cooling process in this study does not cause the  
 356 decomposition of C<sub>3</sub>S into γ-C<sub>2</sub>S polymorph and CaO<sub>free</sub> in the clinker. The decomposition of C<sub>3</sub>S directly influences  
 357 the quality of the cement because the γ-C<sub>2</sub>S polymorph is much less reactive than C<sub>3</sub>S, 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



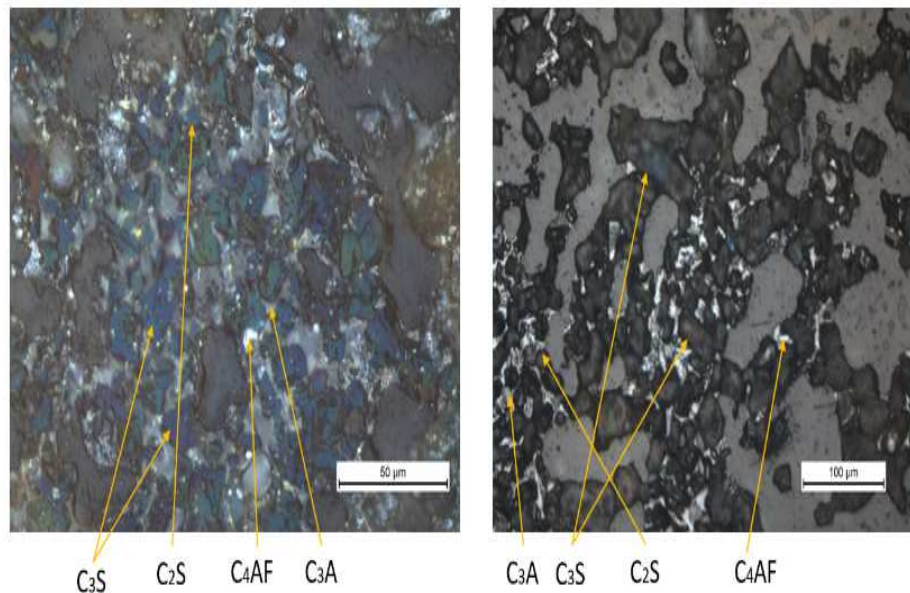
361  
 362 **Fig. 6** β-C<sub>2</sub>S and α-C<sub>2</sub>S polymorph of the CP 97 TM and CP 97 clinker

363 The formation of orthorhombic polymorph of C<sub>3</sub>A (Fig. 7) was observed in the CP 97 clinker. This could be due  
 364 to the presence of Na<sup>+</sup> ions which replaced Ca<sup>2+</sup> ions and led to the change from the cubic system to the  
 365 orthorhombic system [64].



366  
 367 **Fig. 7** Polymorph of C<sub>3</sub>A 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.

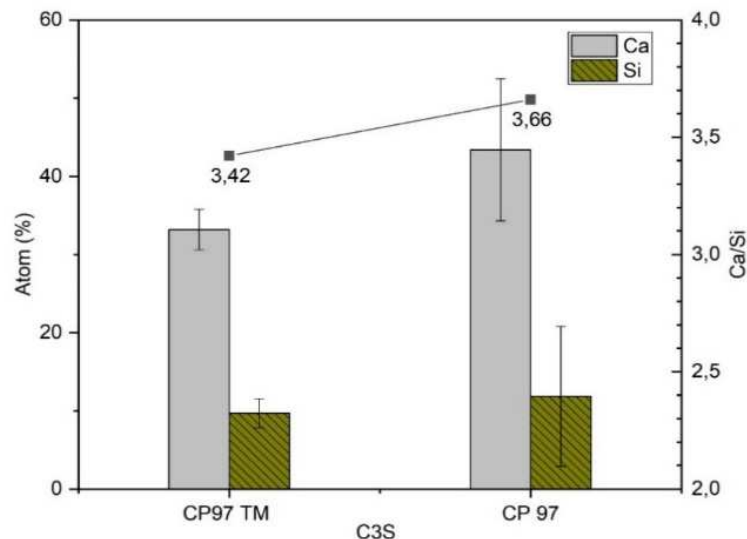


369  
370 **Fig. 8** Observation by optical microscope on the polished section of CP 97 TM (left) and CP 97 (right) clinker

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.



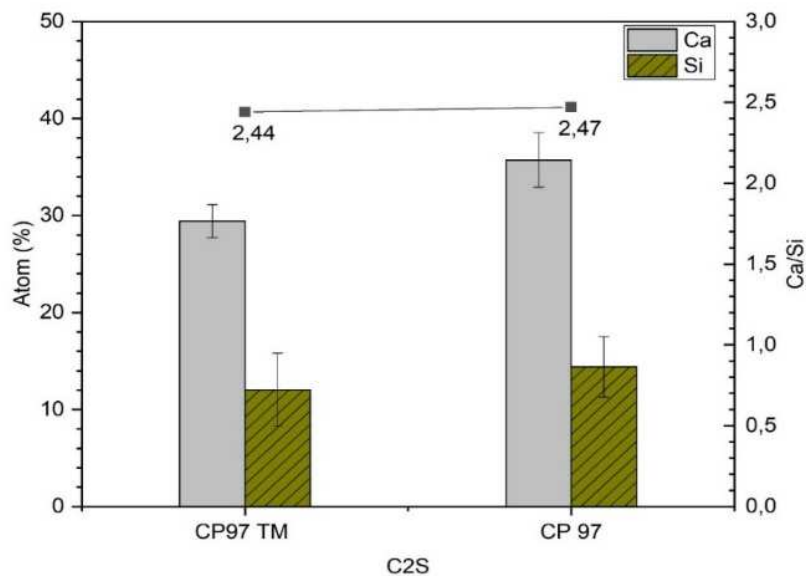
380  
381 **Fig. 9** Chemical composition and the ratio of major elements of  $C_3S$  phase

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.



