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Manufacturing equivalent Clinker by indirect mechanosynthesis process

Othmane Bouchenafa *1, Rabah Hamzaoui*1, Louiza Azem1, Abdelkrim Bennabi 1, Johan Colin1

ABSTRACT

This study is focused to the proposition of new cement manufacturing process. It is widely known that the cement production is responsible for a significant CO_2 release each year (approximatively 4 billon ton). So, it is became necessary to find another cement manufacturing process with a minimum CO_2 emission.

The aim of this work is to manufacture equivalent clinker by indirect mechanosynthesis process. It consists to combine between mechanical activation of the raw materials (mixture of limestone and clay) and heat treatment less than 900 °C.

The equivalent clinker obtained by this method shows the presence of the alite (tricalcim silicate) C3S and belite (dicalcium silicate) C_2S and Tricalcium aluminate C_3A. CO_2 emission by this technique is estimated by 0.3 Ton for 1 Ton of equivalent clinker.

Keywords: Equivalent Clinker, mechanosynthesis, cement, low CO_2 emission.

1| INTRODUCTION

The demand for cement is growing steadily. Significant growth is occurring in countries such as China and India, as well as in areas such as the Middle East and North Africa. [1]
The global cement production will keep rising due to the demographic expansion and the infrastructure demand related this expansion. Global cement production is set to grow by 12-23% by 2050 from the current level. [2]
Some estimates put the cement industry total as high as 5% of total global anthropogenic CO_2 emissions. [3]
Many solutions have been studied and used to reduce these CO_2 emissions, as the clinker substitution, Carbone capitation and storage (CCS), use of alternative fuels [1].

The cement manufacturing process has been known since the beginning of the 19th century. [4]
The Portland cement is produced by milling a mixture of calcareous materials (limestone) and argillaceous materials (clay), and materials containing silica and iron oxide, burning them at a temperature between 1300 and 1500°C, and a fine milling to produce clinker.
In order to obtain cement, only gypsum, water and grinding aids are allowed to add. [5]

The objective of this study is to improve the process of the clinkerisation by introducing the mechanosynthesis (indirect mechanosynthesis) and thus reducing CO2 emissions.
The indirect mechanosynthesis is consisting on coupling a mechanical activation with short duration and adding another process for obtaining the final product. In our case, we have used a heat treatment. The combination between a shot milling duration and a heat treatment is also called "*Mechanically Activated Annealing process*" [6]
The mechanosynthesis is a high-energy ball milling technique wherein the powder particles are subjected to mechanical energy transfer inducing plastic deformation both equilibrium and metastable phases can be synthesized by this process; in addition, there is a reduction of the particle sizes with modification of the shape and reduction of the grain sizes. During the process, the powder particles are regularly flattened, cold-welded, fractured and rewelded. [6, 7]
Mechanosynthesis provides a way to mix and combine solids ranging from the scale of a powder particle to the micrometric scale, while the crystallite (grains) will shrink to a nanoscale size and will provide nanostructured materials. [7,8]
In the case of the mixing of different powders and elements, it is possible to produce during the milling process amorphous alloys, nanocrystalline, nanocomposites, solid solutions, intermetallic and materials with non-equilibrium structures at room temperature [6-8]

Hamzaoui et al. [9] used a planetary ball mill to activate fly ash at different milling times 1h, 6h, and 9h. They observed that the fly ash particle size reduction was optimal at 1h where, for 50% CEMI substitution by milled fly ashes, the compressive strength gain of cement-fly ashes pastes increased after 28 curing days. In addition, they found that the maximum compressive strength gain reached an improvement of +23.9% with fly ashes milled for 3 h after 90 curing days.
Bouaziz et al. [10] used also the mechanosynthesis for the slag activation for 1h to 9h of milling. The particle size reduction was optimal for 3h of milling. For 45% of CEM-I replacement, the authors shown that the optimal compressive strength gain corresponds to 3 h of milling and reached +8.8% for 120 curing days.

In order to obtain an equivalent clinker, we have used a mix of limestone and clay and used an indirect mechanosynthesis.

2| Materials and methods

2.1 Raw materials, clinker and cement (OPC)

2.1.1 Limestone

The limestone used for this study was provides from OMYA. It is constituted of >97% of calcium carbonate ($CaCO_3$) in calcite structure.

2.1.2 Clay

The clay used in this work is Proclay kaolinite provided from Beaujard–Poigny site (France). It contains Kaolinite and quartz.

2.1.3 Conventional clinker.

In our study, for comparison to the equivalent clinker, we have used clinker provided from Vicat Company.

The chemical compositions of the raw materials, clinker and ordinary Portland cement are conducted by X-ray fluorescence; the results are summarized in table 1.

