



Article

The Use of Callovo-Oxfordian Argillite as a Raw Material for Portland Cement Clinker Production

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Abstract: Excavated soils and rocks are materials obtained in construction works that could represent an ecological issue if a durable and efficient reuse process is not set. The radioactive waste disposal planned by the French National Radioactive Waste Management Agency will generate large quantities of excavated soil (mainly as Callovo-Oxfordian argillite). The re-use of excavated soils is a recent question. There is a lack in the literature concerning the recycling of such materials. Therefore, this paper aims to investigate the possibility of using Callovo-Oxfordian argillite (COx argillite from the French URL) as a raw material for Portland cement clinker production. COx argillite was first characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF) then a Portland cement clinker was synthesized at laboratory scale. The produced clinker was characterized to verify the chemical and mineralogical composition. After adding gypsum, the reactivity of the resulting cement was assessed by setting time and isothermal calorimetry measurements. The compressive strength was assessed on standard mortar prisms at 1, 14 and 28 days. The results show that a Portland cement clinker containing 64% C₃S, 14% C₂S, 10% C₄AF, 7% C₃A and 1% CaO can be produced when 22.24% of raw meal was substituted by the COx argillite. The setting time and isothermal calorimetry results show that the produced cement shows an equivalent reactivity to conventional ordinary Portland cement. The compressive strength at 28 days is 56 MPa, showing that the produced cement can be considered as CEM I 52.5 N Portland cement.

Keywords: clinker; argillite; circular economy; hydration; recycling



Citation: Kleib, J.; Amar, M.; Aouad, G.; Bourbon, X.; Benzerzour, M.; Abriak, N.-E. The Use of Callovo-Oxfordian Argillite as a Raw Material for Portland Cement Clinker Production. *Buildings* **2022**, *12*, 1421. <https://doi.org/10.3390/buildings12091421>

Academic Editor: Haoxin Li

Received: 12 August 2022

Accepted: 8 September 2022

Published: 10 September 2022

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1. Introduction

The management of excavated soils becomes one of the major issues that the environment and construction sector have to face. Excavated soils and rock are often obtained through activities of mining, tunneling or foundation works. When these materials are not beneficially reused, they are often stored or dumped and cause far-reaching environmental harm [1,2]. Recent studies pointed out the interest in using excavated soil as secondary building material, seeking therefore economic and environmental benefits [2–4].

Nowadays, the using of partial replacement of raw materials in the clinker raw meal by wastes or by-products is gaining a lot of attention [5,6]. This action allows, on one hand to preserve natural resources, which presents a challenge for the cement industry, and on another hand to recover wastes and industrial by-products. Decades ago, it was the case with blast furnace slag; today the use of by products is greater and comes not only from the industry [7]. Waste recovery makes it possible to participate to the circular economy and to meet the global requirements for reducing the carbon footprint as agreed in the COP22, Kyoto, and according to the IEA/WBCSD Roadmap [8–12]. Different types of wastes have been studied in the literature in order to produce cement, and mainly

OPC cement. Aouad et al. used sediment from the north of France to produce OPC cement [13]. Their results showed that 39% of sediment can be added to the raw meal, and the compressive strength of sediment-based cement is equivalent to the reference cement (without sediment) and exceeds it by 20% in the long term. Sediments, coming from different French regions were also tested by Faure et al. [14] and their study showed that 10–15 wt% of the raw meal can be replaced by various types of sediment without significantly affecting the clinker characteristics. The recycled concrete aggregate and fine fractions were used by Diliberto et al. [15] in order to produce OPC cement. Tsakiridis et al. [16] added 10.5% of steel slag in the OPC clinker raw meal without affecting negatively the quality of the cement.

The French National Radioactive Waste Management Agency, Andra, is responsible for the long-term management of radioactive wastes produced in France. Cigeo (Industrial Centre for Geological Disposal) is one of Andra's projects for the disposal of high-level (HLW) and intermediate level long-lived (IL-LLW) radioactive wastes. The Cigeo project concerns the radioactive waste disposal planned at 500 m below ground level in the geological layer formed by the Callovo-Oxfordian (COx) argillite [17,18].