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- 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 C<sub>3</sub>S 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 C<sub>2</sub>S phase
- 396 The result of the SEM - EDS analysis of the C<sub>2</sub>S 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 C<sub>2</sub>S phase (C/S = 2). However, this ration is similar for the two clinkers.
  - Same as the C<sub>3</sub>S phase, the C<sub>2</sub>S 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 C<sub>2</sub>S phase of the CP 97TM and CP 97 clinkers incorporates 1.42 wt% and 3.03 wt% of the minor elements respectively.

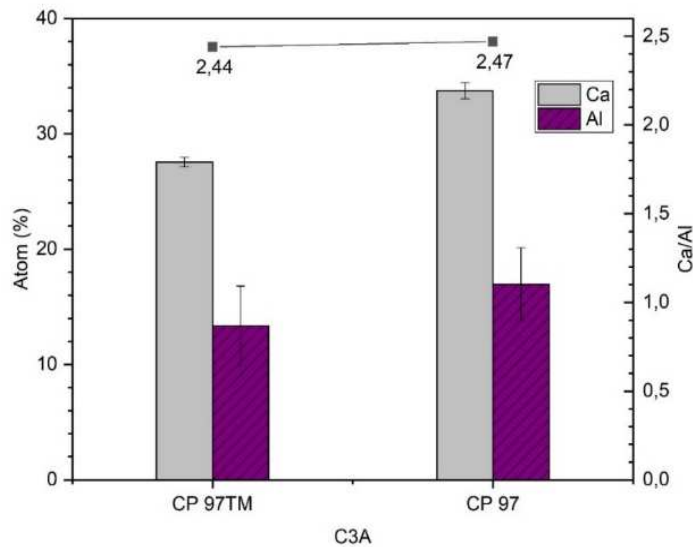
405 The result of the SEM - EDS analysis performed on the C<sub>3</sub>S and C<sub>2</sub>S phases shows that the substitution of

406 sediment for the raw materials does not affect the ratio of major elements of the C<sub>2</sub>S phase whilst it considerably

407 affects the ratio of major elements of the phase C<sub>3</sub>S. This is interesting because the C<sub>3</sub>S 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.

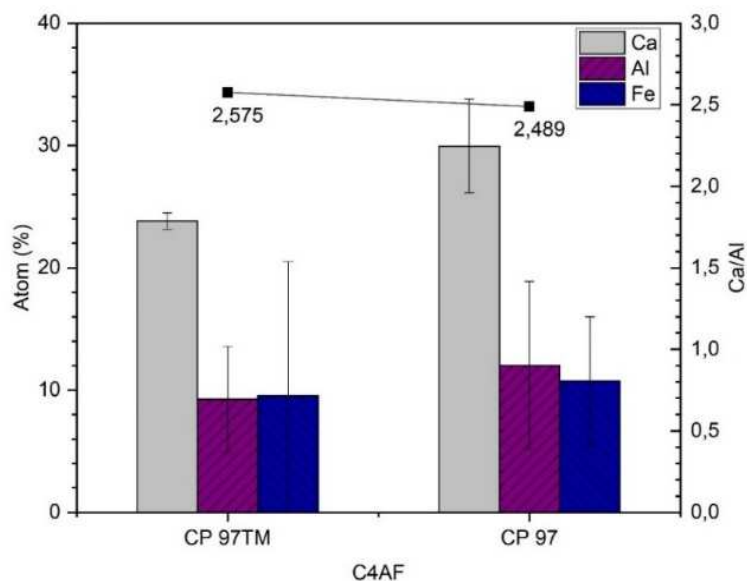


410

411 **Fig. 11** Chemical composition and the ratio of the major elements of C<sub>3</sub>A phase

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

- 413 • The major elements identified in the C<sub>3</sub>A phase are Ca, Al and O. The C/A (CaO/Al<sub>2</sub>O<sub>3</sub>) ratio in the two  
414 clinkers is higher than the theoretical value (Ca/Al = 1.5) of this phase. However, this ratio is relatively  
415 similar for the two clinkers.
- 416 • The C<sub>3</sub>A phase contains the minor elements such as Fe, Si in the CP 97 TM clinker and Si, Fe, Mg, alkali  
417 (Na, K) in the CP 97 clinker. However, the amount of Mg incorporated into this phase is 10 times less than  
418 that in the C<sub>3</sub>S phase.
- 419 • The presence of alkali (Na, K) identified in this phase of the CP 97 clinker is in accordance with than  
420 previously observed by XRD analysis which shows the incorporation of alkali promotes the formation of  
421 orthorhombic polymorph of C<sub>3</sub>A phase (Fig. 7). The amount of alkali in this phase of the CP 97 clinker is  
422 five higher than that of the C<sub>3</sub>S phase.
- 423 • The C<sub>3</sub>A phase of the CP 97 TM and CP 97 clinkers incorporates 3.42 wt% and 4.55 wt% of the minor  
424 elements respectively.



425

426 **Fig. 12** Chemical composition and the ratio of the major elements of the C<sub>4</sub>AF 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].

