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Beneficial reuse of dam fine sediments as clinker raw material

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Abstract

The accumulation of fine sediments (< 200 µm) occurs in hydroelectric dams due to watershed erosion and solid transport. A rigorous and sustainable sediment management is required. Although most of these materials are transferred into the watercourse downstream, a significant quantity might have to be managed as on-land waste in the future. Considering that sediments contain silica, alumina, calcia and iron oxide as main chemical constituents, they could be useful candidate raw materials in the cement industry for the manufacture of clinker. This work concerns sediments from French dams. Whatever their origin, each sediment is suitable for a beneficial reuse as silico-aluminous raw material for clinker production. The characteristics of the raw sediments can lead to specific microstructures in the clinkers. However, clinker characteristics can still be controlled by adjusting raw mix proportions, maintaining a rather high sediment content in the mix (between 10 and 15 wt%).

Keywords

Dam fine sediment, Clinkering reactions, Portland cement industry, Valorization

Highlights

- 7 dam sediments from different French regions are suitable for clinker production
- Clinkers produced using 10 to 15% of sediment are similar to industrial ones
- Special features (polymorphisms and phase ratios) can be induced by sediments
- Key-criteria: Grain size, silica ratio and minor elements (Mg, Na, K) in sediments composition

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1. Introduction

In France, the annual volume of dredged material is estimated at 50 Mm^3 [1]. More than 90 % of this come from marine and estuarian dredging operations. The remaining fraction is attributed to continental extraction (waterways and dams). Although the total volume of removed sediment from dams can slightly vary from one year to the next, the order of magnitude is several tens of thousands of cubic meters. Erosion of rocks and soils at the watershed level generates solid particles that are transported by watercourses. Dam construction leads to a local reduction of the water velocity. Schleiss *et al.* [2] estimated that between 0.5 and 1.0% of the reservoir capacity is lost each year in the world because of sediment accumulation. A segregation occurs between the coarse particles (gravels and sands) that deposit at the reservoir entrance and the fine particles (silts and clay) that can remain in suspension. Further transport of these particles yields a final accumulation close to the dam construction [3]. Nowadays, most of the solid particles are transferred from the reservoir upstream to the watercourse downstream ensuring the ecological and sedimentary continuity. However, technical or environmental reasons could constrain the hydroelectric dam operator to an on-land management of these materials. According to the European Directive 2008/98/CE [4], sediments extracted from reservoirs become waste. Following the waste management hierarchy, beneficial reuse solutions prevail over disposal options. With this in mind, coarse and fine particles need to be clearly distinguished. According to Owens *et al.* [5], the limit can be set at 63 µm, *i.e.* the transition from silt to sand class. Particles greater than 63 µm are not a critical issue since they are commonly reused as sand or aggregate. By contrast, the beneficial reuse of fine sediments, *i.e.* particles smaller than 63 µm, is more challenging since no recycling solution is implemented.

In the literature, several reuse options for fine sediments were considered such as (i) construction of functional soils [6-7], (ii) sub-base layers in road or pavement construction [8-10], (iii) raw material for traditional ceramic bricks manufacturing [11-13] and (iv) partial replacement of sand in concrete production [14-17]. Beneficial reuse of fine sediment as a raw material to produce clinker was also investigated by different authors [18-20]. Aouad *et al.* [18] worked on a contaminated sediment from a waterway in Northern France. They obtained a satisfying clinker by introducing this sediment with a mass ratio of 39.1 wt%. The product reactivity was confirmed both by calorimetry and compressive strength tests on final cement pastes. Dalton *et al.* [19] studied one sedimentary resource sampled in an US marine harbor. The finest fraction was selected (< 300 µm). Tests were performed both at the lab and industrial pilot scales. Although the obtained products could be described as clinkers, some biases were induced by the unadjusted thermal treatments, *e.g.*

no quenching and insufficient sintering temperature. Finally, Anger *et al.* [20] investigated three different sediments from French hydroelectric reservoirs considering a reuse in cement industry as a replacement for clay in clinker manufacture. Microstructural analyses of the produced clinkers showed that all the studied sediments could be successfully recycled into clinker production.

In parallel to the sediment accumulation issue and the need to find some sustainable beneficial reuse solutions, clinker production in cement industry requires an adequate mix of CaO (lime), SiO_2 (silica), Al_2O_3 (alumina) and Fe_2O_3 (iron oxide). These essential elements are traditionally brought to the raw meal by limestone, for calcium, and by clay rocks for the silico-aluminous content. During the clinkering process, a temperature of 1450 °C is reached and lime combines with the three other main oxides to form the usual anhydrous phases, namely alite C_3S, belite C_2S, calcium aluminate C_3A and calcium alumino-ferrite C_4AF – also written $C_2(A,F)$[1]. Along with CO_2 emissions, the consumption of large volumes of natural resources is often described as an environmental issue for the cement industry [21-22]. Knowing that (i) 1.7 t of raw materials are required per ton of clinker [23] and (ii) 12.5 Mt of clinker were produced in France in 2015 [24], the amount of consumed resources to produce clinker can be estimated at 21.3 Mt per year (fuels not considered). Therefore, the replacement of non-renewable geological resources by sediments as alternative raw materials seems relevant. A positive side effect can be pointed out since the valorization contributes to the reduction of waste disposal. Due to the chemical composition similarity between the traditional raw materials used in the cement industry and the fine sediments extracted from hydroelectric reservoirs, this replacement could be technically promising. Moreover, large quantities of sediment could potentially be reused, which makes the cement industry a relevant option for dredged material valorization. Also, it can be noticed that cement plants are quite solicited to incorporate alternative raw materials into the meal. Besides, the literature presents the valorization of various types of waste in the cement industry: wastes from construction and demolition operations [25-28], the metal industry [29-31], extractive activities [32] and residues from household waste incineration [33-34].

Based on literature results and previous studies, this paper investigates and compares a significant number of sediment resources from French reservoirs, namely seven, as alternative raw materials. The objective is to take into account the pedological and geological variability from a watershed to another that directly influences the characteristics of the particles generated by erosion and accumulated in reservoirs. The effect of sediment characteristics has been examined, especially by looking at the relation between the phase polymorphism and the characteristics of the sediment introduced into the clinker raw meal. Also, compared to previous studies, a scale change is operated

[1] In cementitous notation, A, C, F, H and S refer respectively to Al_2O_3, CaO, Fe_2O_3, H_2O and SiO_2.

with the production and characterization of mortars prepared with Portland cement originating from clinker produced with sediments.

2. Materials and methods

2.1 Pretreatment of raw materials

Seven sediments were investigated. They came from four different French regions: four sediments from the Alps named ALP1, ALP2, ALP3 and ALP4, one from Brittany labelled BRT1, one from the North-Eastern part of France called EST1 and a last one close to the Mediterranean Sea referenced as MED1. Locations, labels and allotted colors are given in Figure 1. According to the reservoir context and the water level, fine sediments were either collected by a grab from a barge or with a mechanical or manual shovel. Sealed plastic containers were used for transport. For each sediment, a first preparation step consisted of air-drying associated with homogenization. Drying was carried out at 40 °C. Afterwards, the compact blocks formed during drying were de-agglomerated using a jaw crusher. It was then checked that 100 % of each sediment could pass through a 200 µm sieve. Sediments were then considered as "*pretreated materials*". They were stored at 40 °C until their use.

Concerning the rocks extracted from quarries for clinker production, the initial materials were also pre-treated through coarse crushing. For lab experiments, they were finely ground using a planetary ball mill until the crushed materials could be sieved through a 125 µm mesh. These materials were kept at 105 °C. For the synthesis of clinker, the calcareous rock, referenced as LIM1, was mixed together with a silico-aluminous material. In this respect, two clay resources namely CLY1 and CLY2 were used for comparison and were partially or totally substituted by sediments in raw meal formulations.

In the following sections, "*raw materials*" will refer to the "*pretreated materials*".

2.2 Raw materials characterizations

- *Physical properties*

Particle size distributions of the raw materials were analyzed by laser diffraction using a MALVERN INSTRUMENTS Mastersize 2000 device. The suspensions used for analyses were prepared by mixing 2 g of powder with 50 mL of deionized water, followed by ultrasonic dispersion for two minutes. Results are presented in Figure 2 and Table 1. According to Owen's criteria [5], most sediments can be considered as fine since the particle size is less than 63 µm. The only exception is EST1 since 18.6 vol% is between 63 µm and 2 mm. Regarding the quarried materials, their particle size distributions fulfill the requirements for their use as raw materials in clinker production.

Densities were assessed by helium pycnometry (MICROMERITICS AccuPyc 1330 equipment). Specific surface areas (SSA) were estimated by two different methods: (i) the Brunauer-Emmett-Teller (BET) technique [35] and (ii) the Blaine method. BET SSA measurements were performed with gaseous N_2 on a MICROMERITICS Tristar II apparatus. SSA measurements were preceded by a degassing step at 120 °C for 15 hours. Blaine SSA determinations were carried out according to the NF EN 196-6 standard [36] with an instrument from CONTROLAB Company. Blaine protocol consists in measuring the time required for the transfer of a known air volume through a compacted powder bed. This duration is related to specific surface area and fineness. SSA and pycnometry results are given in Table 2. For lime and most clays, the densities are close to the values of the constituents, except for BRT1 and EST1. This difference is due to the presence of organic matter as witnessed by thermal analysis (see *Mineralogical properties* subsection). Concerning the specific surface area, the values are quite dependent on the technique [37]. Blaine SSA values are lower than BET SSA values. This difference can be attributed to the surface roughness and porosity of the particles. BET corresponds to N_2 forming a single monolayer over the surface of the exposed material while the Blaine technique relies on a gas going through a compacted powder.

- *Chemical properties*

Elemental compositions of materials were obtained by X-Ray fluorescence (XRF). Fused beads were prepared for XRF analysis using a melting agent that contained lithium tetraborate (99.5 wt%) and lithium iodide (0.5 wt%). 1 g of the analyzed sample was mixed with 10 g of melting agent (1:10 mass ratio) in order to prepare the bead. A PANalytical Zetium device was used to carry out the elemental composition measurements operating with a 1 kW generator and a Rh anode. The elemental chemical composition of each raw material is presented in Table 3. For all clay minerals, the main oxides are SiO_2, Al_2O_3 and CaO. The compositions have been plotted in a Rankin's diagram (see Figure 3). The four alpine sediments and BRT1 are located in the same region on the diagram, slightly different from the CLY1 and CLY2 location. EST1 and MED1 are different since they contain respectively slightly less alumina and more lime than the other sediments.

- *Mineralogical properties*

Mineralogical compositions were obtained by X-Ray Diffraction (XRD). Two types of investigations were performed: powder analysis and clay species identification. Both were performed on a BRUKER D8 Advance device mounted on a Bragg-Brentano geometry θ-θ. The apparatus was equipped with a copper anticathode ($\lambda = 1.5406$ Å), a high speed LynxEye XE detector and operated at 40 kV and 40 mA. For powder analyses, measurements were made between 3 and 70 °2θ, with a 0.012 °2θ step and a time per step of 0.6 s. Crystalline phases were

identified using the BRUKER DIFFRACPlus EVA software and the ICDD PDF4+ database. To perform the semi-quantitative XRD analyses, zincite (ZnO) was added to the sample (10 % by mass). XRD quantifications were carried out by the Rietveld method on a BRUKER TOPAS software. Concerning the distinct identification of clay minerals and their semi-quantification, a preferential orientation of the clay minerals in the sample according to the 001 plan was needed in order to increase the intensity of the basal X-ray reflexions. To do so, a suspension was prepared from fine sediment: wet sieving (40 µm mesh) and centrifugation (8000 revolutions per minute – 30 min). The supernatant was extracted with a pipette and placed on a glass slide. In order to make possible identification according to d-spacing, three different treatments were performed: natural air-drying at room temperature, polyalcool atmosphere (adapted to swelling clays) and thermal treatment at 490 °C (differentiation between kaolinite and chlorite). Angles between 3 and 35 °2θ were explored with a step size of 0.008 °2θ and a time per step of 0.84 s. Clay species were semi-quantified using the relative peak intensities according to the technique described by Holtzapffel [38]. Results of powders and clay semi-quantifications are presented in Table 4.

CLY1 and CLY2 present the highest percentage of quartz, which is in accordance with the chemical analysis. The sediments contain quartz (between 17 and 35 wt%), clay minerals (between 26 and 36 wt%) and carbonated phases (between 26 and 46 wt%). MED1, a calcareous sediment, contains the highest percentage of carbonates. In the four alpine sediments and EST1, the clay minerals are mostly illite and some chlorite. CLY1 and CLY2 contain kaolinite and some illite. MED1 and BRT1 contain illite, chlorite and kaolinite. Whatever the nature of the silico-aluminous materials, alkaline ions are present, either potassium in illite and microcline, or sodium in albite.

Thermal behaviors of raw materials were analysed by thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA). Measurements were carried out on a SETARAM Setsys 16/18 thermobalance, using calcined alumina as inert reference. The reference and the analysed materials were placed in platinum crucibles. TGA and DTA were followed in the 30-1000 °C range with a heating ramp of 5 °C/min. Mass loss for each raw material is given in Table 5 with the corresponding temperature range and the associated phenomenon. The sediments present greater mass losses than CLY1 or CLY2. This is explained by both the presence of carbonates (Table 4) and organic matter (OM). Organic matter content is analysed for the fine sediments by loss on ignition according to NF EN 12880 protocol [39], *i.e.* a calcination operation in a muffle electric furnace at 550 °C for 2 hours. 2 g of material were used each time. Organic matter contents are given in Table 6. The OM content has influence upon the density (see Table 2): BRT1 and EST1 which present the lowest densities have the highest OM.