The characterizations of this clay layer have shown that the argillite exhibits a homogeneity and a geological stability as well as physical properties (especially a low permeability) that allow this layer to host radioactive waste disposal [19,20]. This disposal will lead to the generation of millions of cubic meters of excavated COx argillite. The storage of such a volume during the operating period and the remaining volume after closure is a key issue. Therefore, the re-use of the excavated COx clay has become a goal in order to fix the in situ storage problem. Gharzouni et al. investigated the possibility of producing alkali-activated materials/geopolymers based on COx argillite [19]. Different thermal treatments were applied to COx argillite such as traditional calcination at different temperatures and flash calcination. Dupuy et al. [21], used also COx argillite to produce alkali-activated materials with a pH close to 11 and presenting a wide range of setting time up to 24 h.

The characterization of COx argillite realized in different studies shows the presence of three main components: clay, calcite and quartz [17,22–25]. These phases are essential to produce clinker in the cement industry [13,26,27]. The main objective of this paper is to investigate the possibility of using COx argillite as part of the meal blend to produce ordinary Portland cement. Therefore, COx argillite is incorporated to the raw meal. The produced clinker is characterized by X-ray diffraction and X-ray fluorescence to verify its chemical and mineralogical composition. The compressive strength and reactivity of the cement made with COx argillite are investigated on mortar and cement paste, respectively.

2. Materials and Methods

2.1. Materials

The raw materials used in this study are pure CaCO_3 , Fe_2O_3 and SiO_2 , in addition to the Callovo-Oxfordian argillite. Prior to characterization and use, the COx argillite is dried, crushed and ground with a cross beater mill SK300, down to a fineness of less than 200 μm .

The reference cement used is the ordinary Portland cement CEM I 52.5 N produced at industrial scale by EQIOM. It is a cement specified in European standard NF EN 196-1 [28] for general construction use. The physical, mineralogical and chemical characteristics of this cement are presented in Tables 1–3, respectively.

Table 1. Physical properties of CEM I 52.5 N cement.

Material	Density (g/cm^3)	Blaine Specific Surface (cm^2/g)	BET Specific Surface (cm^2/g)	LOI 950 °C (wt%)	D10 (μm)
OPC	3.15	3720	9800	1.91	1.31

Table 2. Mineral phases of CEM I 52.5 N cement.

Method	Clinker	C ₃ S (wt%)	C ₂ S (wt%)	C ₃ A (wt%)	C ₄ AF (wt%)	CaO Free (wt%)
Schlafer–Bukolowki method—Bogue formula	OPC	61.63	15.76	9.14	9.18	1.60
Rietveld method	OPC	64.87	12.47	8.83	9.04	1.19

Table 3. Chemical composition of CEM I 52.5 N cement.

Composition (%)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	Na ₂ O	K ₂ O	MgO	ZnO	P ₂ O ₅	LOI (950 °C)	Total
OPC	63.75	19.95	5.31	2.98	3.03	0.55	0.93	0.86	-	-	1.9	99.99

2.2. Clinker Synthesis at Laboratory Scale

The theoretical composition of the targeted clinker (COx clinker) is represented in Table 4.

Table 4. Theoretical mineralogical composition for the COx clinker.

Phases	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO
Percentages	64	18	10	7	1

In order to reach the targeted composition in Table 4, a theoretical oxide composition was calculated (see Table 5).

Table 5. Theoretical oxide composition for the COx clinker.

Oxide	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
Percentages	68.86	23.12	4.74	3.29

To reach such a composition, a backward calculation is performed to calculate the weight ratio of each raw material in the meal. The raw materials, CaCO₃, Fe₂O₃, SiO₂ and COx argillite are mixed together through a wet process to facilitate the homogenization of the raw meal. Then the raw meal is dried at 105 °C. Pellets are made and fired up to 1450 °C in a static furnace. After 15 min at the clinkering temperature, the clinker is cooled in the furnace to room temperature (Figure 1). The obtained clinker is ground using a vibratory disc mill RS 200 Retsch to a specific area of about 4300 cm²/g (in accordance to the Blaine air permeability method mentioned in the European standard NF EN 196-6 [29]).

To produce cement, gypsum is added with an SO₃/Al₂O₃ ratio of 0.6 using the Equation (1) [30]:

$$\text{Amount of gypsum used} = \text{Al}_2\text{O}_3 \text{ content} \times [0.6/101.96] \times [80.06/0.461] \quad (1)$$

where 101.96 = molar mass of Al₂O₃; 80.06 = molar mass of SO₃; 0.461 = molar mass ratio of SO₃/natural gypsum used (for pure gypsum 80.06/172.16 is 0.461).