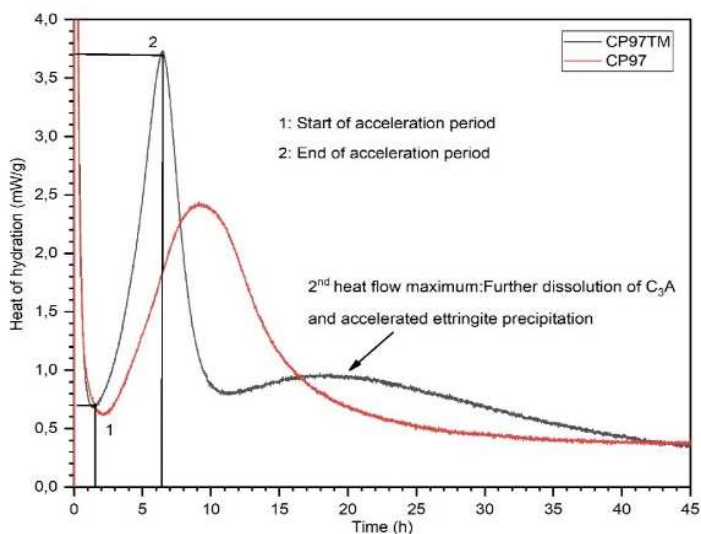
445 **Table 11** Chemical composition of the OPC 97 TM, OPC97 cements measured by XRF analysis

Oxides (wt%)	OPC 97 TM	OPC 97
SiO <sub>2</sub>	20.5	19.7
Al <sub>2</sub> O <sub>3</sub>	4.7	5
Fe <sub>2</sub> O <sub>3</sub>	3.1	3.1
CaO	65.5	62.4
MgO	ND	0.6
Na <sub>2</sub> O	ND	ND
K <sub>2</sub> O	ND	0.5
SO <sub>3</sub>	1.9	2.5
TiO <sub>2</sub>	ND	0.3
P <sub>2</sub> O <sub>5</sub>	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)

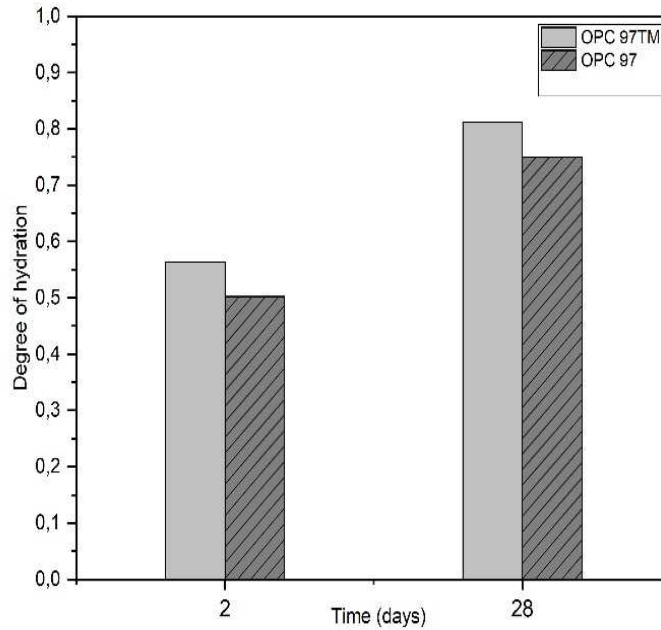
458 **3.2.3. Degree of hydration of cements**

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 <sub>3</sub> S	0.24	73.96	66.33	17.75	15.92
C <sub>2</sub> S	0.21	4.77	10.58	1.00	2.22
C <sub>3</sub> A	0.4	5.93	7.51	2.37	3.00
C <sub>4</sub> 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 **Fig. 14** Degree of hydration of cement pastes (W/C = 0.5)

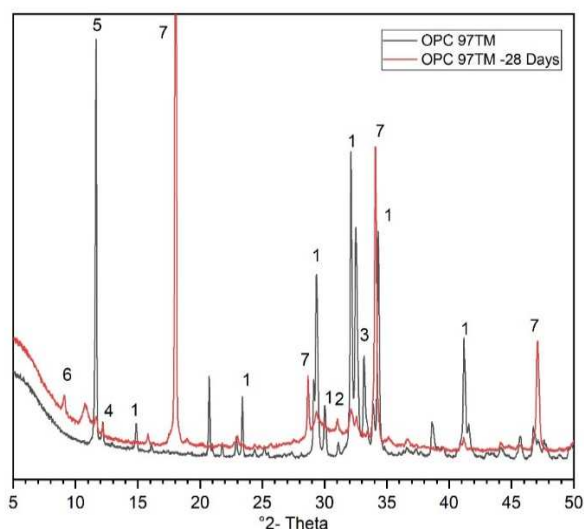
467 The measurement result shows that the OPC 97 possesses hydration behavior similar to the OPC 97 TM cement  
 468 because the degree of hydration of the two cement pastes increases over time of hydration. The degree of  
 469 hydration of OPC 97 cement reaches 0.51 after 2 days and 0.76 after 28 days. 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  $\text{Ca(OH)}_2$  content formed during cement paste hydration was also measured by TGA analysis. Table  
 473 13 presents the  $\text{Ca(OH)}_2$ /initial cement mass ratio of the two cement pastes over time of hydration.

474 **Table 13**  $\text{Ca(OH)}_2$ /initial cement mass ratio over time of hydration

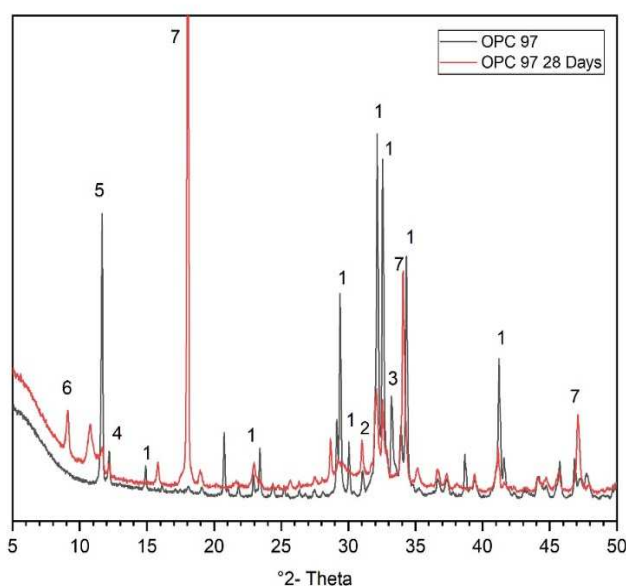
Time (days)	OPC 97 TM	OPC 97
2 days	20.15%	16.31%
28 days	29.04%	25.33%