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(1) Université Paris-Est, Institut de Recherche en Constructibilité, ESTP, 28 avenue du Président Wilson, 94234 Cachan, France.
* Corresponding author(s): obouchenafa@estp-paris.eu, rhamzaoui@estp-paris.eu

Table 1 | Chemical composition of the raw materials

Oxide	Limestone	Kaolinite	Clinker
CaO	97.78	0.72	71.85
SiO_2	0.97	67.70	14.66
Al_2O_3		23.62	3.02
FeO_3	0.22	2.04	3.97
Na_2O			
SO_3	0.14	0.59	2.26
MnO	0.08		
SrO	0.21		0.28
TiO_2		3.52	0.27
P_2O_5		0.72	0.24
MgO			1.8
K_2O	0.18		1.3
Others	0.42	1.09	0.35

2.2 Methods

2.2.1 Equivalent clinker process

For the production of clinker two processes are used: mechanosynthesis (mechanical activation) and heat treatment

2.2.1.1 Mechanical activation (mechanosynthesis)

Mechanical activation is carried out by planetary ball miller (RETSCH PM 400). This device is composed of four vials mounted on a planar disc. With the rotation of the disc, the vials move in a circular and in opposite direction compared to the disc rotation. The ball-to-powder weight ratio is 4. For the preparation of the equivalent clinker, we put in the vial 80% of limestone (160 g) and 20% of clay (40g).
To avoid the contamination, the vials are sealed. The rotation speeds of the disc and the vials are $\Omega = 400$ rpm and $\omega = 800$ rpm, respectively. Different milling durations are used from 15 minutes to 60min.
Thirty-millimeter diameter steel balls and 500 ml volume steel vials are used.

2.1.1.2 Heat treatment

Different temperatures are used from 400° to 900°C for 1 hour using an Electric industrial oven (Kaesermann & Sperisen).

2.2.2 Characterization of powders

The chemical composition of all the products is obtained by an elemental analysis conducted with X-ray fluorescence spectroscopy and carried out using S2 RANGER instrument from Bruker.

X-ray investigation is performed using Bruker D2 phaser diffractometer with a continuous scanning mode and Cu Kα radiation ($\lambda = 0.1541$ nm). The lines are measured in the 2θ range (5–70) ° by an increment of 0.02° for 0.15 s. The software used for building the X-ray diffraction diagrams is DIFFRAC.EVA with ICDD PDF2. In order to improve the relevance of the time evolutions of X-ray diffraction diagrams, X-ray investigation is conduced according to different milling durations from the same vial sampling.

IR spectroscopy is performed by a Thermo Scientific Nicolet IS10 instrument equipped with Smart iTR (with Diamond Plate) accessory. With this ATR (Attenuated Total Reflectance) accessory, the IR spectroscopy is able to analyze solids, liquids, pastes and gels. The results are analyzed with Omnic Software.

In order to have an idea about the fineness of the equivalent clinker, the specific surface area was determined by two methods, Blaine method (Air permeability) and the BET method (nitrogen adsorption).

Blain method is done by Blaine permeabilimeter with automatic time measurement according to EN 196-6 and ASTM C204 from Controlab.
The BET method is performed with the use of a Gemini VII 2390 instrument from Micrometrics. The Analyses is performed using a static volumetric technique in which the adsorptive flows into a tube containing the sample and into a balance tube simultaneously. The internal volume and the temperature surrounding both tubes is maintained in identical conditions. Helium gas is used to determine samples density.

3| Results and discussion

3.1 X-ray diffraction analysis

In this study, we have given the name Equi. Clinker A for the product of the indirect mechanosynthesis process after 15min of milling and 1hour of heat treatment. For the name of Equi. Clinker B concerning the product of 1 hour of milling and 1 hour of heat treatment.

The X-ray diffractions analysis of the conventional clinker and the two types of equivalent clinker produced are shown in Figure 1. The patterns give information about the impact of our process on the clinkerization of the mixture of limestone and the clay.

The X-ray pattern of the conventional clinker shows various structures as the di-calcium silicate (β-C_2S) Ca_2SiO_4 PDF# 00-001-1012, tri-calcium silicate (C_3S) Ca_3SiO_5 PDF# 00-055-0738, Calcium Aluminium oxide (C_3A) $Ca_3Al_2O_6$ PDF# 00-014-0693, Calcium Aluminum iron oxide PDF# 00-010-0032 Ca4 Al2 $Fe_2{}^{+3}O_{10}$ and Lime CaO.

We observe the presence of the Alite and belite the compounds that supposed to be in the clinker and responsible of the C-S-H and C-H production after cement hydration reactions. In addtion, there are few peaks of CaO (lime) which show that all lime has reacted for the Alite and the belite production.