2.3 Clinker synthesis

- *Formulation strategy*

From the chemical composition of each raw material (*i.e.* quarried rocks, sediments; see Table 3), clinker raw meals were formulated applying the empirical moduli used in the cement industry. These moduli correspond to ratios between the main oxides and they are used to target raw meals with the correct stoichiometry. The three most common parameters - named Lime Saturation Factor (LSF), Silica Ratio (SR) and Alumina Ratio (AR) - are given in Equations 1, 2 and 3, respectively [40].

$$LSF = \frac{\%CaO}{2.80 \times \%SiO_2 + 1.20 \times \%Al_2O_3 + 0.65 \times \%Fe_2O_3} \times 100 \quad \textbf{Eq. 1}$$

$$SR = \frac{\%SiO_2}{\%Al_2O_3 + \%Fe_2O_3} \quad \textbf{Eq. 2}$$

$$AR = \frac{\%Al_2O_3}{\%Fe_2O_3} \quad \textbf{Eq. 3}$$

Each of them is supposed to control one or several characteristics of the final clinker. LSF ensures the right stoichiometry between calcium oxide and the three other main chemical components. Theoretically, if the target for LSF is between 92 to 98, a right balance is found between providing enough CaO to complete the clinkering reaction and limiting the free (uncombined) lime content [39]. Working on German industrial clinkers, Locher noticed that the LSF range is actually wider (90 to 104) [41]. Concerning the Silica Ratio, it helps to fix the relative proportion between silicate phases, C_3S and C_2S, and the aluminate ones, that is to say C_3A and C_4AF. Aluminate phases are commonly liquid at high temperature (above 1300 °C) and they both form the interstitial phase. Thus, SR operates also as a relevant index for the liquid phase content during the clinkering process. Suitable clinker SR is in the range 2.0 to 3.0 [40] but a more restrictive and optimized domain can be given: 2.4 to 2.6 [42]. Finally, AR controls the relative mass contents in the interstitial phases between the iron-free mineral C_3A and the only clinker phase that contains iron, *i.e.* C_4AF. A large [40] and a narrow [42] range can be identified for the Alumina Ratio, [1.0 ; 4.0] and [1.5 ; 1.8] respectively.

Two different formulation strategies were considered. The first one consisted in maximizing the dam sediment content with a total replacement of the clay fraction by this alternative raw material. These mixes were called "*binary mixes*". As the limestone is relatively pure, it can be considered that the whole silico-aluminous fraction is brought to the meal by the material coming from the dredging operation. Using only two different constituents, the chemical adjustment possibilities for the raw meal are limited to one compositional parameter. LSF was chosen since combination of lime is the most critical factor. A LSF value of 97 was targeted yielding the

formulation of *binary mixes* (Table 7). It can be observed that CLY1 and CLY2 contents in binary mixes were lower than every sediment mass ratios, whatever the origin. It can be explained by the higher CaO content of the dredged materials compared to the quarried clay rocks. As a consequence, sediments replaced on one hand the whole silica, alumina and iron oxide supply and, on the other hand, a fraction of limestone. That is why the most calcareous sediment, *i.e.* MED1, showed the highest substitution level in binary preparations with 34.81 wt%. As replacement percentages are relatively high, the effect of sediment on clinker properties is supposed to be exacerbated. SR and AR were not adjusted in these formulations. It explains why some of the theoretical SR and AR values could be outside of the usual ranges. None of the SR was in the optimum range [2.4 ; 2.6]. In most cases, they were lower – due to the high alumina content – except for EST1 and CLY2 rock. Depending on the alumina-to-iron ratio of each sediment, AR of binary mixes could also be higher, *e.g.* MED1-Bin, or lower, *e.g.* BRT1-Bin and EST1-Bin, than the supposed optimum domain.

The second formulation strategy consisted in using CLY1 or CLY2 plus a sediment as a silico-aluminous bearer. In other words, a clay rock from a quarry is partially substituted and complemented by an alternative dredged material (Table 8). As three components were introduced into each mix ("*ternary mix*"), it allowed the adjustment of another compositional parameter. The second most important one, SR, was chosen and a value of 2.4 was targeted. To reach this value, the adequate complementing clay had to be selected, that is to say the aluminous CLY1 for EST-Ter and the siliceous CLY-2 for all the other meals (SR < 2.4 in binary). In addition to ternary mixes with sediment, a reference mix – named CLY-Ter – was also studied with both CLY1 and CLY2 as silico-aluminous sources. After resolving the equations, clinker raw meal formulations were obtained and are presented in Table 8. Compared to binary mixes, sediment contents were diminished to values less than 20 %, except for ALP4-Ter. These mass ratios ranging from 10.78 to 18.43 wt% are closer to what is actually observed concerning the use of alternative materials in a cement plant. With respect to the ALP4-Ter case, the calculated AR was already rather close to 2.4 in the binary mix ALP4-Bin (2.32). It justifies why the ALP4 content was kept relatively high, even in ternary meal. Regarding the last compositional parameter, which was not intentionally adjusted, it can be noticed that the transition from binary to ternary mix tended to buffer AR too. Indeed, all the calculated AR were located in the optimum range for ternary meals.

- *Lab clinker preparation*

Clinkers were prepared at the lab scale. To do so, powdered raw materials were initially dried at 105 °C until reaching a constant mass. Then, 100 g of raw meal were prepared according to the mass contents obtained by calculation and presented in Tables 7 and 8 for binary and ternary raw meals, respectively. Dried powders were homogenized using a three-dimensional Turbula mill for

one hour. In a rotary kiln of a cement plant, clinker nodulization results from both the rotative movement and the presence of a liquid phase. Using a static electric lab furnace, nodulization is impossible. To overcome this laboratory issue, a granulation step was added to the process in analogy to what is done in the industrial semi-dry plants. In the literature, other authors suggested this methodology to ensure the shaping of raw meal and an intimate homogenization of the particles at the lab scale [25;43]. Granules with diameters from 5 to 10 mm were obtained using a water-to-powder ratio of 0.22. Afterwards, free water was fully evaporated in an oven at 100 °C. Pellets were then sintered in a bottom lift furnace using a Pt-Rh crucible. After a residence period of 45 min at the clinkering temperature of 1450 °C, clinker granules were air-quenched. This rapid cooling methodology was necessary to make sure that C_3S formed at 1450 °C would not decompose into C_2S and calcium oxide, a reverse reaction that occurs if slow cooling is used.

2.4 Anhydrous clinker characterization

Several analyses and characterizations were performed on lab clinkers. The first one consisted in assessing the success of lime combination with the other oxides to synthetize the four usual phases, two silicates (C_2S, C_3S) and two aluminates (C_3A, C_4AF). The usual experimental technique is based on an acidic titration of the remaining uncombined lime in the clinkering product, also known as "free lime", after a selective chemical attack by ethylene glycol. This method was first suggested by Schläpfer and Bukowski in 1933 [44]. After grinding, 1 g of clinker is stirred in ethylene glycol heated at 70 °C. This specific attack transforms free lime into calcium glycolate, $(CaCH_2O)_2$. After vacuum filtration, calcium glycolate is titrated with HCl 0,1 mol.L^{-1} and the end-point is detected with bromocresol green indicator. The acidic titration reaction is given in Equation 4.

$$(CaCH_2O)_2 + 2HCl \rightarrow (CH_3O)_2 + CaCl_2 \qquad \textbf{Eq. 4}$$

The upper limit which is usually accepted for free lime content is 2 wt%, even if proportions between 2 and 3 % can be tolerated [42]. Due to the formulation step with the LSF adjustment, the free lime content is theoretically supposed to be correct. However, depending on the raw material properties, free lime content might differ from the expected values.

Clinker chemical analyses were performed by XRF with a protocol similar to what was described for the elemental analysis of raw materials. NF EN 197-1 [45] set two different chemical limits for Portland clinker – referenced as "K" in the standard – when used as a component of Portland cement. These restrictions and the typical composition range for Portland clinker according to Baroghel-Bouny [46] are given in Table 9. Knowing the main oxide contents, Bogue defined in 1929 a numerical method to estimate the potential phase composition. Four equations, one for each crystalline phase, were suggested and are given in Equations 5 to 8.

$$C_4AF = 3.0432\ Fe_2O_3 \quad \textbf{Eq. 5}$$

$$C_3A = 2.6504\ Al_2O_3 - 1.6920\ Fe_2O_3 \quad \textbf{Eq. 6}$$

$$C_2S = -3.0710\ CaO + 8.6024\ SiO_2 + 5.0683\ Al_2O_3 + 1.0785\ Fe_2O_3 \quad \textbf{Eq. 7}$$

$$C_3S = 4.0710\ CaO - 7.6024\ SiO_2 - 6.7187\ Al_2O_3 - 1.4297\ Fe_2O_3 \quad \textbf{Eq. 8}$$

These equations were employed on lab clinkers with a correction for CaO: the lime proportion was substracted from the total CaO content.

Clinker XRD analyses were carried out following the same experimental methodology as the one used for bulk raw materials. In addition to the crystalline phase identification in the complete diffraction diagram, several specific windows were selected for the determination of C_3S, C_2S and C_3A polymorphs according to literature. Concerning tricalcium silicate, two angle ranges were examined: 36.0 to 38.0 °2θ and 55.5 to 57.5 °2θ [47]. Regarding dicalcium silicate forms, both 30.5 to 32.0 °2θ and 32.7 to 33.6 °2θ areas were studied [48-49]. For tricalcium aluminate, two other windows were taken into account: between 18.0 and 22.5 °2θ and from 47.0 to 48.0 °2θ [49-50].

2.5 Fresh and hardened state behaviors

Concerning the clinker referenced as ALP1-Ter, standard tests from the cement industry were performed pursue more deeply the demonstration of the beneficial reuse potential of dam sediment in clinker manufacture. A cement equivalent to a CEM I made with clinker ALP1-Ter was compared to an industrial CEM I 52.5N Portland cement (named hereafter Control CEM I) for all the experiments. Both cements were prepared in order to reach an identical SO_3 content (2.6 wt%) and the same Blaine fineness (3600 cm²/g) after clinker and gypsum co-grinding. The chemical composition and the potential phase contents of the Control CEM I are shown in Table 10.

First, the setting times (initial and final) were measured with a Vicat apparatus after the assessment of the water-to-cement ratio (w/c) to reach normal consistency according to NF EN 196-3 [51]. The evaluation of standard consistency and required water content gives information on the fresh state workability of the hydraulic binder. Several parameters come into play: cement fineness, solid particle flocculation and hydration kinetics (consistency modification due to paste stiffening) [52]. Then, strength tests were performed on mortar in agreement with NF EN 196-1 [53]. Flexural and compressive strengths were measured on prismatic samples after curing times of 2, 7 and 28 days. The aim of this test was to determine the strength class of ALP1-Ter cement according to NF EN 197-1 [45] with (i) the compressive strength reached after 28 days (32.5, 42.5 or 52.5 MPa) and (ii) the early-age strength development (normal N or rapid R). Another parameter that was

investigated is the cement heat of hydration. This test was performed by the semi-adiabatic technique given in NF EN 196-9 [54]. In this methodology, a mortar incorporating the tested cement is made and cast in a semi-adiabatic cell. The temperature evolution is followed for 120 h and compared to the temperature of an "inert" mortar (for which hydration is complete). The cumulative hydration at a given time t, labelled Q(t), can be calculated according to Equation 9.

$$Q(t) = \frac{C_{Tot}}{m_c} \times \theta_t + \frac{1}{m_c} \times \int_0^t \alpha\, \theta_t \cdot dt \qquad \textbf{Eq. 9}$$

In Equation 9, C_{Tot} refers to the heat capacity of the complete calorimeter ($J.K^{-1}$), m_c corresponds to the cement mass contained in the mortar sample (g), t is attributed to the hydration time (h), α is a coefficient related to the specific heat loss of the calorimeter and θ_t indicates the difference of temperature between the tested sample and the reference inert mortar at time t. The last investigated parameter is the shrinkage of mortar in a controlled drying atmosphere (20 °C and 50 % RH) according to NF P15-433 [55]. In these conditions, a large part of the total shrinkage is explained by drying shrinkage: evaporation of pore water through the surfaces. In addition to dimensional variations, mass evolution was also followed for 28 days.

3. Results and discussion

The measured clinker properties are presented in three sections. Section 3.1 refers to the clinkers obtained with binary mixes; limestone was blended with a unique silico-aluminous material which was either a quarried clay (CLY1 or CLY2) or a dredged sediment. Section 3.2 focuses on ternary mixes in which silica, alumina and iron oxide are introduced by an adequate blend of one sediment and one clay rock traditionally used by cement plants. The last section summarizes both approaches and establishes some relationships between the initial sediment properties and the final clinker characteristics.

3.1 Binary clinkers

- *Anhydrous clinker characteristics*

The first important parameter that should be considered is the achievement of lime combination reactions. It was assessed by measuring the remaining free lime in clinker that is the calcium oxide that was not found in the cementitious phases. Results for binary clinkers are given in Figure 4a. Chemical compositions of binary clinkers are given in Table 11. Bogue calculations were used to estimate the potential phase proportions for C_3S, C_2S, C_3A and C_4AF. These values are summarized in Table 11 as well. Using the LSF adjustment, most clinkers present a free lime content below the threshold of 2 wt% and a relatively high C_3S/C_2S ratio. EST1-Bin is different since its lime percentage is 3.62 wt% and the C_3S content is the lowest. This can be correlated with its particle size distribution (see Figure 2 and Table 1) showing the presence of > 100 µm particles

that could be quartz. The presence of large quartz particles is known to promote the formation of significant quantities of C_2S to the detriment of C_3S.

The full diffraction diagrams shown in Figure 5 confirm the presence of the four typical crystalline phases of clinker and show some low intensity peaks for calcium oxide resulting from the presence of free lime traces. Figure 5 does not show any complementary phase. To investigate in greater details the effect of sediment introduction on the clinkering reactions, it was decided to identify not only which of the four main phases were present, but also their polymorphism. The cases of alite, belite and tricalcium aluminate cases are examined. Concerning C_3S, two XRD windows were selected allowing allotropes identification. The corresponding diagrams are given in Figures 6a and 6b. The identified C_3S polymorphs are M_3 when sediments are added, while the usual M_1 polymorphs are formed in CLY1-Bin and CLY2-Bin. As shown in Figure 7 it is related to the MgO content of the sediment according to the empirical diagram from Maki et Goto (1982) [56]. Higher MgO content increases the probability of formation of M_3. MgO comes from dolomite and is also present in the trioctahedral sheets of illite, in the trioctahedral sheets of chlorite and in the brucite sheets of chlorite (see Table 4). Figure 8 shows the C_2S polymorphs present in the different binary mixes. Typical β-C_2S are formed when CLY1, CLY2 and MED1 are used (most common form in clinkers; Figure 8a). However, the high temperature α-belite is stabilized for the other clinkers (Figure 8b). Since clinker preparation protocols are equivalent, the only explanation is a stabilization by Na supplied by the Na-feldspars like albite (no feldspar is usually present in industrial rocks). Concerning C_3A, Figure 9 shows that the typical cubic C_3A phase is formed in CLY1-Bin, CLY2-Bin and MED1-Bin. Orthorhombic C_3A is identified for all the other clinkers. Again, the greater the Na content, the more likely is the stabilization of the orthorhombic form of C_3A.