475 The result shows that the Ca(OH)<sub>2</sub> 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 C<sub>3</sub>S 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)<sub>2</sub>  
 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: C<sub>3</sub>S, 2: C<sub>2</sub>S, 3: C<sub>3</sub>A, 4: C<sub>4</sub>AF, 5:  
 486 Gypsum, 6: Ettringite (Aft), 7: Portlandite)

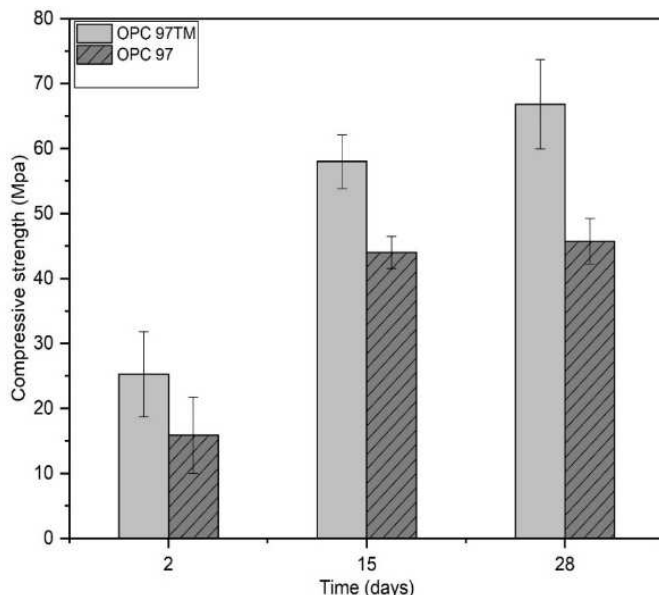


487  
 488 **Fig. 16** X-ray diffraction (XRD) of OPC 97 cement paste over time of hydration (1: C<sub>3</sub>S, 2: C<sub>2</sub>S, 3: C<sub>3</sub>A, 4: C<sub>4</sub>AF, 5:  
 489 Gypsum, 6: Ettringite (Aft), 7: Portlandite)

### 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  $C_3S$  observed by the isothermal calorimetry of OPC 97 cement compared to OPC 97 TM cement (Fig. 13) at an early age.
- The  $C_3S/C_2S$  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  $C_3S$  reactivity is much higher than that of  $C_2S$  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  $C_2S$  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 <sub>3</sub> S	74.693	289811	74.617209	66.64	257381	66.267505
C <sub>2</sub> S	4.719	18378	4.7317564	10.41	39609	10.198071
C <sub>3</sub> A	6.344	24902	6.411481	8	30572	7.8713275
C <sub>4</sub> 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  $\beta$  value in the CEMHYD3D code**

535 In order to determine the  $\beta$  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  $\beta$  value, then we look for the value of the number of cycles that

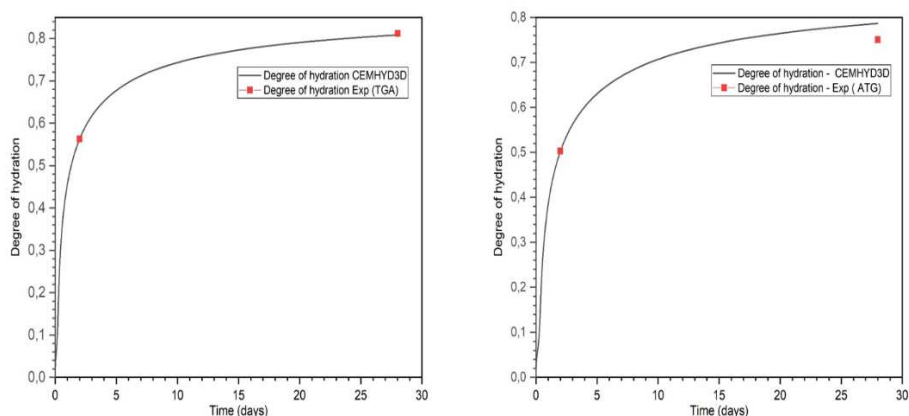
538 allows to reach a degree of hydration corresponding to the experimental value of the degree of hydration at 2  
 539 days.  
 540 The  $\beta$  value is determined according to Eq(15) and Eq(16) equations with the cycle number values previously  
 541 found. In our case, the  $\beta$  values are 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

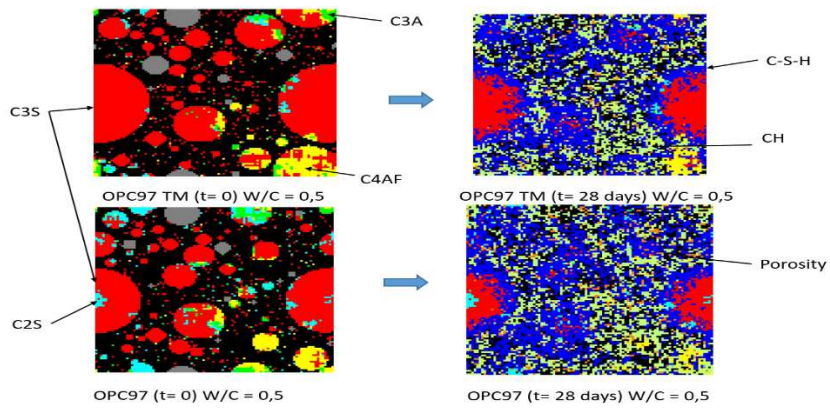
549 Fig. 18 shows the degree of hydration estimated by the CEMHYD3D code comparing with the experimental  
 550 values measured by the TGA analysis at 2 and 28 days of hydration. A good consistency between the numerical  
 551 and experimental values was observed. The result in the CEMHYD3D code also 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:

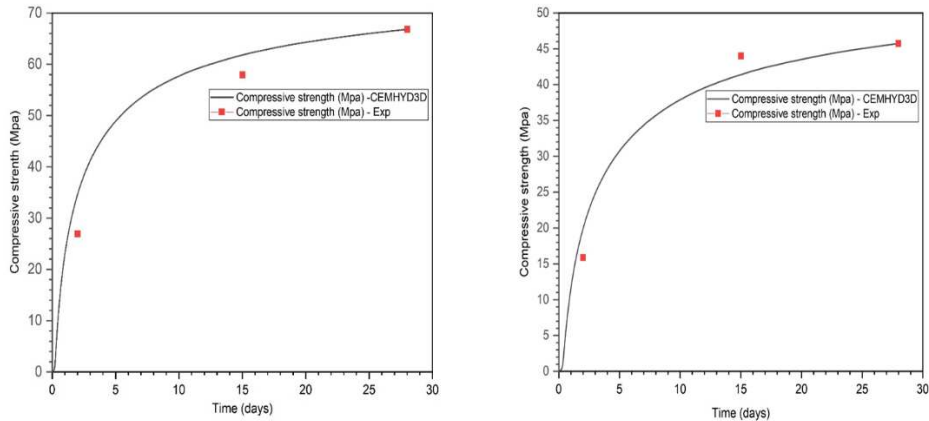
- 558 • At the initial state, all the mineral phases of the two cements are present. The size of the anhydrous  
 559 cement grains is in accordance with the experimental result.
- 560 • After 28 days of hydration, the hydrate formation such as C-S-H phase,  $\text{Ca(OH)}_2$  and the consumption of  
 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**

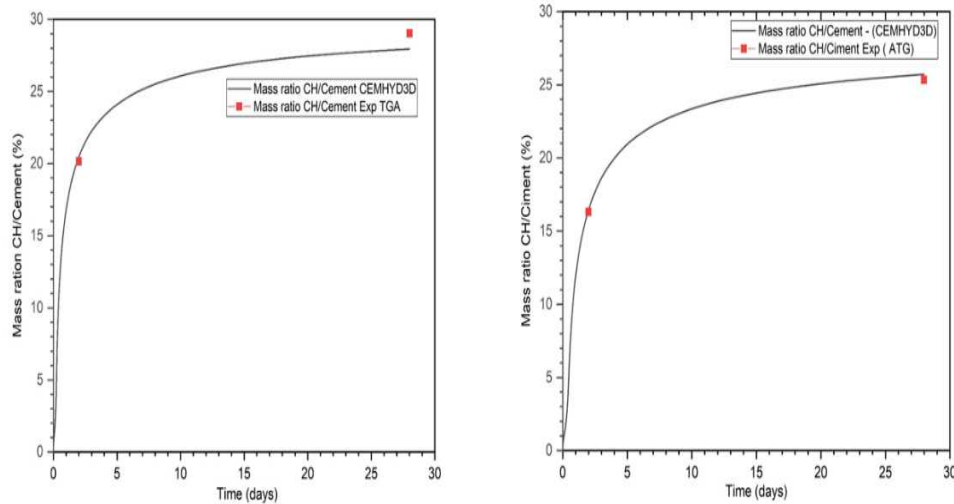
569 The CEMHYD3D code uses Eq(12) equation to estimate the compressive strength of cement paste over time of  
 570 hydration. The numerical and experimental result of the compressive strength is presented in Fig. 20. The  
 571 compressive strength estimated by the CEMHYD3D code is in accordance with 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)<sub>2</sub> quantification in the CEMHYD3D code**

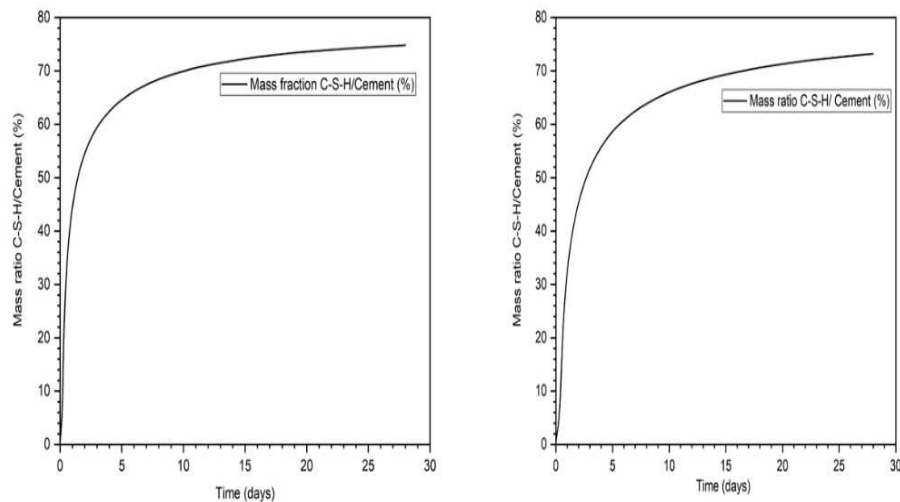
578 Because the Ca(OH)<sub>2</sub> phase is a data which can be determined using the TGA analysis, we chose to compare the  
 579 numerical and experimental quantity of this hydrate to evaluate the reliability of the CEMHYD3D code in our study.  
 580 CEMHYD3D code presented the evolution of Ca(OH)<sub>2</sub> volume over time of hydration, a Ca(OH)<sub>2</sub> density value equal  
 581 of 2.24 (g/cm<sup>3</sup>) is used to convert from volume fraction to mass fraction. Fig. 21 shows the Ca(OH)<sub>2</sub>/ 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 SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> 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 C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF 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 C<sub>3</sub>S phase and an orthorhombic polymorph in C<sub>3</sub>A phase due to the presence of minor oxides such as  
611 MgO, Na<sub>2</sub>O.  
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 SO<sub>3</sub> 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 C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF phases are relatively similar,  
618 while the ratio in C<sub>3</sub>S 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 C<sub>3</sub>S 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 C<sub>3</sub>S in the clinker-based sediment which is less reactive than the M1 polymorph.  
624 - The zinc presence in the sediment does not modify the C<sub>3</sub>A formation in the clinker. The zinc is present in  
625 all phases except in the C<sub>2</sub>S 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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635 No applicable

