

Physico-chemical and Mechanical Characterization of Artisanal Pseudo-cement Made in Madagascar

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Abstract

Cement is an essential material for construction, which is one of the world's leading industries and one of the largest employers. Of vital importance for housing and basic infrastructure, the cement industry plays a key role in economic development and poverty reduction in emerging and developing countries. Cement production remains fundamentally local, except for some fragmented markets such as those in sub-Saharan Africa. It requires heavy investments that require financing and long-term profitability that are difficult to access in developing countries. There is therefore a need to promote new local materials for the construction of basic infrastructures in Africa. The aim of the present research work is to elaborate pseudo-cement from michefer, pozzolan, kaolinitic clay, calcined chlorite. The purpose of this study is to attempt to partially substitute clinker in Portland cement with pozzolanic materials such as natural and artificial pozzolans. These mineral compounds are mainly composed of silica and alumina which has a certain chemical activity called "pozzolanic" that allows them to react with lime to form compounds similar to cement hydrates in order to reduce production costs while obtaining good mechanical performance. Laboratory analyses were carried out to determine their physico-chemical parameters, and then we made normal mortar specimens to optimize the pozzolan and lime content. On all crushing tests carried out, the proportions of optimal lime which give the maximum resistances are equal to 35% for pozzolan, 25% and 55% for michefer, 45% for kaolinitic clay and finally the optimal quantity of the mixture of calcined chlorite and rice husk ash is of ratio (70-30) to obtain good binder.

Keywords

Pseudo-Cement, Clinker, Pozzolans, Pozzolanicity, Michefer, Cement, Mortars

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1. Introduction

1.1. Background

The cement is made of clinker and grinded gypsum and produced from a burned mixture of limestone and clay in certain percentages [1]. Cement is the essential material for civil engineering construction works. Demand for cement has increased significantly as a result of rapid development in the construction sector worldwide, especially as a result of the construction boom in emerging countries [2]. Currently, cement manufacturing emits a significant amount of carbon dioxide (CO_2), which is well known for its impact on the greenhouse effect. Carbon dioxide comes from the transformation of the main raw material limestone [CaCO_3 , $\text{CaCO}_3 \cdot \text{MgCO}_3$ or $\text{CaMg}(\text{CO}_3)_2$] under the effect of temperature into lime (CaO) [3-4]. Over the last 190 years of existence of Portland cement the fundamentals of manufacturing chemistry have not undergone any significant changes, while considerable engineering advances have been made in the hardware and software of cement manufacture in order to achieve optimum cost and quality. Portland cement clinker can be described as a four-component system consisting of the four major oxides: CaO , SiO_2 , Al_2O_3 and Fe_2O_3 [5]. Several materials rich in oxides such as fly ash, blast furnace slags, pozzolans or volcanic ash can thus be used as substitute materials for Portland cement clinker. The aims of this study are to: (i) Valorise local materials by studying their physico-chemical properties, in order to achieve improvements in economy and sustainability; (ii) Attempt to partially substitute clinker in Portland cement with pozzolanic materials such as natural and artificial pozzolans; (iii) Lower the manufacturing costs of building materials and (iv) Increase the mechanical resistance of this binder.

1.2. Cement Manufacturing Process

Five main steps constitute the cement manufacturing process:

- 1) Extraction and pre-homogenization of raw materials;
- 2) Preparation of raw materials to form raw meal (or paste for wet process);

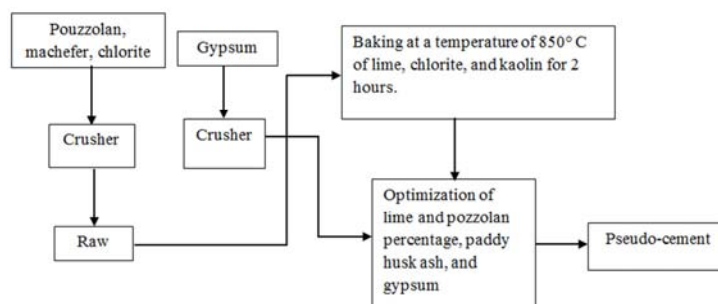


Figure 2. Different steps of pseudo-cement manufacturing process.

- 3) Cooking at 1450°C of the flour leading to the creation of the clinker;
- 4) Grinding clinker and additions to make cement, and;
- 5) Storage and shipment of cement.