- *Hardened state properties*

Differences can be observed at 2 or 7 days (Figure 10). This can be attributed to differences in clinker reactivity, in mass percentage of each phase, in the gypsum quantity or in the fineness after grinding. Nevertheless, all the samples show suitable strengths after 28 days. The important increase between young age and 28 days for samples using sediments might be linked to the formation of the C_2S α-polymorph which is delayed (compared to C_3S) but which is also known to be a highly reactive belite polymorph.

3.2 Ternary clinkers

- *Anhydrous clinker characteristics*

A study, which was similar to the investigations on binary clinkers, was also carried out on clinkers obtained from ternary meals. Free lime contents were evaluated and results are reported in Figure 4b. The diagram presented in Figure 4b demonstrates that all the clinkering products

exhibited a free lime content less than the typical limit of 2 wt%, or slightly higher for ALP4-Ter. Hence, it can be said that the clinkering reaction were relatively successful. Combination of lime with the three other oxides was efficient. Interesting observations come from the comparison of the free lime content between binary and ternary mix for a same sediment source. The most remarkable example is the EST1 sample, since free lime content was reduced from 3.62 wt% for the binary clinker to 1.70 wt% for EST1-Ter. This improved raw meal burnability can be explained by the decrease of the sediment fraction in the meal, from 26.27 % to 10.78 %, and its substitution by an aluminous clay rock (CLY1) that increased the melt content. A high liquid phase proportion facilitates the combination of lime, especially the transition from C_2S to C_3S. Melt acts as a medium for Ca^{2+} ion diffusion [40]. Although the EST1 content was maintained at a relatively high level (> 10 wt%), the negative effect of coarse PSD and high silica ratio were fully corrected using an appropriate industrial clay from the cement industry. This good result for a ternary blend was obtained only by mix adjustment and without any modification of the clinkering process, particularly the burning time. Contrary to the EST1 sediment, all the other resources – MED1, BRT1 and alpine materials – were complemented by a clay rock CLY2 with a high silica ratio. Due to the reduction of the liquid phase fraction, ternary mixes were in most cases harder to burn than for binary mixes. Free lime contents increased although they still remained in a satisfactory range.

After the successful assessment of lime combination, chemical compositions of ternary clinkers were determined, and analyses are presented in Table 12 along with potential mineralogical compositions which were calculated according to Bogue calculations. Table 12 shows that the chemical composition tends to be more uniform from one clinker to another due to the simultaneous use of one dam sediment and one quarried clay, which allows a good adjustment of the chemical parameters. For instance, the SiO_2 content was increased for all the clinkers prepared by incorporating a sediment with low SR, *i.e.* ALP1, ALP2, ALP3, ALP4, BRT1 and MED1, in comparison to the binary clinkers. Chemical compositions comply with the typical range as defined by [46]. Moreover, the ternary clinkers satisfied both criteria concerning the MgO content and the ratio between lime and silica as defined in NF EN 197-1. In parallel, the mineralogical compositions according to Bogue calculations were also stabilized due to SR adjustment during the mix formulation step. The ratio between silicate and aluminate phases was relatively constant between all the ternary clinkers, with an interstitial phase (C_3A and C_4AF) that accounted for 18.5 to 20.3 wt%. It should be noticed that only three components were used to obtain homogeneous and well-proportioned clinkers (Table 8). The adjustment could even be better, particularly by setting the alumina ratio, *i.e.* controlling the composition of the liquid phase. Depending on the expected clinker, iron oxide or alumina – often in the form of bauxite – can be added to the raw meal.

Since adequate ratios between crystalline phases were demonstrated for ternary clinker, attention was then focused on the polymorphs. Specific XRD windows allowing alite identification are shown in Figure 11. First, in Figure 11a, the presence or absence of the diffraction peak located at 36.7 °2θ helps in discriminating which samples contain alite with the M3 allotrope and which ones are free from this monoclinic form. It can be observed that all the ternary samples prepared with sediment do contain M_3-C_3S. In contrast, CLY-Ter clinker did not present the typical reflection peak at 36.7 °2θ. This observation for the reference CLY-Ter clinker was not very surprising since the binary clinkers prepared with the individual quarried clays did not initially present M_3-alite. Considering, as a second step, the 55.5 to 57.5 °2θ window in Figure 11b, it can be mentioned that the control lab clinker CLY-Ter presented the expected characteristic pattern of M_1-C_3S. Regarding the clinkers produced with sediment in ternary blends, it should be noticed that a broad double peak can now be distinguished between 56.2 and 56.7 °2θ. This pattern could be interpreted as a coexistence of M_1 and M_3 polymorphs. Compared to the binary clinkers, a relevant evolution to consider is the relatively equal intensity between the peak at 36.4 (M_1) and the peak at 36.6 (M_3). Intensities were almost equivalent for all the ternary clinker whereas the M_3 peak was clearly the strongest in binary clinkers produced with sediment (Figure 6). To sum up, the main conclusion concerning alite polymorphism during the transition from binary to ternary mix was a distinct increase of monoclinic M_1-C_3S proportion and, in parallel, a relative decrease of M_3-C_3S. The decrease of sediment content and its replacement by clay low in magnesium oxide reduces the quantity of incorporated magnesium that acts as a stabilizing agent in the M_3 form due to substitutions in crystal lattice.

Concerning C_2S polymorphism, the same windows as for binary clinkers were chosen for ternary products. These selected angle ranges are presented in Figure 12. Figure 12a, which focuses on the angle range 30.5 to 32.0 °2θ, shows similar diffraction patterns for all the studied clinkers, except for ALP4-Ter. The common feature is an association of two close peaks: a first one just below 31.0 °2θ and another one at 31.6 °2θ. This combination is typical of the β-C_2S phase, which is industrially the most frequent polymorph. With a moderate level of stabilizing agents and a moderate to rapid cooling rate, β-belite is the obtained form of C_2S. Theoretically, this polymorph is metastable at room temperature and should be transformed into the unreactive orthorhombic γ-C_2S. However, due to chemical stabilizers and/or the size of crystallites [40], this transition to the γ-form does not occur. In ternary clinkers, it should also be noticed that no peak could be observed at 33 °2θ contrary to observations for binary clinkers observations. It means that the high temperature α-C_2S form was no longer contained in clinkers from ternary blends, except for ALP4-Ter. This observation can be explained by the reduction in alkali content, especially Na_2O which is known to promote the α-form when combined with rapid cooling [57]. Thus, considering the results for

binary and ternary blends, it is clear that the sediment content in clinker raw meal may modify the polymorphism of C_2S. High replacement ratios are likely to preserve high temperature forms whereas a mix with a reduced amount of alternative raw material would favor the cooling transformations towards α'_H, α'_L and the traditional β-form. Even if most sediments – MED1 excluded – tend to add stabilizers for high temperature belite, all these polymorphs are supposed to present a hydraulic reactivity. The unreactive γ was never observed, neither the typical "dusting" phenomenon due to the 13 % volume change when crystals evolve from monoclinic-β to orthorhombic-γ.

During the binary clinkers characterization, it was shown that C_3A was the third phase with a polymorphism affected by sediment addition. Crystallographic changes of this mineral were also investigated for ternary mixes, using the usual 47.0 to 48.0 °2θ angle range. This portion of XRD patterns is given for each ternary clinker in Figure 13. The main comment that can be made on Figure 13 is the prevalence of the 47.8 °2θ peak for all the ternary clinkers, except for ALP4-Ter. It means that the cubic polymorph, that is to say the undistorted lattice form, was dominant. This result can be explained by a reduced amount of sodium impurities provided by sediment and contained in Na-feldspars and, to a lesser extent, in clay minerals.

- *Fresh and hardened state properties on mortar*

It was previously shown that ternary clinkers did not show any particular feature in comparison to the binary ones. Furthermore, the characteristics were rather homogenous from one ternary clinker to another due to a more precise adjustment of the raw meal chemistry, except for ALP4-Ter. Thus, it was decided to investigate more deeply one clinker formulation. For its greater availability, ALP1-Ter was selected. Several standard tests, on the mortar and in the fresh state, were carried out on a Portland cement produced with fine-grained sediment, yielding results which were never observed before in literature. The properties of ALP1-Ter cement were compared (i) to the cement standards when available and (ii) to the hydration characteristics of an industrial Portland cement, considered as reference in the experimentation. As a reminder, both cements were prepared to obtain a similar Blaine fineness (3600 cm²/g) and identical SO_3 contents (2.6 wt%).

First and foremost, setting times were measured after establishing the water-to-binder ratio which yields standard consistency. Results are given in Table 13. Since the production in the laboratory of ALP1-Ter lab cement was limited (2 kg), the number of possible w/c trials to reach standard consistency was reduced. It explains why there is no strict value given in Table 13. According to the accomplished tests, it can be said that w/c ratio of ALP1-Ter cement at standard consistency was slightly lower than 0.245. In comparison, the reference CEM I presented a w/c ratio of 0.260. According to Zhang [58], standard consistency generally lies in the range 0.24 to 0.30. Thus, the studied ALP1-Ter cement required a rather low water amount while maintaining an

interesting workability. Concerning setting times, it can be mentioned that the initial setting time is 30 minutes shorter for ALP1-Ter cement compared to the control sample. This observation could be explained by the difference in C_3A content which plays a main role in early reactivity. According to the NF EN 197-1 standard [45], a 52.5 strength class cement must exhibit an initial setting time greater than 45 min. This condition was satisfied by ALP1-Ter and by the reference cement as well. Regarding the final setting times, they are similar from one cement to another (around 3 hours). According to Siddiqi [59], a final setting time less than 10 h should be recommended for any binder. Again, this requirement was fulfilled by ALP1-Ter cement. Therefore, a hydraulic reactivity was demonstrated by the alternative laboratory cement. Short setting times ensure rapid hardening and quick strength development.

The heat generated by ALP1-Ter cement hydration was followed for 120 h using semi-adiabatic calorimetry and compared to the Portland cement made with an industrial clinker. Cumulative heats of hydration for both cements are presented in Figure 14. After 120 h, the cumulative heat of hydration is stabilized for both Portland binders. Mortar manufactured with ALP1-Ter cement generated 413 J/g, which was 8.7 % higher than the control CEM I (380 J/g). Each clinker phase exhibits a very different heat of hydration. Two of them mainly participate in total heat generation: C_3A (1000 to 1200 J/g) and C_3S (500 to 525 J/g) [60]. Therefore, the higher content in tricalcium aluminate of the laboratory clinker could explain the greater heat generated during its hydration compared to the control sample, especially at the very beginning of setting. Although the total heat generated by ALP1-Ter cement was rather high, it is still tolerable for a CEM I binder. For different reasons (thermal cracking risks and delayed ettringite formation), a limitation of heat of hydration might be required. ALP1 sediment could still be valorized using supplementary cementitious materials in addition to ALP1-Ter or adjusting the raw meal to synthesize less C_3A.

Mortar compressive strength with ALP1-Ter cement was assessed after 2, 7 and 28 days in standard conditions. Results are given in Figure 15 and Table 14 and compared to the industrial reference CEM I. After 28 days, ALP1-Ter cement presented a compressive strength of 57.9 MPa. According to the strength value after a curing time of 2 days (< 30 MPa), ALP1-Ter cement can be classified as a 52.5N binder. It can be noticed that at any curing time, compressive strengths of the laboratory cement made with sediment were higher than the reference Portland cement. ALP1-Ter cement showed a high reactivity and strength gain at the earliest ages (2 and 7 days). The maximum compressive strength difference between the tested cement and the control sample was observed after 7 days (17.3 % higher). In contrast, this discrepancy tended to diminish at a later age, *i.e.* 28 days. The described strength development is rather consistent with the semi-adiabatic

calorimeter results and relatively short setting times. In summary, mechanical performances of the Portland cement prepared with 11.4 wt% of sediment were fully acceptable.

Dimensional and mass variations of mortars stored in a cabinet with controlled atmosphere were assessed during 28 days (Figure 16). Mortar shrinkage with ALP1-Ter cement was stabilized after 21 days at 390 µm/m (Figure 16a). This value is low compared to the reference Portland cement (500 µm/m). Generally speaking, the lower the shrinkage, the more performant the cement. Shrinkage limits are no longer given in cement standards. However, the withdrawn NF P15-301 standard set a maximum limit at 1000 µm/m for a cement that reaches 55 MPa after 28 days. This criterion is respected for ALP1-Ter cement and the reference one as well. Moreover, studying 8 different industrial CEM I cements, Massazza observed that shrinkage in the same conditions lies in a range from 329 to 461 µm/m [61], which is similar to the manufactured ALP1-Ter mortar. Blaine fineness is often presented as a key-explanation for drying shrinkage. However, in this study, Blaine fineness was kept constant in order to avoid this bias. Therefore, the small difference in shrinkage between the ALP1-Ter mortar and the control one can mainly be attributed to the progress of the hydration reaction that was greater for the laboratory ALP1-Ter sample in an equivalent time. More water participated in hydration reactions compared to the other sample, meaning less water is available for evaporation in the porous system. To complete dimensional interpretations, it can be observed in Figure 16b that whatever the drying time, mass loss was lower for ALP1-Ter mortar compared to the control CEM I. This result is consistent with dimensional variations, since mass loss and shrinkage are both related to the evaporated water quantity. To sum up, it can be said that ALP1-Ter shrinkage is absolutely satisfying.

As a conclusion of this result part concerning the “advanced” experiments related to ALP1-Ter cement, it can be said that this alternative binder fulfilled all the tested requirements either in a fresh or a hardened state.

3.3 Link between sediment properties and clinker characteristics

It’s interesting to represent the different mineralogical compositions in a framework, as proposed by Haurine *et al.* in 2016 [13] in order to classify the sediments according to their interest in being used in the tile and brick industry. In the present work, we have chosen a representation that highlights the presence of alkaline ions which are known to play a significant role during sintering. The poles are the following: (1) clay minerals and microcline since they contain potassium (especially illite as shown in Table 4 and microcline), (2) albite which can supply sodium during sintering, and (3) quartz. All sediments are quite distinct from CLY1 and CLY2. Thus a chemical and a mineralogical framework to predict the effect of sediment addition on clinker

563 characteristics can be proposed (Figure 17). From Figure 17a, the following points can be
564 underlined:
565 - The greater the CaO content, the greater amount of sediment can be used in the raw meal.
566 - When the quantity of SiO_2 increases, the burnability decreases.
567 - The interstitial phase is abundant when the composition in enriched with alumina.
568 Figure 17b presents the mineral compositions of the sediments in a mineralogical framework. One
569 pole corresponds to K rich phases, a second pole to Na rich phases and the last pole to quartz. If the
570 composition contains a significant amount of albite, then orthorhombic C_3A and α-C_2S are present
571 in the clinker. These frameworks are simplified and obviously they need to be completed with
572 similar studies on a variety of sediments. Nevertheless, they could be a useful decision support tool
573 for a cement company to decide if a sediment could be incorporated into a raw meal as it is or if it
574 needs to be mixed with other sources of raw materials.