#### 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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#### 646 **Reference**

- 647 1. INSEE: <https://www.insee.fr/fr/statistiques/3589283>
- 648 2. Kajaste, R., Hurme, M.: Cement Industry Greenhouse Gas Emissions - Management Options and  
649 Abatement Cost. *J. Clean. Prod.* 112, 4041–4052 (2015)
- 650 3. Ademe: Déchet, Chiffres-clés. (2015)
- 651 4. Pan, J.R., Huang, C., Kuo, J.J., Lin, S.H.: Recycling MSWI bottom and fly ash as raw materials for Portland  
652 cement. *Waste Manag.* 28, 1113–1118 (2008). <https://doi.org/10.1016/j.wasman.2007.04.009>
- 653 5. Ferreira, C., Ribeiro, A., Ottosen, L.: Possible applications for municipal solid waste fly ash. *J. Hazard. Mater.*  
654 96, 201–216 (2003). [https://doi.org/10.1016/S0304-3894\(02\)00201-7](https://doi.org/10.1016/S0304-3894(02)00201-7)
- 655 6. Mukiza, E., Zhang, L.L., Liu, X., Zhang, N.: Utilization of red mud in road base and subgrade materials: A

- 656 review. *Resour. Conserv. Recycl.* 141, 187–199 (2019). <https://doi.org/10.1016/j.resconrec.2018.10.031>
- 657 7. De Larrard, F., Colina, H.: *Le béton recyclé.* (2018)
- 658 8. Chen, G., Lee, H., Young, K.L., Yue, P.L., Wong, A., Tao, T., Choi, K.K.: Glass recycling in cement production-  
659 an innovative approach. *Waste Manag.* 22, 747–753 (2002). [https://doi.org/10.1016/S0956-](https://doi.org/10.1016/S0956-053X(02)00047-8)  
660 053X(02)00047-8
- 661 9. Renaut, M.: *Calcination des déchets industriels : synthèse de ciment et stabilisation / solidification des*  
662 *résidus de combustion - Thèse de doctorat,* (2017)
- 663 10. Dubois, V.: *Etude du comportement physico-mécanique et caractérisation environnementale des*  
664 *sédiments marins – Valorisation en technique routière - Thèse de doctorat,* (2006)
- 665 11. Scordia, P.: *Caractérisation et valorisation de sédiments fluviaux pollués et traités dans les matériaux*  
666 *routiers,* (2008)
- 667 12. Tribout, C.: *Valorisation de sédiments traités en techniques routières : contribution à la mise en place d’un*  
668 *protocole d’acceptabilité. Thèse de doctorant de l’Université Toulouse III,* (2010)
- 669 13. Miraoui M.: *Mise en œuvre d’une démarche de prétraitement et de traitement des sédiments de dragage*  
670 *en vue d’une valorisation dans le génie civil - Thèse de doctorat*
- 671 14. M.Dia: *Traitement et valorisation de sédiments de dragage phosphatés en technique routière - Thèse de*  
672 *doctorat,* (2013)
- 673 15. S.Brakni: *Première approche vers une valorisation de granulats artificiels à base de sédiments de dragage -*  
674 *Thèse de doctorat,* (2008)
- 675 16. Amar, M.: *Étude expérimentale et numérique de la valorisaion des sédiments de dragage dans les matrices*  
676 *cimentaires - Thèse de doctorat,* (2017)
- 677 17. Zhao, Z., Benzerzour, M., Abriak, N.E., Damidot, D., Courard, L., Wang, D.: Use of uncontaminated marine  
678 sediments in mortar and concrete by partial substitution of cement. *Cem. Concr. Compos.* 93, 155–162  
679 (2018). <https://doi.org/10.1016/j.cemconcomp.2018.07.010>
- 680 18. Taylor HFW: *Cement chemistry.* (1997)
- 681 19. Dalton, J.L., Gardner, K.H., Seager, T.P., Weimer, M.L., Spear, J.C.M., Magee, B.J.: Properties of Portland  
682 cement made from contaminated sediments. *Resour. Conserv. Recycl.* 41, 227–241 (2004).  
683 <https://doi.org/10.1016/j.resconrec.2003.10.003>
- 684 20. Aouad, G., Laboudigue, A., Gineys, N., Abriak, N.E.: Dredged sediments used as novel supply of raw  
685 material to produce Portland cement clinker. *Cem. Concr. Compos.* 34, 788–793 (2012).  
686 <https://doi.org/10.1016/j.cemconcomp.2012.02.008>
- 687 21. Faure, A., Smith, A., Coudray, C., Anger, B., Colina, H., Moulin, I., Thery, F.: Ability of Two Dam Fine-Grained  
688 Sediments to be Used in Cement Industry as Raw Material for Clinker Production and as Pozzolan  
689 Additional Constituent of Portland-Composite Cement. *Waste and Biomass Valorization.* 8, 2141–2163  
690 (2017). <https://doi.org/10.1007/s12649-017-9870-8>
- 691 22. Faure, A., Coudray, C., Anger, B., Moulin, I., Colina, H., Izoret, L., Théry, F., Smith, A.: Beneficial reuse of  
692 dam fine sediments as clinker raw material. *Constr. Build. Mater.* 218, 365–384 (2019).  
693 <https://doi.org/10.1016/j.conbuildmat.2019.05.047>
- 694 23. XP 94- 047 : Détermination de la teneur pondérale en matières organiques d’un matériau - Méthode par  
695 calcination. (1998)
- 696 24. Association Française de Normalisation (AFNOR): NF EN 1097-7 : Détermination de la masse volumique  
697 absolue du filler - Méthode au pycnomètre. (2008)
- 698 25. Association Française de Normalisation (AFNOR): NF EN 196-6 : Méthodes d’essai des ciments -  
699 Détermination de la finesse. (2018)
- 700 26. NF EN 12457-2. Leaching-Compliance Test for LeachingofGranular Waste Materials and SludgesPart 2: One  
701 Stage Batch Test at a Liquid to Solid Ratio of10 l/kgfor Materials with Particle Size Below 4 mm (without or  
702 with Size Reduction); BSI: London, UK, 2002.
- 703 27. Centre d’information sur le ciment et ses applications: Ciments et Bétons.
- 704 28. ANGER, B., THERY, F., LEVACHER, D.: Caractérisation des sédiments fins des retenues hydroélectriques en  
705 vue d’une pré-orientation vers des filières de valorisation matière. 97–102 (2015).  
706 <https://doi.org/10.5150/cmcm.2015.020>
- 707 29. Dia, M., Ramarosan, J., Nzihou, A., Zentar, R., Abriak, N.E., Depelsenaire, G., Germeau, A.: Effect of