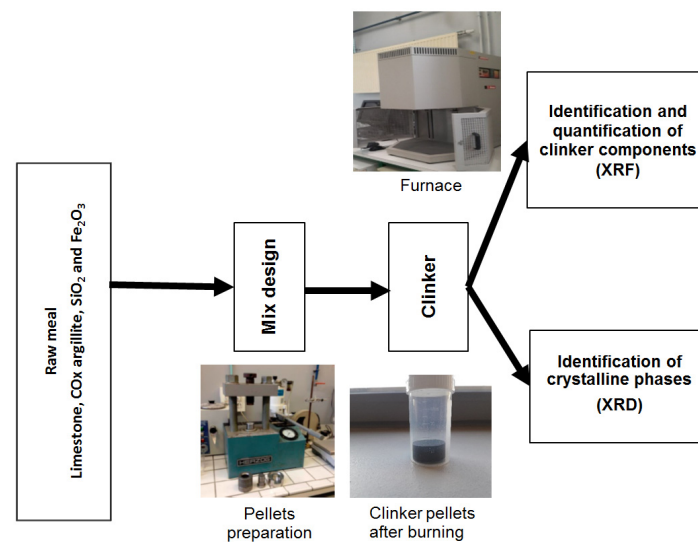


Figure 1. Clinker preparation procedure.

2.3. Characterization Methods

The particle size distributions were determined using a COULTER laser granulometry type LS 13320.

Thermogravimetric analysis (TG/DTG) was performed using Netzsch STA 409. The thermal analysis was performed in a nitrogen gas atmosphere, within a temperature range from 40 °C to 1100 °C. The program was divided into 3 segments: a linear of 2 °C/min between 40 and 105 °C, an isothermal of 30 min at 105 °C and a linear of 3 °C/min between 105 and 1100 °C.

The chemical composition was determined by X-ray fluorescence (XRF) using a S4-Pioneer equipped with 4 KW generator and Rh anode.

The mineralogical analysis of argillite and the produced clinker was determined by X-ray diffraction (XRD) using a Bruker D2 apparatus with Cu K α radiation. The X-ray patterns were acquired in the 2 θ (10–80°) with a step size of 0.02° and 1 s per step. TOPAS software was used to conduct the Rietveld analysis in order to quantify the crystalline phases.

The reactivity of COx cement paste was followed by isothermal heat flow calorimetry measurements performed at 20 °C using a home-made calorimeter with flowmeters that allowed the calorimeter to equilibrate in less than 5 min [31]. A water/cement ratio of 0.5 was applied, and all the materials were kept at 20 °C before mixing in order to eliminate errors related to the temperature variation during testing.

The compressive strength tests were carried out at 1, 14 and 28 days on mortar prisms 40*40*160 mm, according to the European standard AFNOR NF EN 196-1 using a standard sand [28]. These tests were carried out using an Instron 5500R-4206-006 press with a loading capacity of 1500 KN. The strain rate applied was 144 KN/min, as required by the European standard AFNOR NF EN 196-1 [28].

The VICATRONIC I06 091 device was used to determine the initial setting time in conformity with the NF EN 196-3 standard.

3. Results and Discussions

3.1. COx Argillite Characterization

Figure 2 represents the particle size distribution of the COx argillite after grinding. The results show that 90% of the particles have a diameter < 60 μ m. Therefore, the particle size of COx is adapted to be used as raw material for cement production that should be less than 200 μ m according to the literature [32].

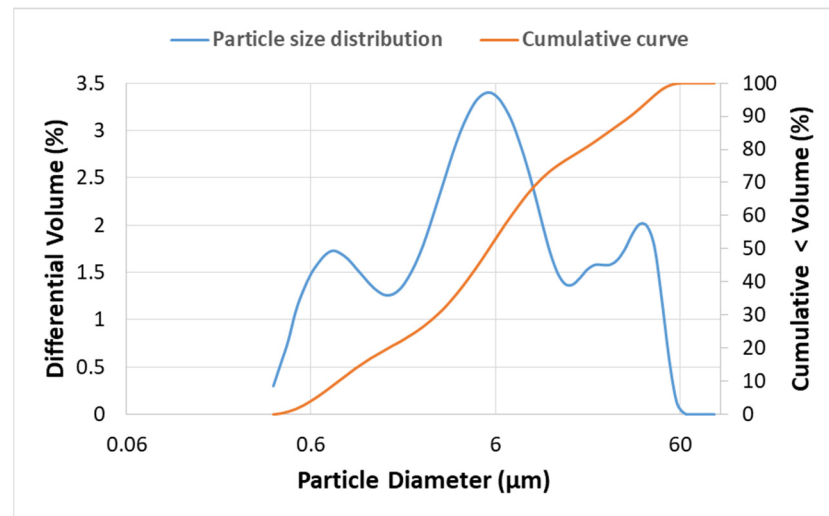


Figure 2. Particle size distribution of COx argillite.