575 **4. Conclusions**

576 Beneficial reuse of waste as alternative raw materials for industry is a challenging, but
577 necessary, objective for the future. Concerning the cement industry, large amounts of natural
578 geological resources are consumed each year to manufacture clinker, component of concrete which
579 is the most widely used construction material. In parallel, great amounts of fine-grained sediment
580 might have to be dredged from French reservoirs in the future. In this context, an industrial ecology
581 approach could be implemented in order to introduce dam sediments into clinker raw meals,
582 reducing at the same time waste disposal and the extraction of quarried rock. Compared to previous
583 studies which were "case-specific", this paper aimed to take into account the soils and geological
584 variations from one French region to another, working simultaneously on 7 sediments from
585 different locations. The essential conclusions are listed below:
586 - In terms of chemical composition, all the studied sediment resources contain SiO_2, Al_2O_3
587 and CaO as the main oxides but with various concentrations. A direct relationship can be
588 made with the mineralogical phases, *e.g.* CaO is carried by carbonates (primarily calcite)
589 while silica is contained in quartz, phyllosilicates and feldspars. Additional minor elements
590 can also be indicated, especially for alpine sediments, like Mg (illite, chlorite and dolomite)
591 and alkalis (feldspars and illite).
592 - Very high sediment replacement ratios (from 25 to 35 wt%) are reached in the total clay
593 substitution strategy, called binary mixes. This approach is challenging since the adjustment
594 of the composition is restricted to the lime saturation factor. According to the identified
595 crystalline phases, the products can be considered as "Portland" clinkers. In several cases,
596 special features are observed due to sediment introduction (lime combination success,

interstitial phase content, polymorphism). The impact of dredged materials on clinkering reactions was never described with such details previously in literature.

- Considering the clinker obtained with ternary meals, it can be said that a replacement of 10 to 15 wt% of the usual raw material by any of the sediments does not significantly impact the clinker properties, even the phase polymorphism. After gypsum addition, a CEM I 52.5N cement can be obtained, with a high hydraulic reactivity and no constraint in terms of fresh state workability and shrinkage. To sum up, fine-grained sediments can be reused in clinker raw meal to produce any type of clinker.

Due to the significant number of investigated sediments, this study provides a solid foundation for future work and in particular to test with an industrial pilot scheme. Moreover, additional practical aspects must be considered such as full-scale drying after dredging operation and transport conditions. It should also be noticed that durability tests are a legitimate extension of this work, particularly the sensitivity to chemical attacks, according to the desired cement type and the expected application.

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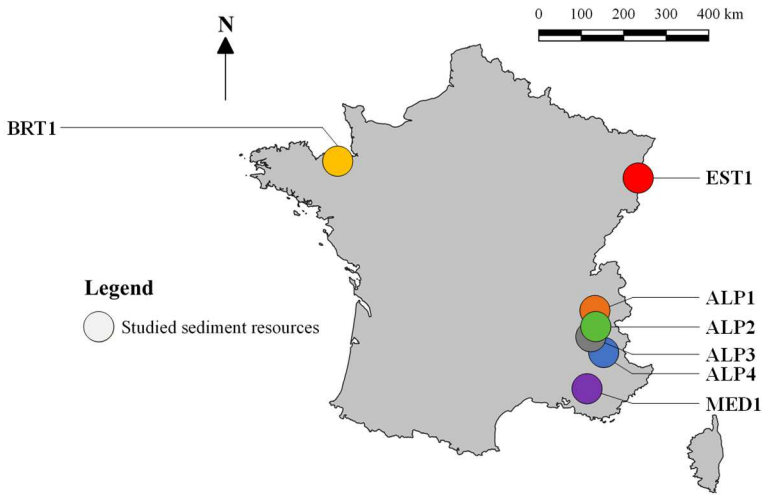
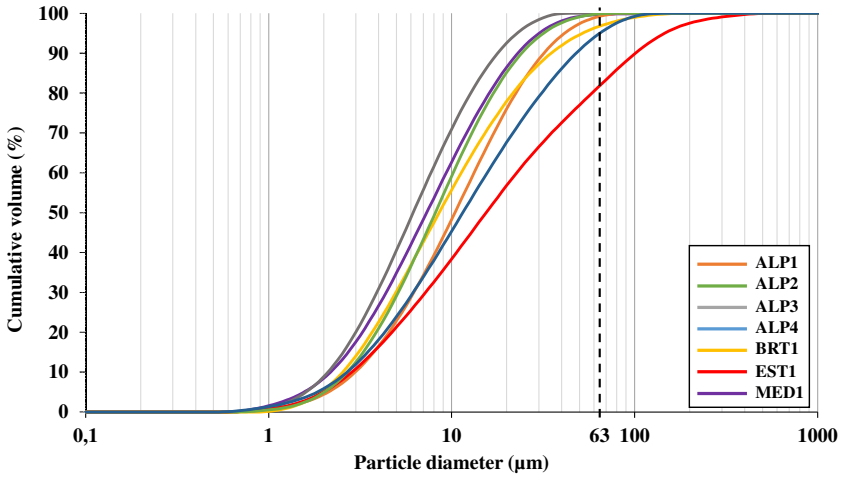
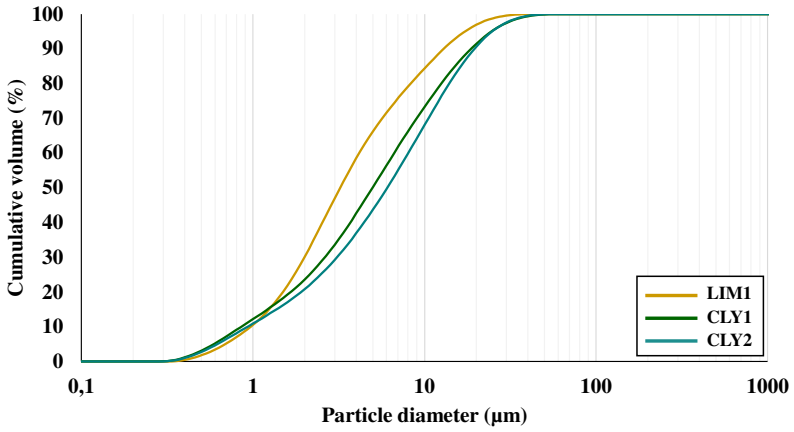


Figure 1 - Location of dam sediments on the French territory and corresponding abbreviations.



(a)



(b)

Figure 2 - Particle size distributions of the raw sediments (a) and the quarried materials (b).

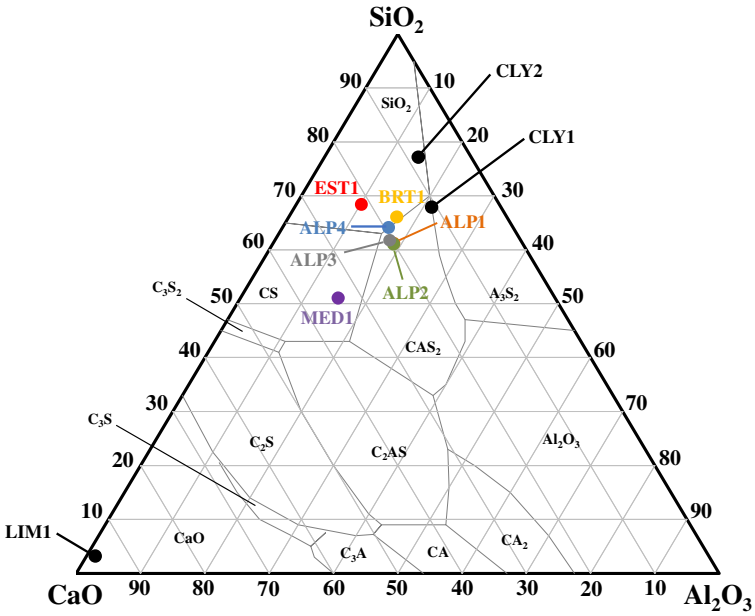
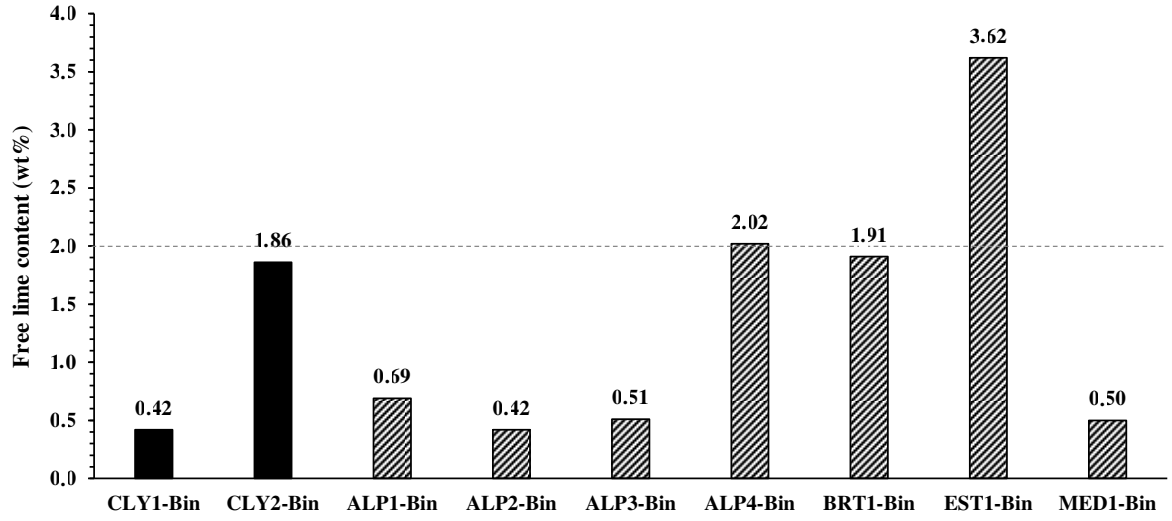
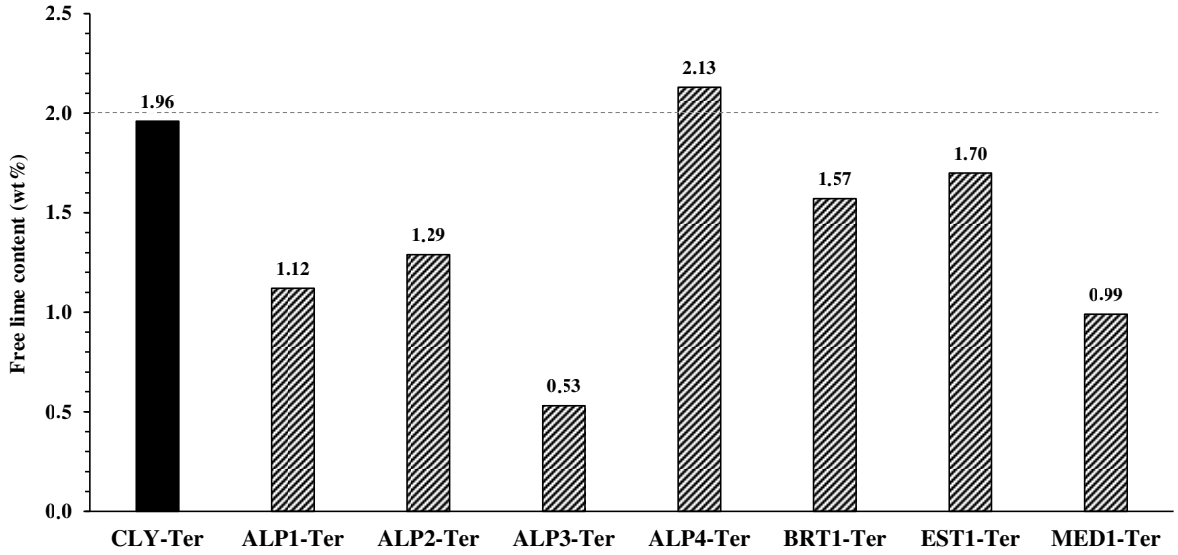


Figure 3 - Raw material locations in Rankin's diagram.



(a)



(b)

Figure 4 - Free lime contents of clinkers from (a) binary and (b) ternary mixes.