- 708 chemical and thermal treatment on the geotechnical properties of dredged sediment. *Procedia Eng.* 83,  
709 159–169 (2014). <https://doi.org/10.1016/j.proeng.2014.09.034>
- 710 30. Teklay, A., Yin, C., Rosendahl, L., Køhler, L.L.: Experimental and modeling study of flash calcination of  
711 kaolinite rich clay particles in a gas suspension calciner. *Appl. Clay Sci.* 103, 10–19 (2015).  
712 <https://doi.org/10.1016/j.clay.2014.11.003>
- 713 31. Lea: *Lea's chemistry of cement and concrete*. Elsevier. (2003)
- 714 32. G.K.Moir: *Advanced Concrete Technology*. (2003)
- 715 33. G.K.Moir; *Mineralised high alite cement*. *World Cem.* 13, 374 (1982)
- 716 34. F.W.Locher: *Cement principles of production and use*. (2006)
- 717 35. Lawrence, C.D.: *The Constitution and Specification of Portland Cements*. (2004)
- 718 36. Neville, A.: *Propriétés des Bétons*, édition Eyrolles, Translated by CRIB. (2000)
- 719 37. Hill, L., Fulvio, T.: *Manufacturing solutions for concrete performance*, World cement.
- 720 38. Baron, J., Ollivier, J.-P.: *Les Bétons*. (1997)
- 721 39. Zayed, A.: *Effect of sulfur trioxide content on concrete structures using Florida Materials*, Research report,  
722 University of south Florida. (2004)
- 723 40. Association Française de Normalisation (AFNOR): *NF EN 197-1: Composition, spécifications et critères de*  
724 *conformité des ciment courant*.
- 725 41. Faure, A.: *Capacité d'un sédiment à se substituer à la fraction argileuse de la matière première de l'*  
726 *industrie des liants hydrauliques - Thèse de doctorat*, (2017)
- 727 42. Kleib, J., Aouad, G., Khalil, N., Zakhour, M.: *Incorporation of zinc in calcium sulfoaluminate cement clinker*.  
728 *Adv. Cem. Res.* 1–7 (2020). <https://doi.org/10.1680/jadcr.19.00125>
- 729 43. Chu, D.C., Kleib, J., Amar, M., Benzerzour, M., Abriak, N.-E.: *Determination of the degree of hydration of*  
730 *Portland cement using three different approaches: Scanning electron microscopy (SEM-BSE) and*  
731 *Thermogravimetric analysis (TGA)*. *Case Stud. Constr. Mater.* 15, e00754 (2021).  
732 <https://doi.org/10.1016/j.cscm.2021.e00754>
- 733 44. Patel, R.G., Killoh, D.C., Parrott, L.J., Gutteridge, W.A.: *Influence of curing at different relative humidities*  
734 *upon compound reactions and porosity in Portland cement paste*. *Mater. Struct.* 21, 192–197 (1988).  
735 <https://doi.org/10.1007/BF02473055>
- 736 45. Snyder, K.A., Bentz, D.P.: *Suspended hydration and loss of freezable water in cement pastes exposed to*  
737 *90% relative humidity*. *Cem. Concr. Res.* 34, 2045–2056 (2004).  
738 <https://doi.org/10.1016/j.cemconres.2004.03.007>
- 739 46. NIST: *Technical Note VCCTL-01*.
- 740 47. Kleib, J., Aouad, G., Abriak, N.E., Benzerzour, M.: *Production of Portland cement clinker from French*  
741 *Municipal Solid Waste Incineration Bottom Ash*. *Case Stud. Constr. Mater.* 15, e00629 (2021).  
742 <https://doi.org/10.1016/j.cscm.2021.e00629>
- 743 48. T. Knudsen: *The dispersion model for hydration of portland cement I. General concepts*. *Cement and*  
744 *Concrete Research*, 14, pp.622–630 (1984).
- 745 49. Mounanga, P., Khelidj, A., Loukili, A., Mounanga, P., Khelidj, A., Loukili, A., Predicting, V.B.: *Predicting Ca (*  
746 *OH ) 2 content and chemical shrinkage of hydrating cement pastes using analytical approach* To cite this  
747 version : HAL Id : hal-01007190. (2004)
- 748 50. B. Lothenbach, F. Winnefeld, C. Alder, E. Wieland, P. Lunk: *Effect of temperature on the pore solution,*  
749 *microstructure and hydration products of Portland cement pastes*. *Cement and Concrete Research*, 37,  
750 pp.483–491 (2007).
- 751 51. van Breugel, K.: *Numerical simulation of hydration and microstructural development in hardening cement-*  
752 *based materials (I) theory*. *Cem. Concr. Res.* 25, 319–331 (1995). [https://doi.org/10.1016/0008-](https://doi.org/10.1016/0008-8846(95)00017-8)  
753 [8846\(95\)00017-8](https://doi.org/10.1016/0008-8846(95)00017-8)
- 754 52. Bentz, D.P.: *Incorporation of Fly Ash into a 3-D Cement Hydration Microstructure Model* Nistir 6050. (1997)
- 755 53. Bentz, D.P.: *Modeling the influence of limestone filler on cement hydration using CEMHYD3D*. *Cem. Concr.*  
756 *Compos.* 28, 124–129 (2006). <https://doi.org/10.1016/j.cemconcomp.2005.10.006>
- 757 54. Kamali, S., Moranville, M., Garboczi, E., Prené, S., Gérard, B.: *Hydrate dissolution influence on the Young's*  
758 *modulus of cement pastes*. *Proc. 5th Int. Conf. Fract. Mech. Concr. Concr. Struct.* 12–16 (2004)
- 759 55. NIST: *Guide to using CEMHYD3D Version 3.0*.