These processes can be described by the following schematic diagram:

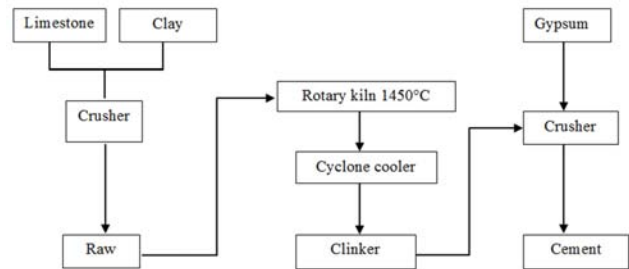


Figure 1. Different steps of cement manufacturing process.

In our study, the manufacturing principle is mainly based on cooking slaked lime to form calcium oxide. The calcination products are then incorporated with pozzolan, machefer, metakaolin, calcined chlorite, paddy husk ash and gypsum to form pseudo-cement (substitution of the clinker by our raw materials).

On the one hand, quicklime combines with alumina and iron oxide to form calcium aluminates and aluminoferrites, and on the other hand, with silica to form dicalcium silicate (belite).

The stages of manufacturing pseudo-cement are as follows:

- 1) Grinding and sieving with an $80\mu\text{m}$ sieve of pozzolan, machefer, gypsum
- 2) Baking at 850°C of lime, chlorite, kaolin for 2 hours.
- 3) Percentage optimization of lime and pozzolan, paddy husk ash, and gypsum
- 4) Optimization of the water content according to the compressive strength
- 5) Physical test (compressive and flexural strength test)

These processes can be described by the following schematic diagram:

2. Material and Methods

These are the standard methods and characterization materials used for chemical analysis of pozzolan, kaolinitic clay, gypsum, and chlorite. The same is true for tests to determine the mechanical performance of normal mortars.

2.1. Chemical Analysis

The chemical analysis of raw materials is an important step in the cement manufacturing process in order to determine the different chemical constituents, the major elements being SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO . The methods used are complexometric and gravimetric analysis.



Figure 3. Materials used for complexometry.

2.2. Analysis by X-ray Fluorescence Spectrometry

It is an elemental analysis technique that qualifies and quantifies the chemical elements present in the sample, its samples being put in the form of pellets or beads. It is based on the emission of a characteristic radiation by the atoms after ionization [6].



Figure 4. X-ray fluorescence spectrometer.

2.3. Preparation of Test Tubes

The purpose of this test is to determine the compressive and flexural strength of normal mortar specimens. An attempt will be made to determine the optimum amount of lime and pozzolan mix for mortar mixing.

The variable parameters in our experiments are:

- 1) The molar ratio of pozzolan/lime
- 2) The age of the sample: 2d, 7d, 28d
- 3) The quantity of water for the manufacture of the test tubes W/C.

The method consists of varying one parameter by setting the other parameters. The steps below are from the NF EN 196-1 standard and are valid for the search of the resistance to compression at 2, 7 and 28 days. The materials used are: mixer; impact device; mould of dimension 4*4*16 [cm]; crushing machine; stopwatch, scale, flat ruler, spatula. The manufacturing process for samples of normal mortar specimens is shown in the figure 5.

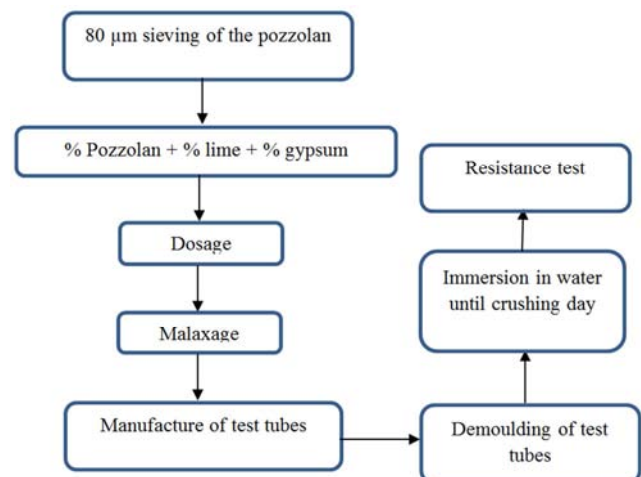


Figure 5. Manufacturing process of the test-tubes.