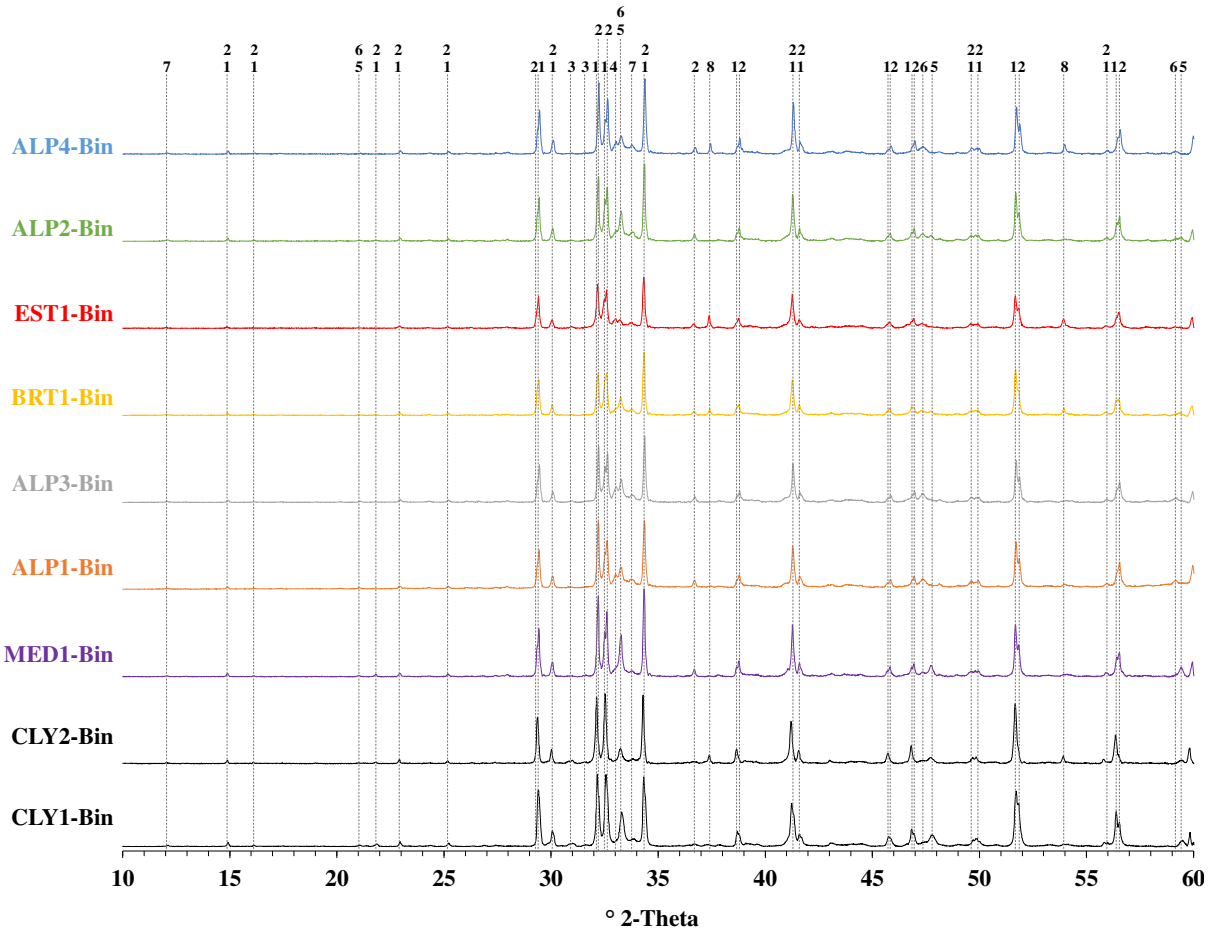
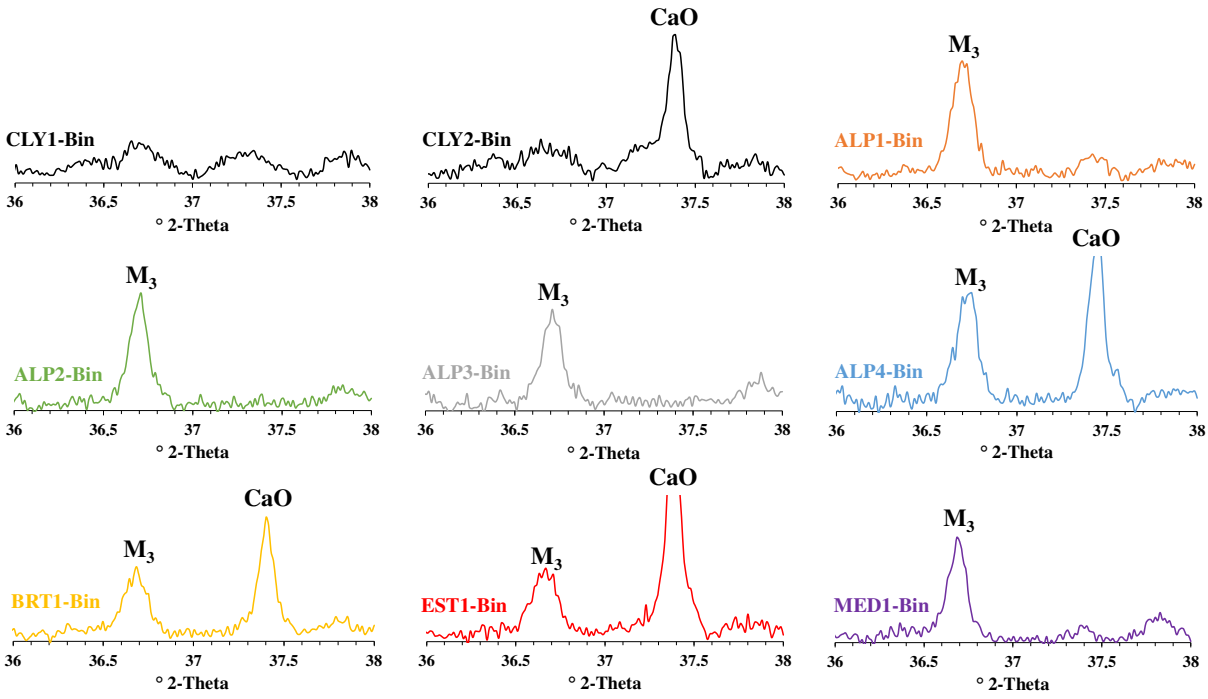
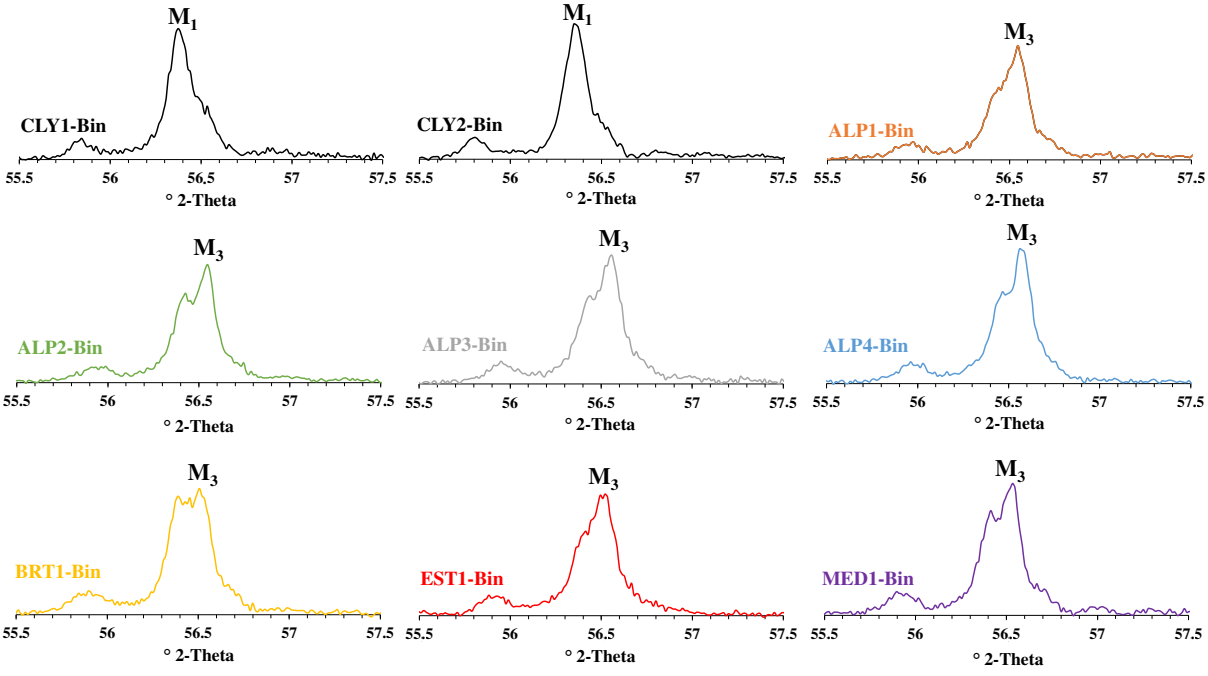


Figure 5 - XRD of binary clinkers *(1: M_1-C_3S ; 2: M_3-C_3S ; 3: β-C_2S ; 4: α-C_2S ; 5: Cubic-C_3A; 6: Orthorhombic-C_3A ;7: C_4AF ; 8: CaO).*



(a)



(b)

Figure 6 - Identification of C_3S polymorphism of binary clinkers in the 36.0 to 38.0 °2θ window (a) and in the 55.5 to 57.5 °2θ window (b). M_1 and M_3 are two alite polymorphs.

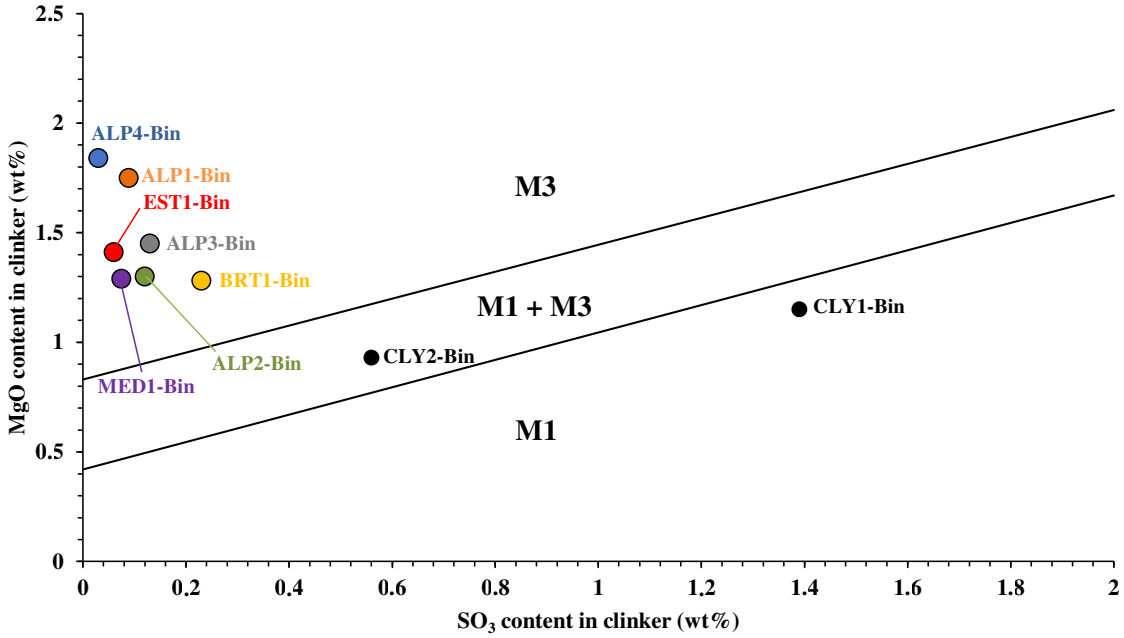
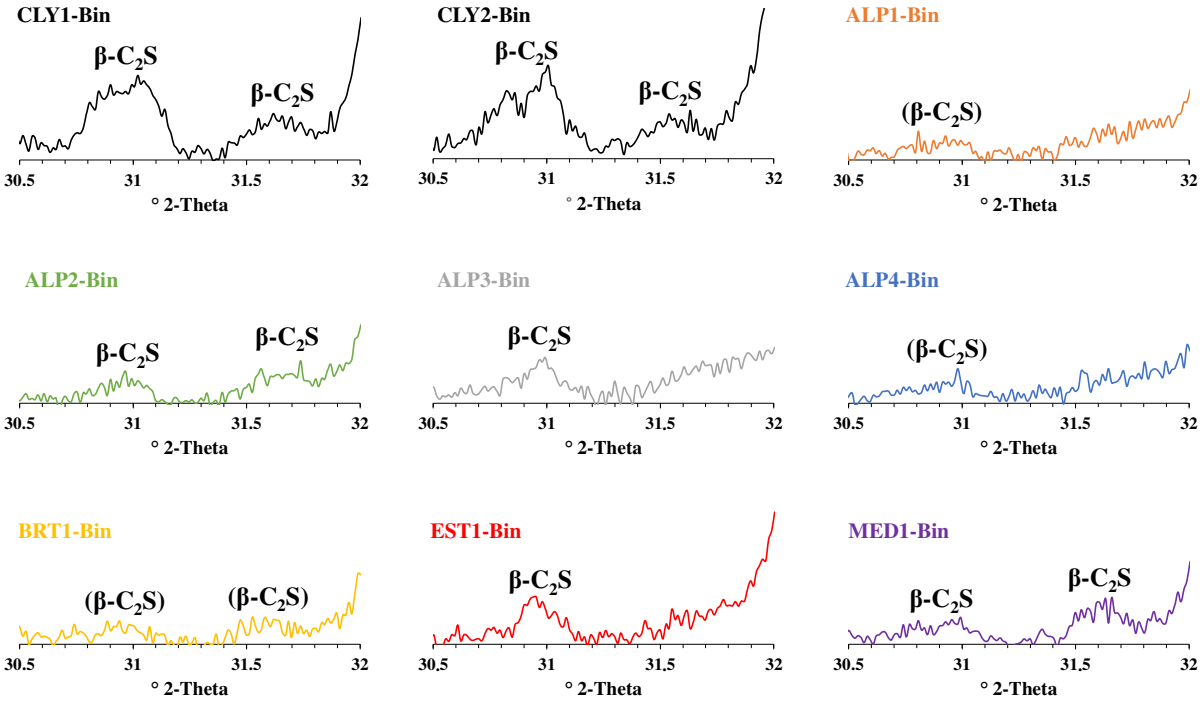
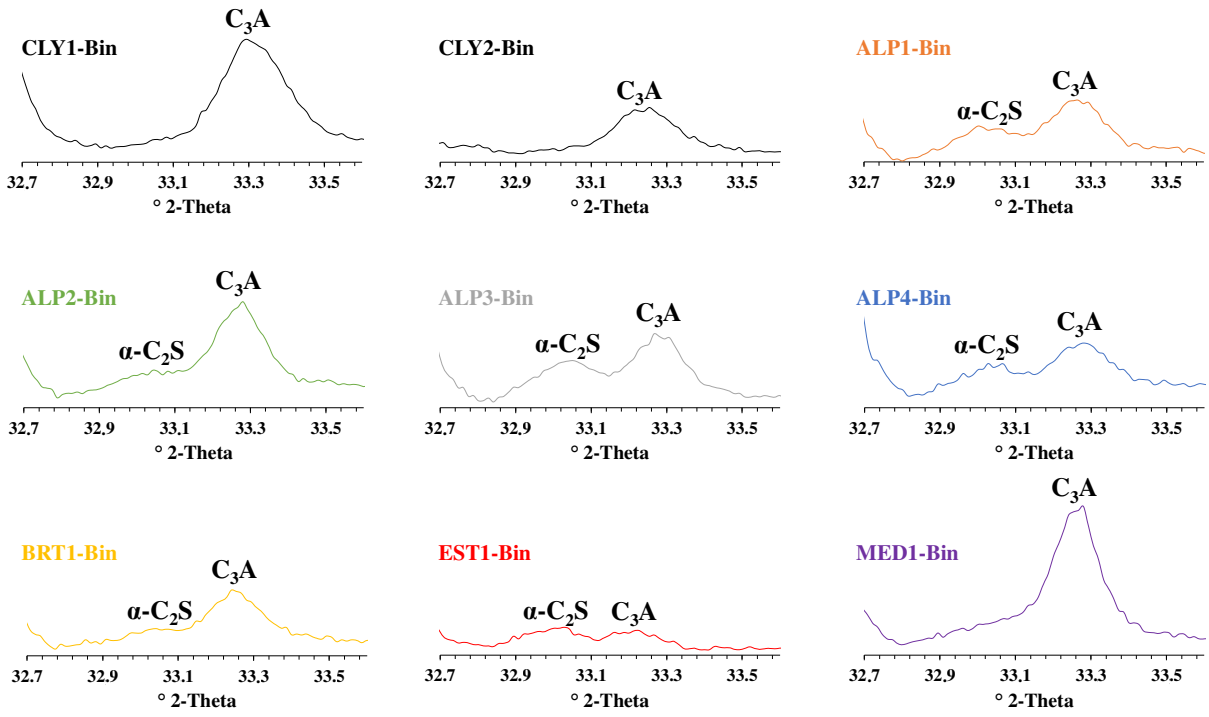


Figure 7 - Relationship between MgO/SO_3 content on polymorphic transformations of alite and location of binary lab clinkers (adapted from [56]).