- 760 56. Bresciani, C.: Simulation numérique de l'hydratation et du développement des propriétés physiques et  
761 mécaniques d'une pâte de ciment afin de sélectionner de nouveaux ajouts minéraux., (2009)
- 762 57. Bentz, D.P.: Guide to Using CEMHYD3D: A Three-Dimensional Cement Hydration and Microstructure  
763 Development Modelling Package. (1997)
- 764 58. Li, T., Xiao, J., Zhu, C.: Hydration process modeling of ITZ between new and old cement paste. *Constr. Build.  
765 Mater.* 109, 120–127 (2016). <https://doi.org/10.1016/j.conbuildmat.2016.01.053>
- 766 59. Kamali, S., Bernard, F., Damidot, D.: Modélisation multi-échelles de la lixiviation des mortiers : effet sur les  
767 caractéristiques mécaniques. 7–12 (2005)
- 768 60. Faure, A.: Capacité d'un sédiment à se substituer à la fraction argileuse de la matière première de l'  
769 industrie des liants hydrauliques - Thèse de doctorat, (2017)
- 770 61. Gineys, N., Aouad, G., Sorrentino, F., Damidot, D.: Incorporation of trace elements in Portland cement  
771 clinker: Thresholds limits for Cu, Ni, Sn or Zn. *Cem. Concr. Res.* 41, 1177–1184 (2011).  
772 <https://doi.org/10.1016/j.cemconres.2011.07.006>
- 773 62. Tang, S., Wang, Y., Geng, Z., Xu, X., Yu, W., A, H., Chen, J.: Structure, fractality, mechanics and durability of  
774 calcium silicate hydrates. *Fractal Fract.* 5, (2021). <https://doi.org/10.3390/fractalfract5020047>
- 775 63. Wang, L., Jin, M., Zhou, S., Tang, S., Lu, X.: Investigation of microstructure of C-S-H and micro-mechanics of  
776 cement pastes under NH<sub>4</sub>NO<sub>3</sub> dissolution by <sup>29</sup>Si MAS NMR and microhardness. *Measurement.* 185,  
777 110019 (2021). <https://doi.org/10.1016/j.measurement.2021.110019>
- 778 64. Bye, G.C.: Portland cement: Composition, production and properties. (1999)
- 779 65. Clark, M.: Petcoke and Nodulisation. *Int. Cem. Rev.* 39 (2003)
- 780 66. Berthomier, M.: Etude de la lixiviation de l'aluminium de matériaux cimentaires à base de CEM III utilisés  
781 dans les canalisations d'eau potable : approche expérimentale et numérique. (2020)
- 782 67. Gineys, N., Aouad, G., Damidot, D.: Managing trace elements in Portland cement - Part II: Comparison of  
783 two methods to incorporate Zn in a cement. *Cem. Concr. Compos.* 33, 629–636 (2011).  
784 <https://doi.org/10.1016/j.cemconcomp.2011.03.008>
- 785 68. HORNAIN H.: SUR LA REPARTITION DES ELEMENTS DE TRANSITION ET LEUR INFLUENCE SUR QUELQUES  
786 PROPRIETES DU CLINKER ET DU CIMENT Réf. ATILH n°04005. *CIMENTS BETONS, Rev. DES Mater. Constr.*
- 787 69. Witzleben, S.T.: Acceleration of Portland cement with lithium, sodium and potassium silicates and  
788 hydroxides. *Mater. Chem. Phys.* 243, 122608 (2020). <https://doi.org/10.1016/j.matchemphys.2019.122608>
- 789 70. Bentz, D.P.: Three-dimensional computer simulation of portland cement hydration and microstructure  
790 development. *J. Am. Ceram. Soc.* 80, 3–21 (1997). <https://doi.org/10.1111/j.1151-2916.1997.tb02785.x>
- 791 71. Bentz, D.P.: CEMHYD3D : A Three-Dimensional Cement hydratation and Microstructure Development  
792 Modelling Package Version 2.0.
- 793