The COx argillite XRD result (Figure 3) shows the presence mainly of calcite and quartz in addition to muscovite, kaolinite and pyrite as crystalline phases. These results are in accordance with older studies conducted on COx argillite in the literature [17,22–25]. This mineralogical composition confirms that COx argillite is a candidate raw material to produce Portland cement clinker equivalent to many other raw materials in use [5].

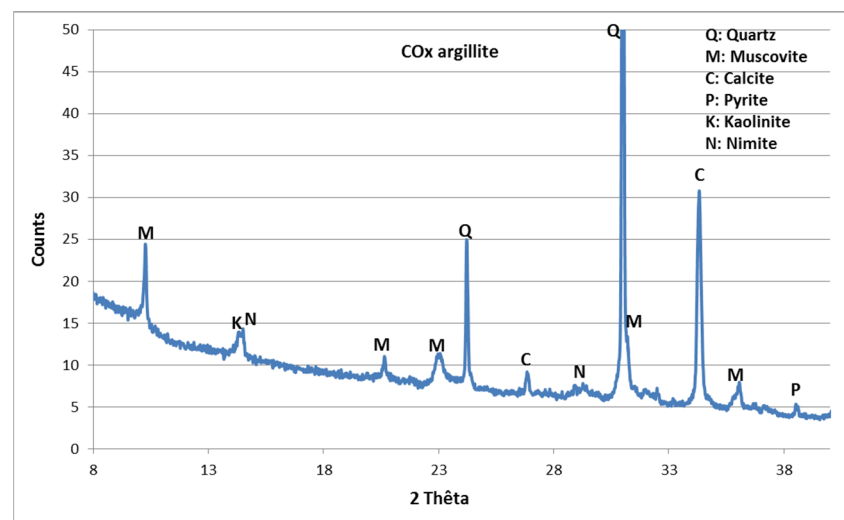


Figure 3. X-ray pattern of COx argillite.

The TG/DTG analysis of the COx argillite represented in Figure 4 shows the formation of three main peaks at:

- 100 °C corresponding to free water evaporation,
- 300–500 °C corresponding to decomposition of the organic matter in addition to muscovite, kaolinite and pyrite,
- 750 °C corresponding to the decarbonation of calcite.

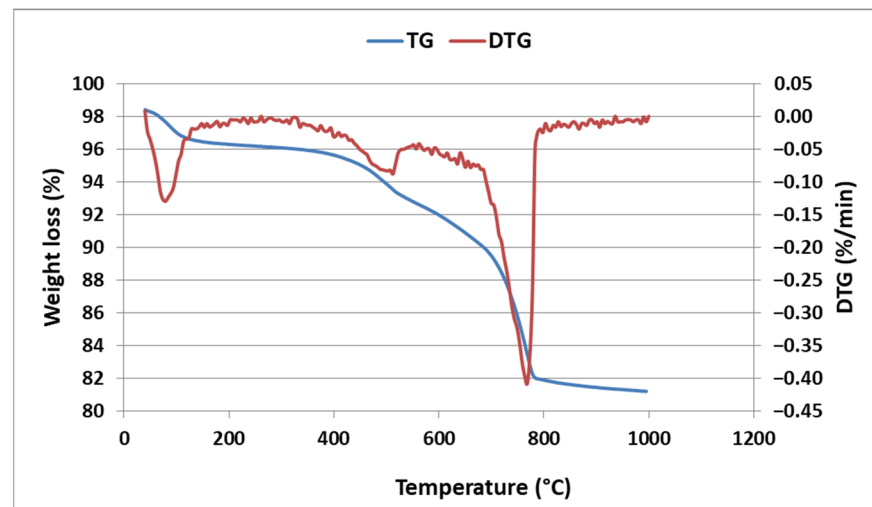


Figure 4. TG/DTG analysis of COx argillite.

Table 6 presents the results of the chemical characterization conducted by XRF of COx argillite. These results show that the four main elements needed for Portland clinker manufacturing (Ca, Si, Al and Fe) are present in the COx argillite. Therefore, COx argillite could act as an alternative to limestone and clay in the manufacturing of Portland clinker.

Table 6. Chemical composition of COx argillite.