(a)



(b)

Figure 8 - Identification of C_2S polymorphism of binary clinkers in the 30.5 to 32.0 °2θ window (a) and in the 32.7 to 33.6 °2θ window (b).

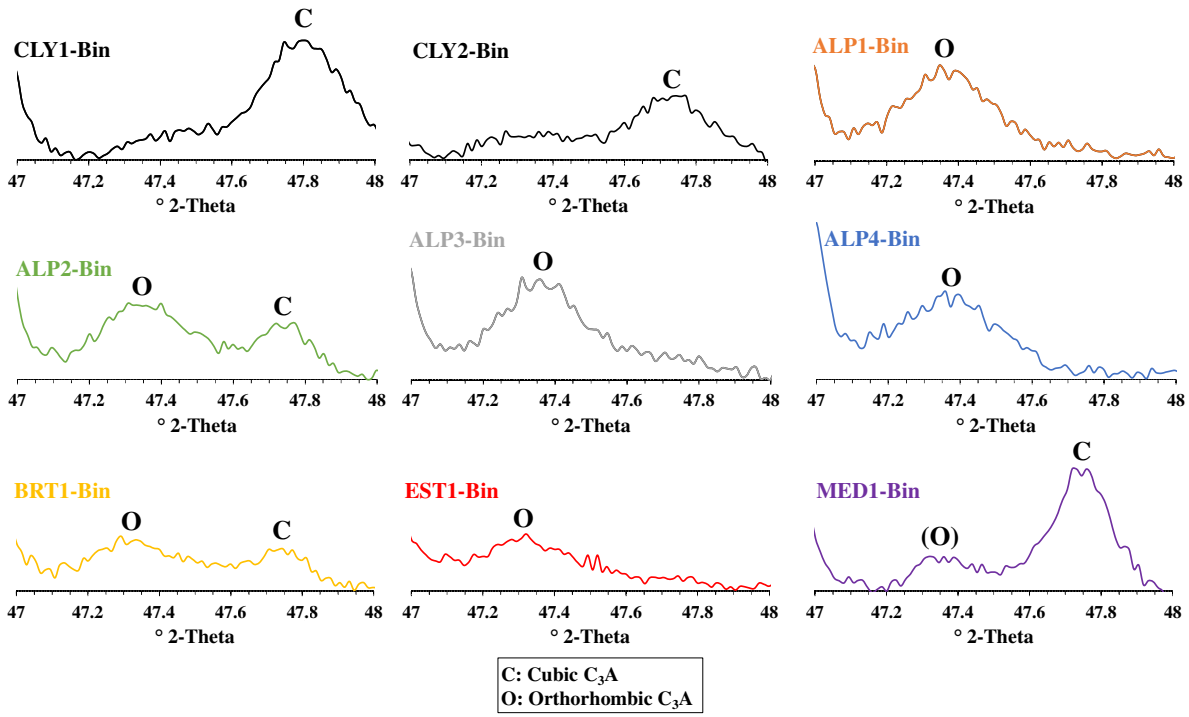


Figure 9 - Identification of C_3A polymorphism of binary clinkers in the 47.0 to 48.0 °2θ window.

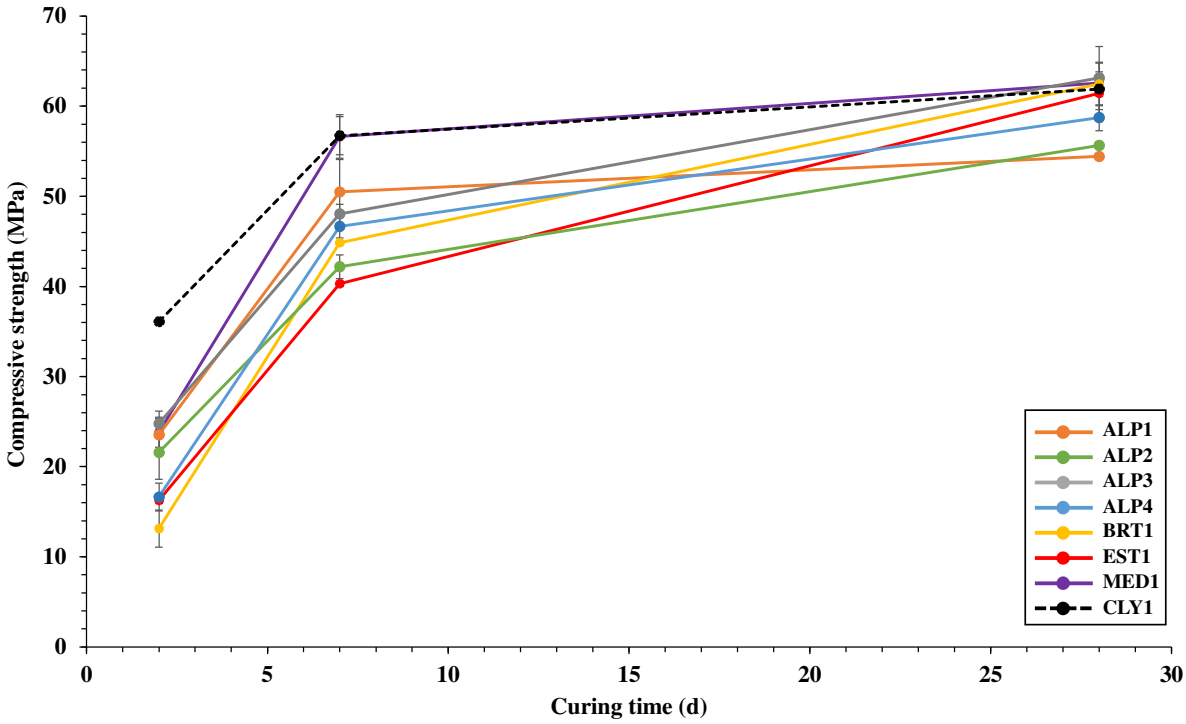
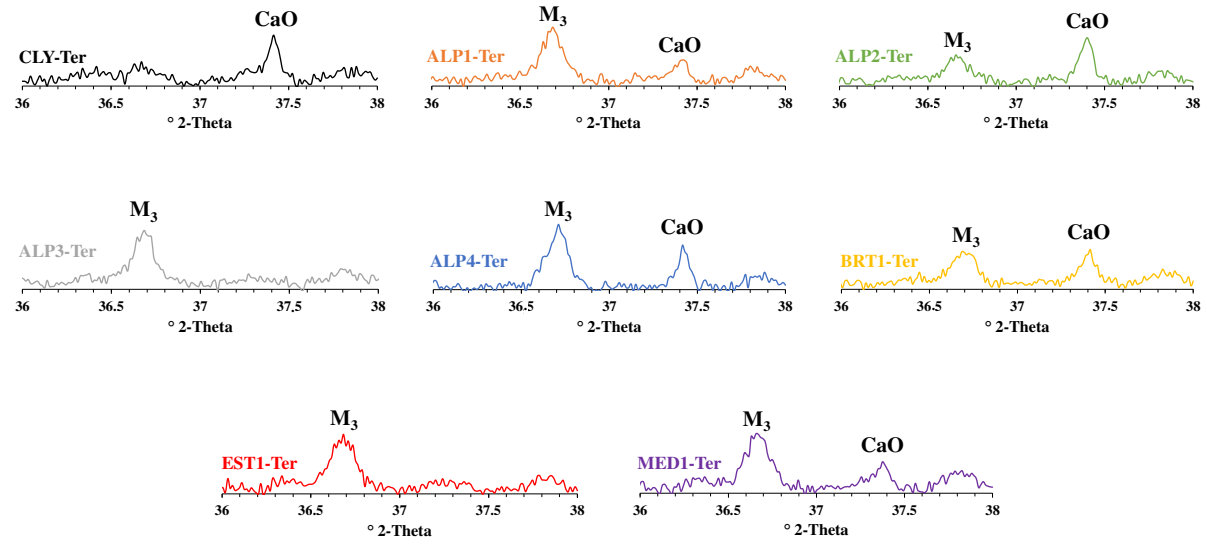
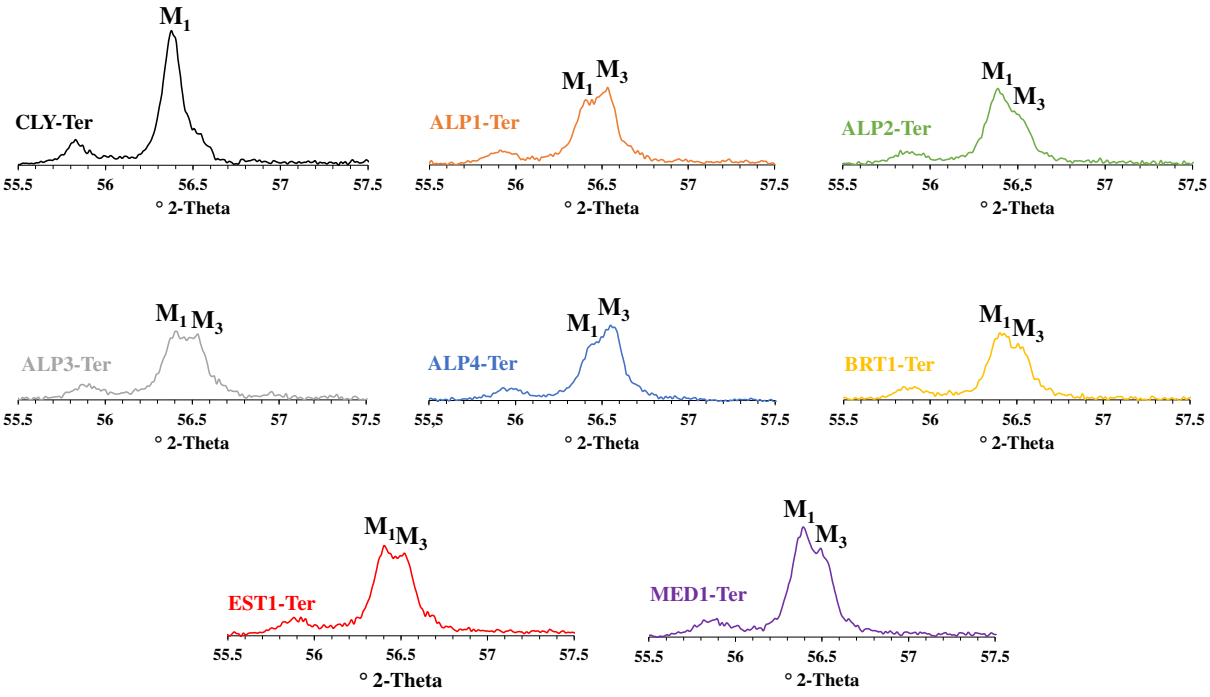


Figure 10 - Compressive strength on cement pastes produced from binary clinkers.

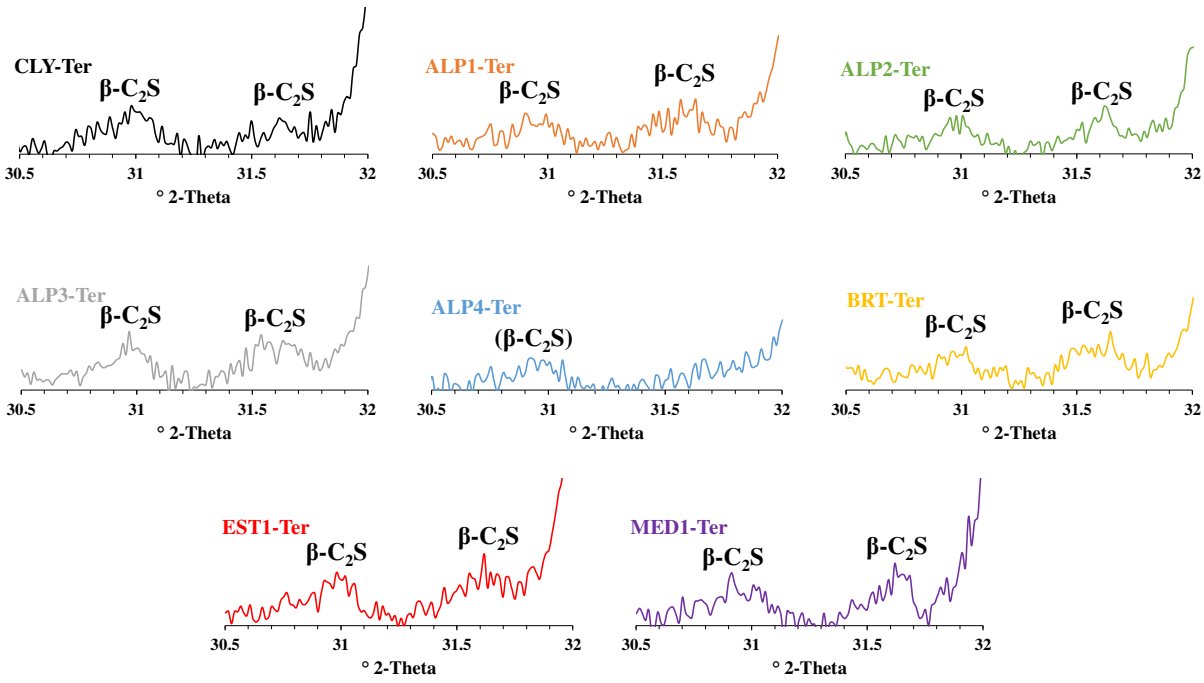


(a)