Comparing to the pattern of the conventional clinker, we have found the same structures: the di-calcium silicate (β-C_2S), tri-calcium silicate (C_3S), Calcium Aluminium oxide (C_3A) and Lime CaO in the Equi. clinker A and B. We have observed the disappearance of several peaks of C_3S in the Equi. clinker A et B found in the conventional clinker at 30.303°, 38.853°, 56.560°, 60.085°, 63.975.° In addition we have found the existence of more Lime peaks in Equi Clinker A and B than in conventional clinker.

The presence of CaO may be due to the fact that this lime has not reacted with other elements such as silica or iron oxide.
From the two observations, we can say that the new clinkerization process is not as efficient as the classical

process and this proposed process should be more improved.

Some additional peaks of C_3A are found in the equi. clinker A and B at 17.236°, 19.161°. We observe also the peak C_3A at 26.675° is more intense in the two new clinkers that in the conventional one.

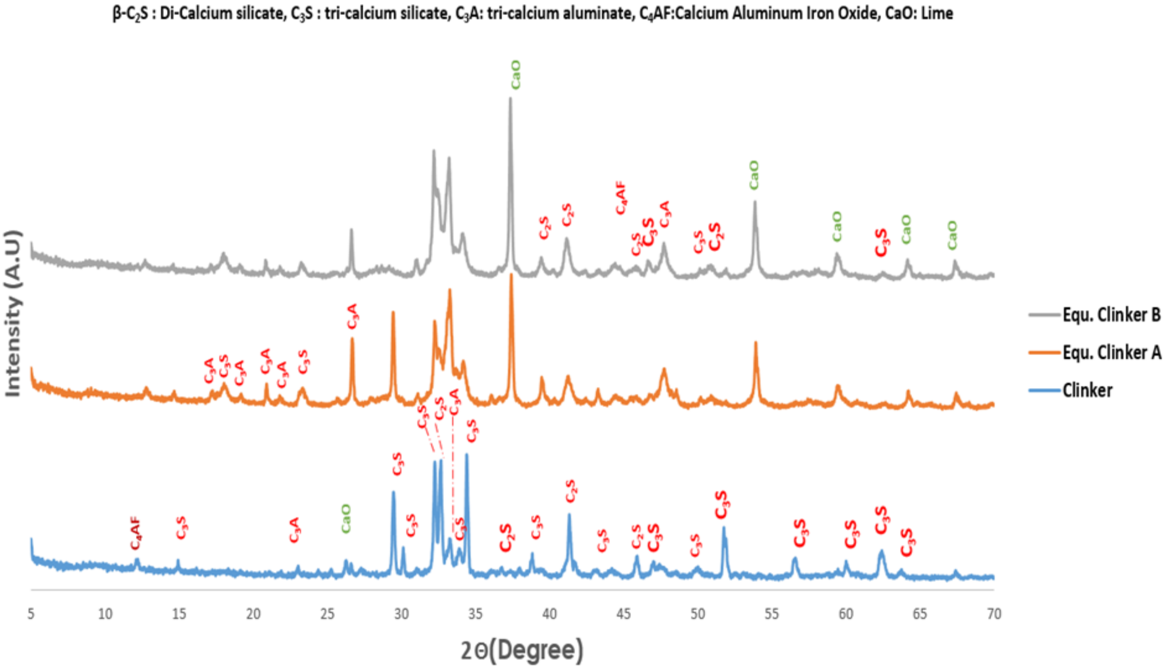
β-C_2S : Di-Calcium silicate, C_3S : tri-calcium silicate, C_3A: tri-calcium aluminate, C_4AF:Calcium Aluminum Iron Oxide, CaO: Lime