Oxide	LOI 950 °C	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	MgO	P ₂ O ₅	SO ₃	K ₂ O	TiO ₂
Percentage	16.2	12.0	12.9	4.7	46.8	2.3	0.2	0.2	3.4	0.7

The results also showed that argillite, unlike another secondary raw material such as sediment [33], does not contain trace elements. Otherwise, the presence of some trace elements, such as zinc, will disadvantage the synthesis of Portland cement and orient the use towards more specific cement [31].

3.2. Raw Meal Design and Characterization

To calculate the appropriate amount of COx argillite that could be incorporated in the meal to substitute the raw materials and to reach the mineralogical composition presented in Table 4, the solver option in Excel is used [15]. The calculation reveals that a maximum of 22.24% of COx argillite can be incorporated in the raw meal. If less than this maximum amount is used, an additional amount of Al₂O₃ must be used, in the aim of reaching the raw meal composition.

The theoretical raw meal composition for the COx clinker is represented in Table 7.

Table 7. Theoretical composition for the raw meal.

Component	CaCO ₃	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	COx Argillite
COx Clinker	72.97	3.79	0.00	1.00	22.24

Before sintering, the particle size distribution (Figure 5) was verified. As shown in Figure 5 the maximal particle size is 69 µm, indicating that the raw meal fineness is in the appropriate range (<200 µm) [32].

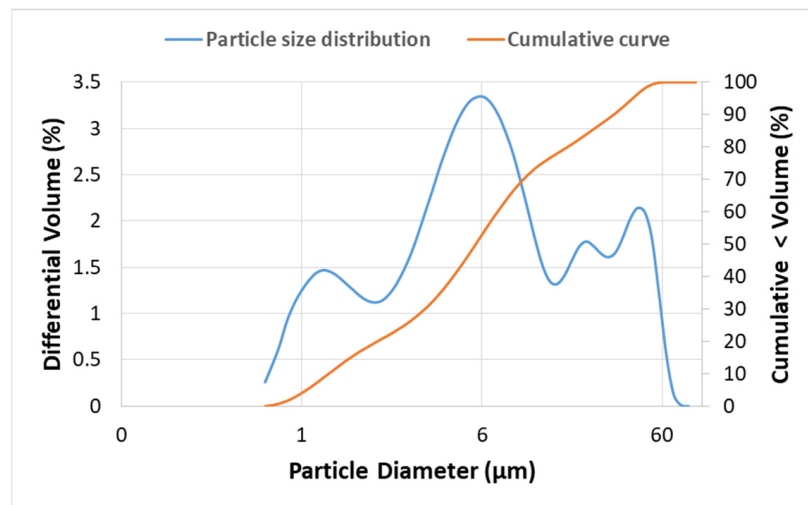


Figure 5. Particle size distribution of COx raw meal.

In addition, the three moduli used in the cement industry which corresponds to the ratio between the main oxides are calculated. These moduli correspond to the lime saturation factor (LSF), silica modulus (SM) and alumina modulus (AM). The three moduli are given in the equations (Equations (2)–(4)) below:

$$\text{LSF} = \frac{\% \text{CaO}}{2.8 \times \% \text{SiO}_2 + 1.20 \times \% \text{Al}_2\text{O}_3 + 0.65 \times \% \text{Fe}_2\text{O}_3} \quad (2)$$

$$\text{SM} = \frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3} \quad (3)$$

$$\text{AM} = \frac{\% \text{Al}_2\text{O}_3}{\% \text{Fe}_2\text{O}_3} \quad (4)$$

The value of LSF is usually between 92 and 102, 2 and 3 for SM and 1 and 4 for AM [34].

Table 8 shows that the experimental and theoretical moduli for COx clinker are equivalent.

Table 8. Experimental and theoretical cementitious modulus for COx clinker.

	LSF	SM	AM
Experimental values	0.97	2.95	1.44
Theoretical values	0.95	2.88	1.44

3.3. Clinker Characterization

After burning, the mineralogical analysis of the produced clinker was verified by XRD analysis (Figure 6). The results show that the main phases of Portland clinker— C_3S , C_2S , C_4AF and C_3A —are obtained in addition to free lime CaO . No secondary phases are detected, indicating that the raw meal composition as well as the clinkering process are adapted.