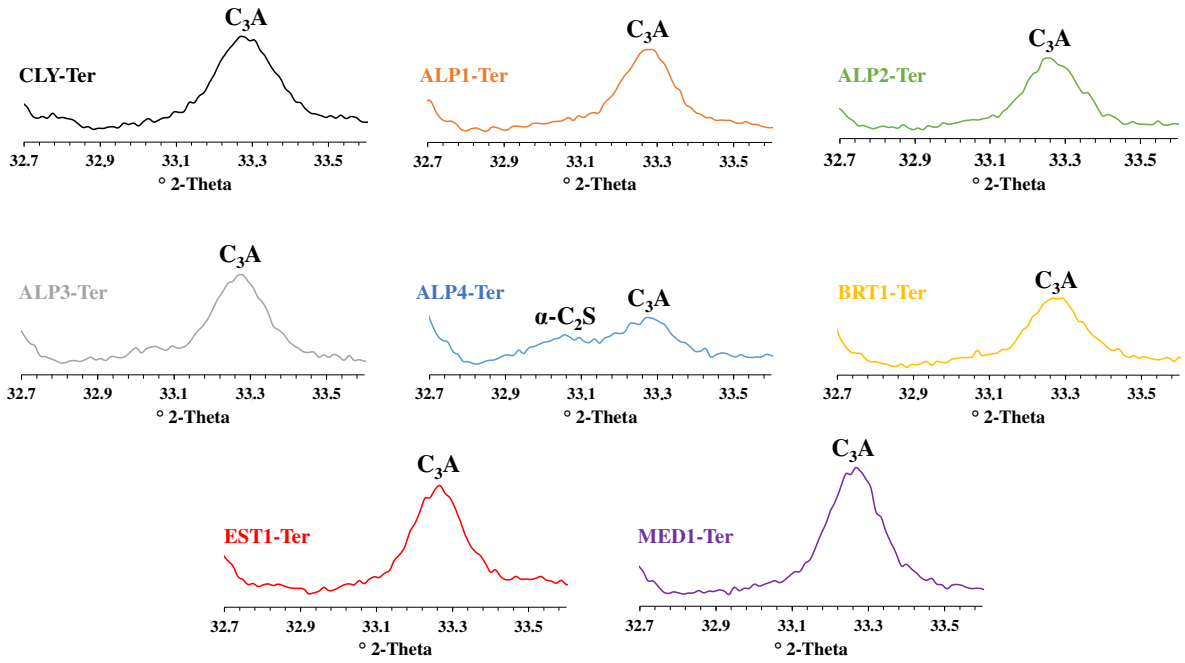


(b)

Figure 11 - Identification of C_3S polymorphism of ternary clinkers in the 36 to 38 °2θ window (a) and in the 55.5 to 57.5 °2θ window (b). M_1 and M_3 are two alite polymorphs.



(a)



(b)

Figure 12 - Identification of C_2S polymorphism of ternary clinkers in the 32.7 to 33.6 °2θ window (a) and in the 32.7 to 33.6 °2θ window (b).

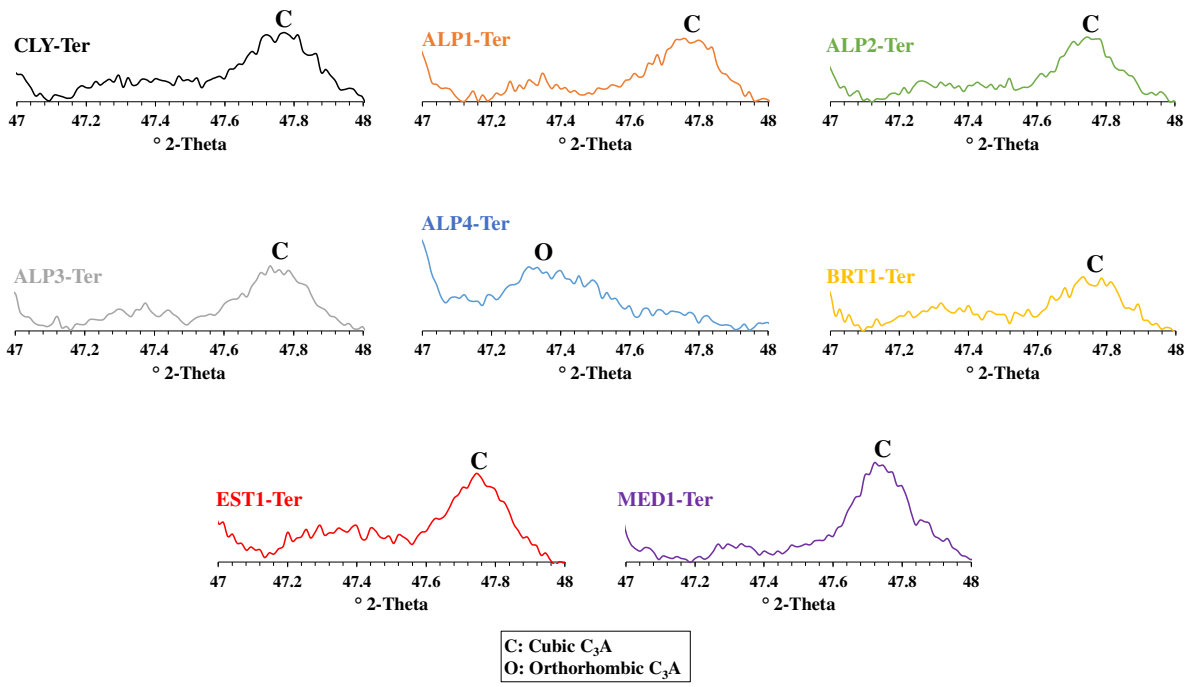


Figure 13 - Identification of C_3A polymorphism of ternary clinkers in the 47.0 to 48.0 °2θ window

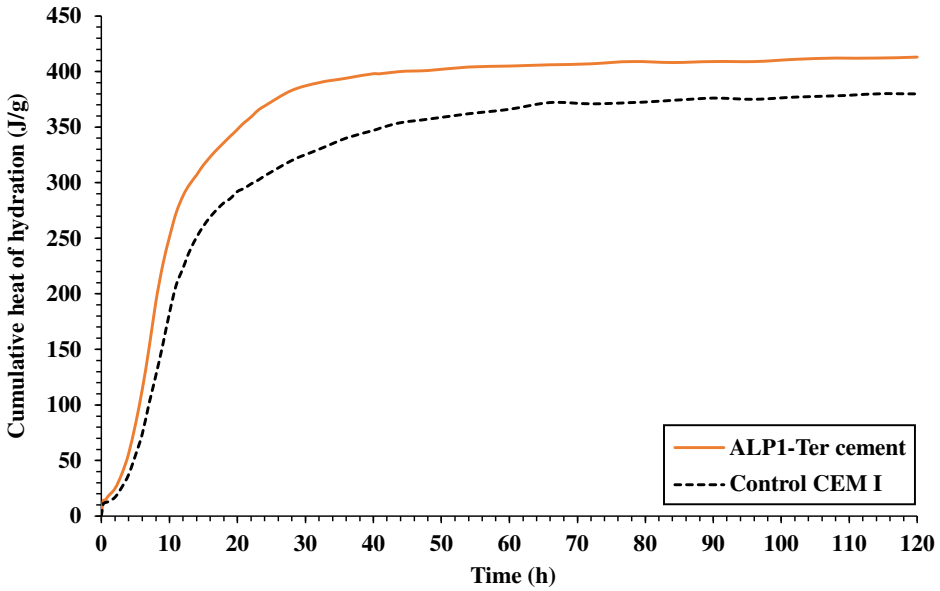


Figure 14 - Cumulative heat of hydration of ALP1-Ter cement and control CEM I.

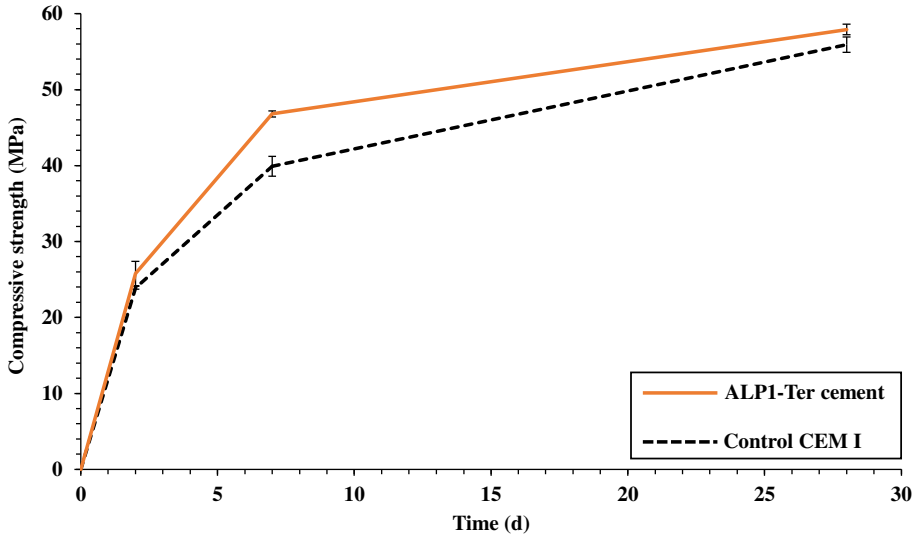
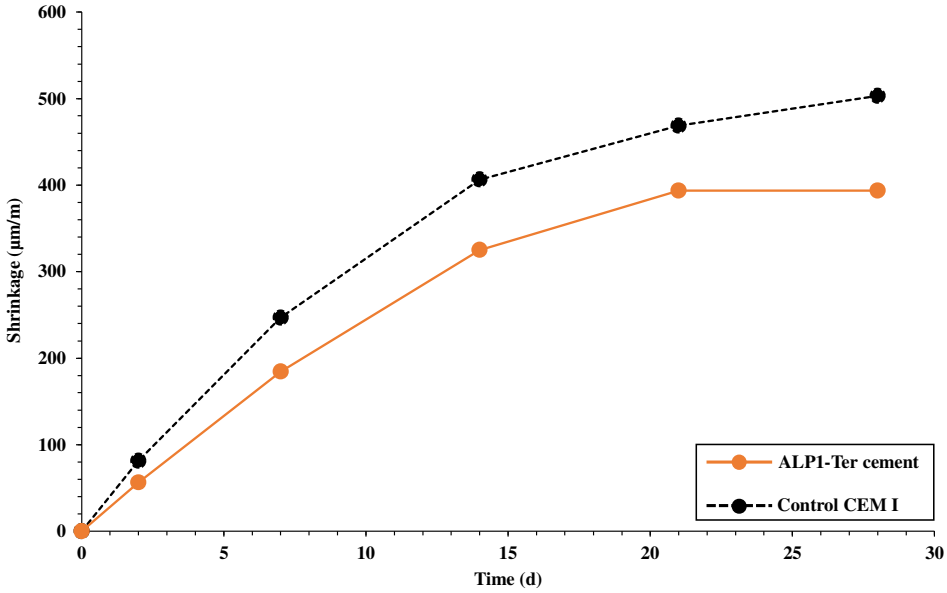
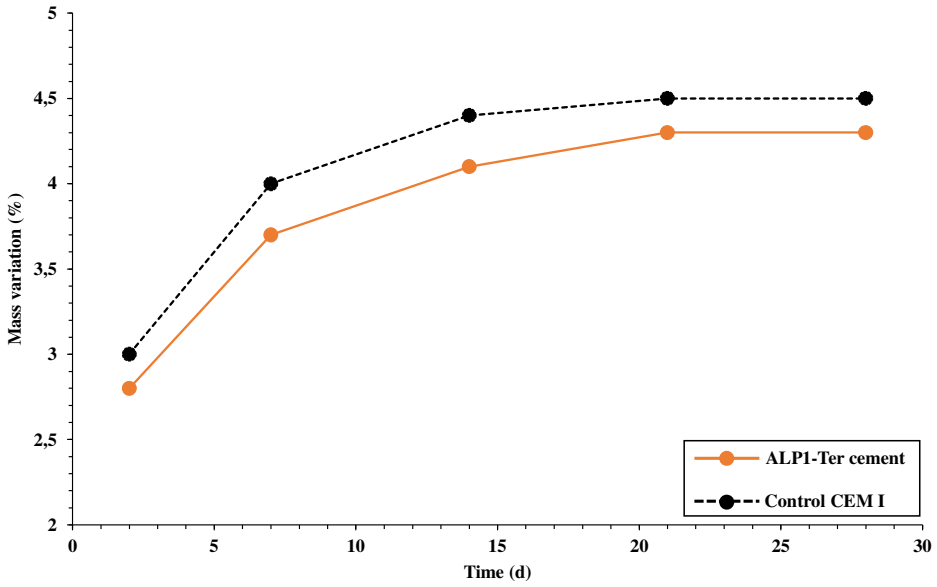


Figure 15 - Compressive strength of standard NF EN 196-1 mortars prepared with ALP1-Ter cement and with the control CEM I.

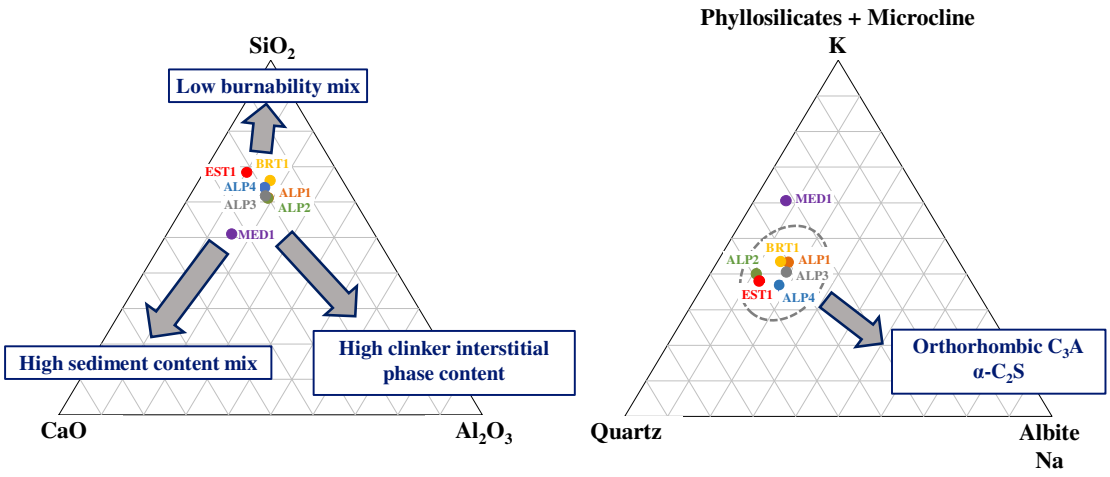


(a)



(b)

Figure 16 – Mortar shrinkage (a) and mortar mass variation (b) versus time for ALP1-Ter cement and control CEM I.