Fig.1 | XDR patterns of the conventional clinker and equivalent clinker A and B

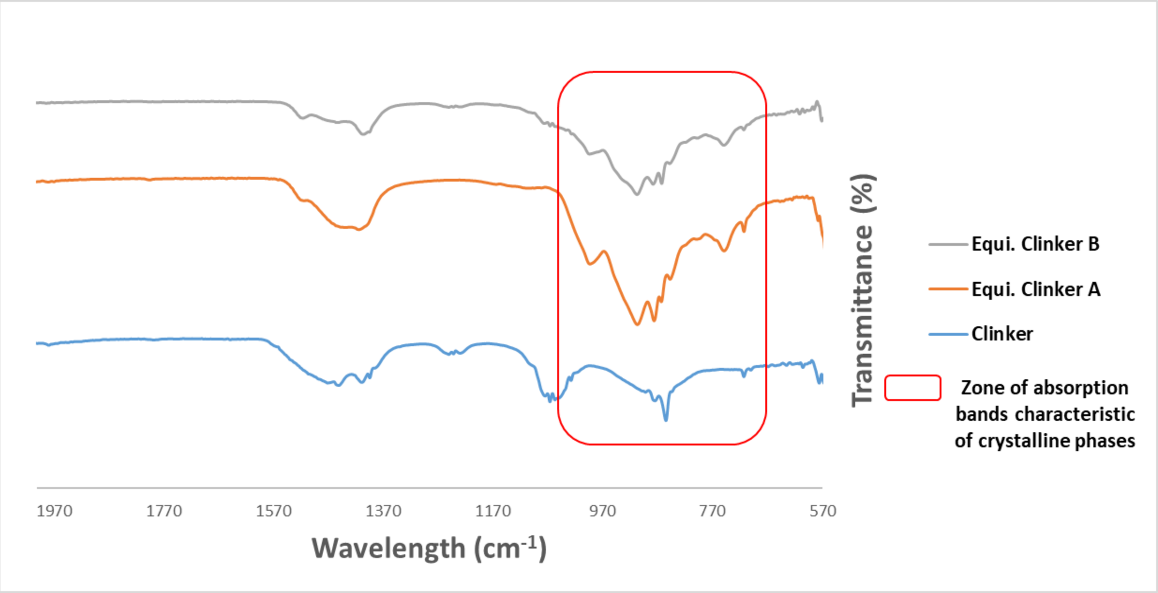

Fig.2 | Infrared spectra of the conventional clinker and the two equivalent clinker

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3.2 FTIR spectroscopy

Figure 2 presents FTIR spectra of equi. clinker A, B and conventional clinker. Assignment of related peak bands of sample is provided by the spectral search feature implemented in the Thermo Scientific Omnic series software.The search is performed with a sensitivity of 80%. Results are summarized in Table 2.

Table 2 | Assignment of FTIR peaks of clinkers using the Thermo-Scientific Omnic series software

Crystalline phases	Wavelength (cm^{-1})
ß-C_2S or C_3S (Si-O)	846, 912 ,992,1025
$CaCO_3$ (C-O)	712,876,
C_3A (Al-O)	861
C_3AF(Fe-O)	700

It is observed the presence of compounds as the ß-C_2S or C_3S by the absorption band Si-O at 992, 912 and 846 cm^{-1} for the two equivalent clinker A and B. The absorption band Si-O is identified at 1025 cm^{-1} for the conventional clinker [11,12]. FTIR data confirm the X-ray diffraction results.

The width band between 1360 and 1568 can be related to calcium carbonate (C-O). In addition, calcium carbonate (C-O) band is identified at 876 cm^{-1} (observed only in the 2 patterns of the two equivalent clinkers A and B) and 712 cm^{-1}(observed in the 3 patterns). For adsorption band (Al-O) observed at 861 cm^{-1} found in the two patterns of the equivalents clinker A and B can be related to C_3A.

In conventional clinker, we have identified band (Fe-O) at 700 cm^{-1} related to C_3AF [11, 12].

3.3 Specific surface area measurement by Blaine permeability and BET method.

In table 3, we give the results of the specific surface analysis done by the use of two different methods Blaine permeability and BET method

Generally, the specific surface of the commercially available cement is between 0.25 m² / g and 0.45 m² / g measured by Blaine method.
We observe from the results that the finesses of the two equivalent clinker A and B are higher than SSA of commercial cement. This high specific surface is due to the milling process. Mechanosynthesis provides a way of mixing and combining solids from the scale of a powder particle down to the micrometric scale, while the crystallite (grains) will scale down to a nanometric size and obtaining nanostructured materials [6, 9, 10].

In addition, we remark that the SSA of the equi. clinker A is high than that of equi. clinker B.

This difference between equi. clinker A and B can be explained by the agglomeration of particles due to the cold-welding during the milling process [9-10].

Table 3 | Specific surface by Blaine permeability and BET method of the equivalents clinker

	BET m²/g	Blaine m²/g
Equi. clinker A	8,4523	1,6213
Equi. clinker B	8,0991	0,7562

Conclusion

It is known that the environmental impact of cement production must be reduced. Our research work aims to reduce this impact and produce a cement with the same performance.
We observe from the structural study that the process of the indirect mechanosynthesis have been able to produce the crystalline phases wanted in the cement as the Alite C_3S and Belite C_2S. The extra amount of lime observed in the two equivalent clinkers is an issue that we must keep work on, and improve our process to increases the production of the C3S and C2S.
Further investigation on the microstructure and the mechanical performances of the equivalent clinker are in progress. Moreover, concerning the energy consumption and the CO2 emissions of the indirect mechanosynthesis process are under investigation.

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