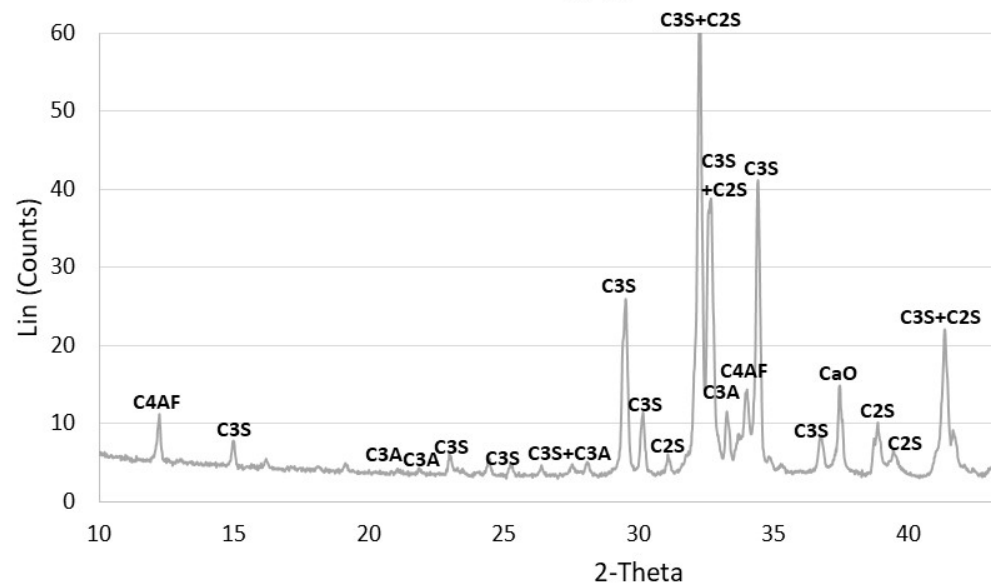


Figure 6. XRD analysis for the COx clinker.

In order to quantify the crystalline phases in the COx clinker, Rietveld analysis was conducted using TOPAS software (Table 9). Regarding the mineralogical composition, the Rietveld results show that COx clinker could be used to produce a sulfate resisting Portland cement (C_3A content less than 3 wt%). [35].

Table 9. Rietveld quantification for COx clinker.

Crystalline Phases	C_3S	C_2S	C_4AF	C_3A	C
COx clinker	61.5	21.2	10.9	2.9	2.9

3.4. Isothermal Heat-Flow Calorimetry of COx Cement Paste

The hydration of the cement paste is an exothermic process, thus the heat release during hydration can be correlated with hydration kinetics. Figure 7 shows the calorimetric curve for COx cement paste. The shape of the curve is similar for an ordinary Portland cement presented in previous studies [13,36–38]. A first peak in phase I is formed after water addition and the anhydrous grain dissolution. In phase II, an induction period of 2 h with low thermal activity is observed. Then acceleration in the calcium silicates and aluminates hydration occurs in phase III and a second exothermic peak is formed after 8 h 45 min. In phase IV, the sulfate is depleted and a slow in the hydration kinetics of calcium silicates and aluminates is observed. In phase IV, a shoulder appears corresponding to the gypsum depletion (at 11 h 30 min). Figure 7 also includes the total heat release in J/g. COx cement paste shows a total heat release of 186 J/g after 24 h of hydration, which correspond to a low heat release cement (<270 J/g) according to the European standard NF EN 197-1 [35], that could be used for massive structures.