(a) (b)

Figure 17 - Proposition of a chemical (a) and mineralogical (b) framework to predict the influence of sediments introduction in clinker manufacture.

	LIM1	**CLY1**	**CLY2**	**ALP1**	**ALP3**	**ALP2**	**ALP4**	**BRT1**	**EST1**	**MED1**
d_{v10} (µm)	1.1	1.0	1.0	3.3	2.4	3.0	3.0	2.5	3.2	2.2
d_{v50} (µm)	3.6	5.6	6.8	11.7	6.9	9.1	12.9	8.6	17.3	7.3
d_{v90} (µm)	14.5	21.0	21.9	35.8	20.0	27.1	53.8	35.0	113.4	23.0
Clay fraction (vol%) < 4 µm	30.1	23.6	20.8	16.5	30.9	20.9	18.1	22.5	16.4	26.6
Silt fraction (vol%) 4 µm - 63 µm	69.9	76.4	79.2	82.7	69.1	78.9	76.6	74.2	65.0	73.1
Sand fraction (vol%) 63 µm – 2 mm	0.0	0.0	0.0	0.8	0.0	0.2	5.3	3.3	18.6	0.3

Table 1 – 10^{th}, 50^{th} and 90^{th} percentiles of sediments particle size distributions and volumic distribution of clay, silt and sand fractions.

	LIM1	CLY1	CLY2	ALP1	ALP2	ALP3	ALP4	BRT1	EST1	MED1
Density ($g.cm^{-3}$)	2.74	2.66	2.75	2.79	2.81	2.70	2.79	2.55	2.59	2.67
BET SSA ($m^2.g^{-1}$)	4.1	47.1	28.3	5.9	7.0	11.7	5.2	17.9	7.8	16.8
Blaine SSA ($cm^2.g^{-1}$)	5852	6377	6154	5741	10502	12498	7547	7132	4931	12069

Table 2 - Density and specific surface areas of raw materials.

wt%	LIM1	CLY1	CLY2	ALP1	ALP2	ALP3	ALP4	BRT1	EST1	MED1
SiO_2	1.79	50.65	61.22	43.52	44.51	42.76	46.95	46.96	49.63	35.04
Al_2O_3	0.76	16.07	11.63	13.40	13.70	12.38	11.58	11.97	7.41	10.46
Fe_2O_3	1.28	5.95	4.82	5.63	5.81	5.22	5.09	5.79	3.07	3.90
CaO	52.71	7.79	6.43	14.18	14.64	14.09	13.78	12.13	15.64	23.14
MgO	0.48	1.64	1.14	2.87	1.83	1.84	3.03	1.72	2.10	1.56
TiO_2	0.02	0.90	0.92	0.60	0.70	0.68	0.56	0.64	0.39	0.48
MnO	0.04	0.03	0.02	0.10	0.16	0.15	0.11	0.05	0.06	0.08
P_2O_5	0.06	0.10	0.05	0.16	0.19	0.17	0.14	0.29	0.13	0.10
SrO	0.03	0.02	0.02	0.05	0.08	0.06	0.05	0.08	0.04	0.07
Na_2O	0.00	0.13	0.06	0.91	0.65	0.83	0.94	0.75	0.70	0.27
K_2O	0.13	3.15	2.24	2.69	2.18	2.50	2.32	2.08	1.58	1.81
SO_3	0.10	1.07	1.27	0.17	0.36	0.28	0.08	0.30	0.11	0.34
LOI	42.54	12.35	10.09	15.60	15.06	18.92	15.28	17.05	19.02	22.72
Total	99.94	99.85	99.91	99.88	99.87	99.88	99.91	99.81	99.88	99.97

Table 3 - Chemical composition of raw materials.

wt%	LIM1	CLY1	CLY2	ALP1	ALP2	ALP3	ALP4	BRT1	EST1	MED1
Silico aluminous phases										
Quartz	1	45	59	29	35	28	30	31	32	17
Clay minerals	-	28	22	29	23	21	22	27	21	31
Albite	-	-	1	12	7	12	12	11	8	4
Microcline	-	3	2	2	5	7	3	5	3	2
Carbonated phases										
Calcite	98	20	15	23	29	30	25	18	28	43
Dolomite	1	-	-	5	1	2	8	-	8	3
Aragonite	-	-	-	-	-	-	-	8	-	-
Mineral phases that contain sulfur										
Pyrite	-	3	4	-	-	-	-	-	-	-
Gypsum	-	1	1	-	-	-	-	-	-	-
Detailed clay mineral compositions										
Illite	-	41	45	62	54	55	68	24	63	45
Chlorite	-	-	-		46	45	32	36	37	25
Kaolinite	-	59	55	38	-	-	-	40	-	30

Table 4 - Mineral composition of raw materials.

Temperature range (°C)	Attributed phenomenon	Mass loss (wt%)									
		LIM1	**CLY1**	**CLY2**	**ALP1**	**ALP2**	**ALP3**	**ALP4**	**BRT1**	**EST1**	**MED1**
105-150	Remaining adsorbed water evaporation and organic matter oxidation	0.1	0.7	0.4	1.1	0.8	1.2	0.8	5.3	3.8	1.5
450-650	Phyllosilicates dehydroxylation – Dolomite decomposition	0.4	1.2	0.9	2.5	2.2	3.1	1.7	4.1	2.8	3.1
650-850	Calcite decomposition	12.9	2.5	2.0	11.4	10.2	17.1	10.5	6.9	10.5	17.1
850-1000	Ending of phyllosilicates degradation	0.0	0.1	0.0	0.2	0.1	0.1	0.2	0.1	0.2	0.1
105-1000	Total mass loss	13.4	4.5	3.3	15.2	13.3	13.9	13.2	16.4	17.3	21.8

Table 5 - TGA for the raw materials between 105 and 1000 °C and associated phenomena.

	LIM1	CLY1	CLY2	ALP1	ALP2	ALP3	ALP4	BRT1	EST1	MED1
Organic matter (wt%)	n.d.	n.d.	n.d.	3.2	3.2	3.9	3.0	8.7	5.6	4.8

Note: n.d. = not determined

Table 6 - Organic matter content of raw materials.

Meal reference	Limestone (wt%)	Silico-aluminous raw material (wt%)									SR	AR
		CLY1	CLY2	ALP1	ALP2	ALP3	ALP4	BRT1	EST1	MED1		
CLY1-Bin	76.70	23.30									1.97	1.83
CLY2-Bin	79.24		20.76								2.81	1.50
ALP1-Bin	72.70			27.30							1.97	1.71
ALP2-Bin	72.13				27.87						2.07	1.68
ALP3-Bin	73.12					26.88					1.97	1.70
ALP4-Bin	73.82						26.18				2.32	1.58
BRT1-Bin	74.20							25.80			2.21	1.49
EST1-Bin	73.73								26.27		3.37	1.43
MED1-Bin	65.19									34.81	2.11	1.89

Table 7 - Composition of binary clinker meals (LSF = 97).

Meal reference	Limestone (wt%)	Silico-aluminous raw material (wt%)									AR
		CLY1	CLY2	ALP1	ALP2	ALP3	ALP4	BRT1	EST1	MED1	
CLY-Ter	78.18	9.67	12.14								1.65
EST1-Ter	75.48	13.74							10.78		1.69
ALP1-Ter	76.50		12.06	11.44							1.59
ALP2-Ter	75.72		10.48		13.79						1.60
ALP3-Ter	76.70		12.14			11.16					1.59
ALP4-Ter	74.84		3.90				21.25				1.56
BRT1-Ter	76.04		7.60					16.36			1.50
MED1-Ter	71.80		9.77							18.43	1.71

Table 8 - Composition of ternary clinker meals (LSF = 97 and SR = 2.4).

Usual composition range in wt% (according to [46])				**NF EN 197-1 requirements [45]**	
SiO_2	Al_2O_3	Fe_2O_3	CaO	CaO/SiO_2	MgO
19-25	2-9	1-5	62-67	> 2.0	< 5.0

Table 9 - Chemical requirements for Portland clinker.

wt%	Control CEM I
SiO_2	19.94
Al_2O_3	5.33
Fe_2O_3	4.21
CaO	65.74
MgO	0.69
TiO_2	0.31
MnO	0.04
P_2O_5	0.07
SrO	0.08
Na_2O	0.09
K_2O	0.41
SO_3	2.69
LOI	0.26
Total	99.86
Mineralogical composition according to Bogue calculations	
C_3S	70.9
C_2S	5.2
C_3A	7.2
C_4AF	13.1

Table 10 - Chemical and mineralogical composition of the control CEM I used as reference in the standard cement tests.

Clinker	CLY1-Bin	CLY2-Bin	ALP1-Bin	ALP2-Bin	ALP3-Bin	ALP4-Bin	BRT1-Bin	EST1-Bin	MED1-Bin
SiO_2	20.02	21.45	20.61	20.72	20.98	20.93	20.21	22.61	20.82
Al_2O_3	6.58	4.85	6.53	6.40	6.58	5.69	5.67	4.06	6,56
Fe_2O_3	3.64	3.02	3.79	3.79	3.69	3.77	3.93	2.83	3.51
CaO	65.20	67.86	65.23	65.89	65.56	66.50	66.75	66.21	66.32
MgO	1.15	0.93	1.75	1.30	1.45	1.84	1.28	1.41	1.29
TiO_2	0.32	0.35	0.34	0.31	0.35	0.19	0.31	0.15	0.28
MnO	0.03	0.04	0.10	0.14	0.11	0.10	0.06	0.10	0.10
P_2O_5	0.11	0.10	0.13	0.15	0.13	0.11	0.20	0.14	0.11
SrO	0.05	0.05	0.06	0.07	0.07	0.06	0.07	0.06	0.07
Na_2O	0.14	0.08	0.41	0.28	0.37	0.35	0.35	0.29	0.16
K_2O	1.17	0.44	0.34	0.26	0.50	0.23	0.27	0.21	0.33
SO_3	1.39	0.56	0.09	0.12	0.13	0.03	0.23	0.06	0.08
LOI	0.14	0.20	0.52	0.50	0.02	0.12	0.58	1.84	0.33
Total	99.94	99.93	99.90	99.93	99.94	99.92	99.91	99.97	99.96
NF EN 197-1 chemical requirements on clinker									
%MgO	< 5 wt%	< 5 wt%	< 5 wt%	< 5 wt%	< 5 wt%	< 5 wt%	< 5 wt%	< 5 wt%	< 5 wt%
%CaO / %SiO_2	3.3	3.2	3.2	3.2	3.1	3.2	3.3	2.9	3.2
Mineralogical compositions according to Bogue calculations									
C_3S	62.1	68.77	56.8	60.6	55.8	59.8	66.6	51.6	60.6
C_2S	10.6	9.70	16.3	13.7	18.0	14.9	7.7	25.9	14.0
C_3A	11.3	7.74	10.9	10.6	11.2	8.7	8.4	6.0	11.5
C_4AF	11.1	9.19	11.5	11.5	11.2	11.5	12.0	8.6	10.7

Table 11 - Chemical and mineralogical compositions of binary clinkers.

Clinker	CLY-Ter	ALP1-Ter	ALP2-Ter	ALP3-Ter	ALP4-Ter	BRT1-Ter	EST1-Ter	MED1-Ter
SiO_2	20.40	20.61	20.74	21.78	20.95	21.12	20.94	21.14
Al_2O_3	5.40	5.86	5.62	5.64	5.54	5.85	6.01	5.73
Fe_2O_3	3.14	3.29	3.23	3.26	3.41	3.54	3.18	3.16
CaO	68.29	67.20	67.68	66.25	67.11	66.61	66.59	67.16
MgO	1.02	1.24	1.06	1.21	1.68	1.19	1.23	1.14
TiO_2	0.30	0.32	0.33	0.31	0.21	0.33	0.28	0.28
MnO	0.02	0.07	0.08	0.09	0.09	0.07	0.08	0.09
P_2O_5	0.10	0.08	0.11	0.11	0.12	0.13	0.09	0.09
SrO	0.05	0.05	0.05	0.06	0.06	0.06	0.05	0.06
Na_2O	0.11	0.17	0.12	0.18	0.31	0.17	0.19	0.13
K_2O	0.42	0.43	0.35	0.38	0.20	0.40	0.55	0.36
SO_3	0.55	0.47	0.30	0.33	0.06	0.41	0.63	0.36
LOI	0.18	0.16	0.30	0.32	0.23	0.10	0.14	0.26
Total	99.98	99.95	99.97	99.92	99.97	99.98	99.96	99.96
Mineralogical compositions according to Bogue calculations								
C_3S	74.27	68.3	70.2	59.4	63.2	59.8	60.0	65.6
C_2S	2.52	7.6	6.5	17.6	12.4	15.4	14.8	11.1
C_3A	9.00	10.0	9.4	9.4	8.9	9.5	10.5	9.8
C_4AF	9.55	10.0	9.8	9.9	10.4	10.8	9.7	9.6

Table 12 - Chemical and mineralogical compositions of ternary clinkers.

	ALP1-Ter cement	Control CEMI
w/c at standard consistency	< 0.245	0.260
Initial setting time (min)	95	125
Final setting time (min)	180	185

Table 13 - Setting times of ALP1-Ter cement and the control CEM I.

Curing time (d)	ALP1-Ter cement		Control CEMI	
	Flexural strength	Compressive strength	Flexural strength	Compressive strength
2	4.9	25.8	5.0	23.9
7	7.4	46.8	7.6	39.9
28	8.3	57.9	8.6	57.9

Table 14 - Flexural and compressive strength values for standard NF EN 196-1 mortar prepared with ALP1-Ter cement and control CEM I.