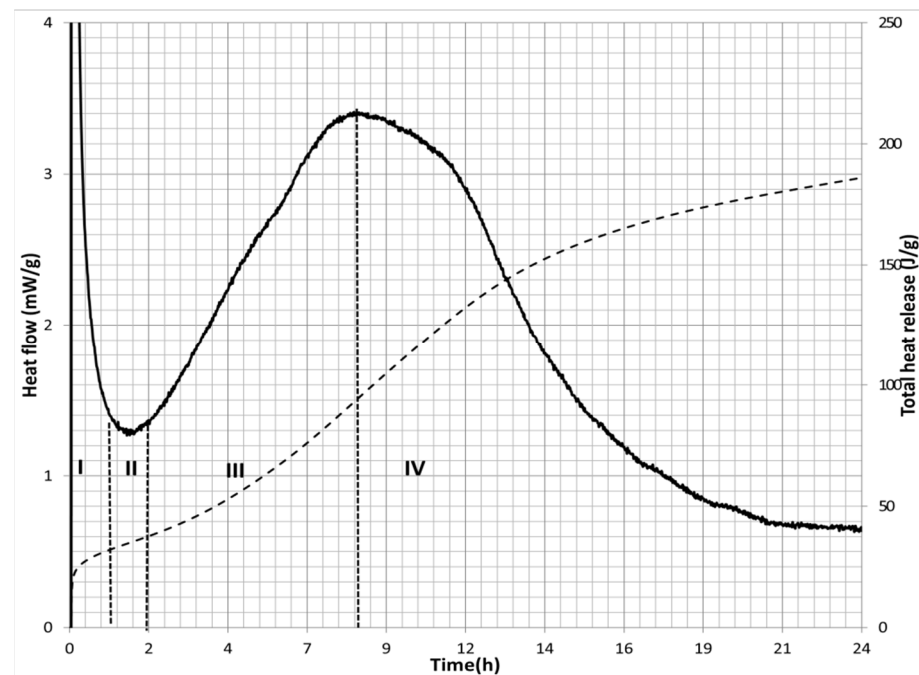


Figure 7. Heat flow release for COx cement paste.

3.5. Setting Time of the COx Cement Mortar

The aim of setting time measurements was to determine the theoretical time needed for the hydration and mechanical properties development. The principle consists in monitoring the depth vs. time to sink the needle into the mixture to a depth of 34 ± 1 mm. The results are presented in Figure 8. The formulations include reference mortar with the commercial OPC (CEM I 52.5) and COx cement.

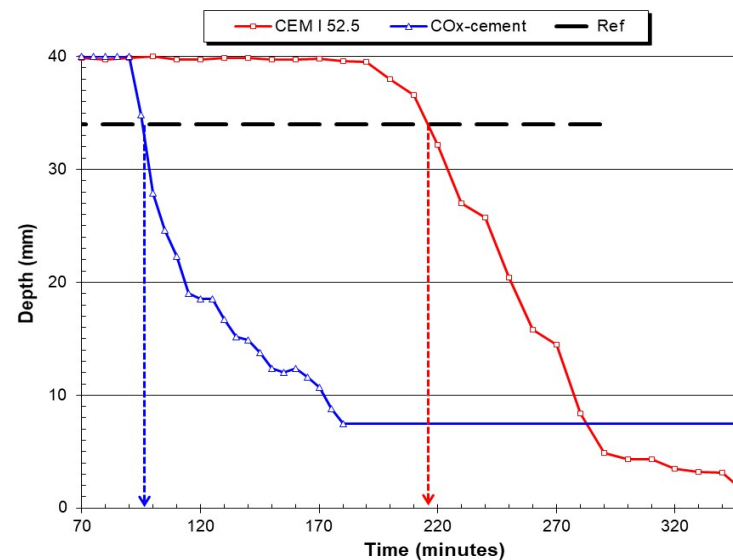


Figure 8. Setting time of the COx cement mortar.

The initial setting time is 96 min for the COx cement and 216 min for the reference CEM I 52.5. This difference is mainly due to the difference in the crystallinity of the cement phases produced in a static kiln (for COx cement) compared to that produced in an industrial rotary kiln (commercial cement CEM I 52.5 N), in addition to the difference in the cooling rate applied [39] and/or the cement fineness.

The same result was obtained by Faure et al. [14] when comparing CEM I 52.5 N cement and a laboratory produced clinker containing 11.4% sediment from the Alps.

It is worth noting that, even though the initial setting time of COx cement is lower than the reference cement CEM I 52.5 N, it is still satisfying the condition of a 52.5 strength class according to the standard NF EN 197-1 (>45 min) [35].

3.6. Compressive Strength of the COx Cement Mortar

The compressive strengths of the produced clinker were tested by measuring the compressive strength on COx cement mortar prisms at 1, 14 and 28 days (Figure 9) according to the AFNOR NF EN 196-1 standard. The compressive strength measured on COx cement mortars were compared to the one made with commercial Portland cement CEM I 52.5 N.

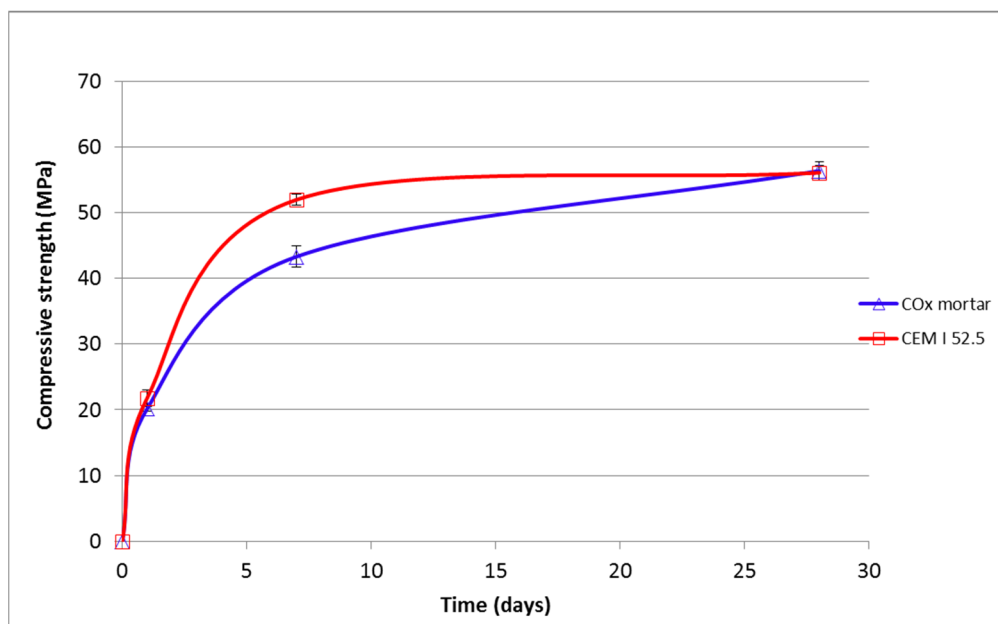


Figure 9. Compressive strength of COx cement mortar.

The compressive strength of COx cement mortar is equal to 20.2, 43.3 and 56.4 MPa at 1, 7 and 28 days, respectively. These values are almost the same as those of commercial cement that has a compressive strength of (21.8, 52.0 and 56.1 MPa at 1, 7 and 28 days, respectively). Only a difference can be noticed at 7 days between the two mortars however the trends of the compressive strength curves are similar. The same result was obtained by Her et al. [39] when comparing the reference cement paste to cement pastes made from clinkers containing recycled pulverized oyster and scallop shell. The authors found that at 3 days, the strength values were lower than reference OPC cement paste but the trends of the compressive strength curves were similar.

The results show that adding 22.4% of argillite in the raw meal could be accomplished without affecting the compressive strength long term. The same results were obtained by Tsakiridis et al. [16] showing that at 28 days, steel slagbased cement had the same compressive strength as the reference cement.

4. Conclusions

Callovo-Oxfordian Argillite provided by Andra was used in this study to be used in a raw meal for the production of an Ordinary Portland Cement clinker. Therefore, after COx argillite characterization, Portland clinker was produced at laboratory scale with the maximum substitution of raw materials by COx argillite. Then, the mineralogy, hydration and mechanical performance of the produced clinker were studied. The main conclusions of this work can be summarized as follow:

- COx argillite contains the main oxides required for a Portland clinker production: SiO_2 , Al_2O_3 , CaO and Fe_2O_3 .
- Up to 22.4% of COx argillite could be used in clinker raw meal, without any other addition to adjust, especially, the Al content.
- The COx argillite-based clinker produced contains the main phases of an ordinary Portland cement without having any secondary phase: C_2S , C_3S , C_3A , C_4AF .
- The hydration of COx cement presents a heat evolution comparable to that of Portland cement, even if the setting seems faster.
- The compressive strength of COx cement mortar at 28 days is equivalent to the one of CEM I 52.5 N commercial cement, with a compressive strength measured on normalized mortar samples, close to 56 MPa after 28 days.

Finally, it can be concluded that Callovo-Oxfordian argillite can be used as a raw material in the process of clinker production without affecting the cement properties. Moreover, this recycling reduces the use of natural resources and contributes to the circular economy and provides environmental benefits. Further studies should focus on the durability of the COx argillite-based cement and on the sintering process to get closer to the real industrial manufacturing.

Author Contributions: Conceptualization, X.B.; funding acquisition, G.A., X.B. and M.B.; investigation, J.K. and M.A.; methodology, J.K., M.A., G.A., X.B. and M.B.; project administration, N.-E.A.; resources, N.-E.A.; supervision, G.A. and M.B.; validation, G.A., X.B., M.B. and N.-E.A.; visualization, J.K. and M.A.; writing—original draft, J.K.; writing—review & editing, M.A., G.A., X.B., M.B. and N.-E.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the French National Radioactive Waste Management Agency (Andra) in collaboration with IMT Nord Europe laboratories.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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