(i). *Malaxage* (step 1): The mixing process is as follows: weigh 225 g of water and pour it into the mixer container; weigh 450 g of cement and introduce it into the mixer container; start the mixer at its minimum speed for 30 seconds; introduce all the sand regularly for the next 30 seconds; turn the mixer to its maximum speed and continue mixing for a further 30 seconds; stop the mixer for 90 seconds during which time the bowl is lowered; scrape off with a rubber spatula all the mortar adhering to the walls and bottom of the bowl; raise the bowl and resume mixing at high speed for 60 seconds; and then turn the mixer on again [7-8].

A mortar is obtained and carried in the mould 4*4*16 on the impact device.



Figure 6. Mixer.

(ii). *Moulding and compaction* (step 2): The moulding and compacting of the specimens is carried out according to the following procedure: introduce the first layer of mortar into each of the 3 cells, using the large squeegee, taking support on the upper edge of the riser, pull once forwards and once backwards to remove the excess mortar; introduce the second layer and put the impact table back into operation for 60 strokes; disassemble. Then remove the excess mortar with the ruler, taking care not to rotate the mould; smooth the surface of the specimens using the same ruler, then clean the edge of the mould [8].

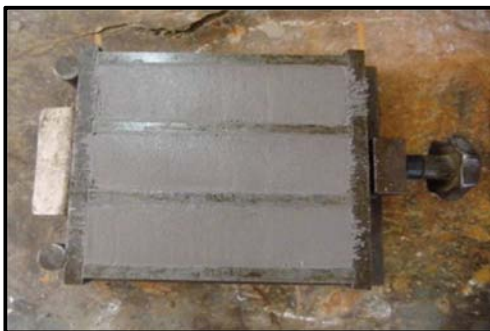


Figure 7. Mould 4*4*16 [cm].



Figure 8. Shock table.

(iii). *Demoulding and storage* (step 3): To carried out the process of demoulding and preservation of the specimens, place the mould in a "cold room" under a temperature of

20°C for 24 hours; remove the mould and immerse the specimens vertically in water at a temperature of 20°C; keep the specimens in the "cold room" according to the duration of the test to be carried out, i.e. 2 days and 28 days [8].



Figure 9. Conservation of test-tubes.

(iv) *The crushing* (step 4): Remove the specimens (after the required time) and allow them to dry for a certain period of time (a few hours); carry out the breaking test on the bending tester by cutting the specimen in half; the breaking load [N] is read directly from the tester. Multiply this value by 0.0025 to obtain the bending strength in [MPa] [8]. Crush each half of the test tube on the compression strength meter. Read the compressive strength directly in [MPa], and average the results of two half test tubes.



Figure 10. Measuring compressive strength.

2.4. Raw Materials

(i). Pozzolan

Pozzolan is a natural rock consisting of basaltic or similarly composed volcanic slag. It has an alveolar structure. The pozzolan is generally red or black, with all intermediate shades. Pozzolan is a light material with a density of less than 1, porous, abrasive, refractory and insulating [9]. They are natural products of volcanic origin composed essentially of

silica, alumina and ferric oxide; they are used in cement works for their pozzolanic properties, i.e. the ability to fix lime at room temperature and to form compounds with hydraulic properties. Pozzolanic materials have the characteristic of being able to react more or less quickly with lime. This results mainly in hydrated calcium silicates and/or hydrated calcium aluminates [10]. The pozzuolana used in this study comes from the Vakinakaratra region in the Betafo district (figure 11). It has black color. Betafo village (19° 50' 24" S, 46° 51' 18" E) is located 22 kilometers from the spa town of Antsirabe on the road to Morondava.

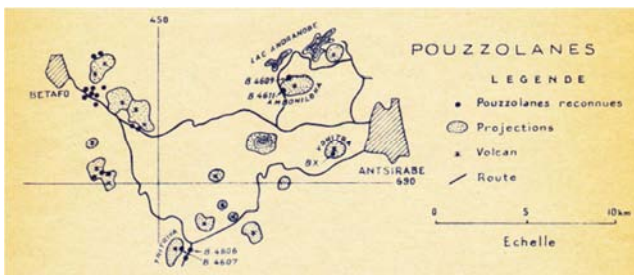


Figure 11. Sampling map.

(ii). Chlorite

A chlorite is an aluminosilicate mineral of iron or magnesium, generally greenish in colour, and similar to mica in structure and physico-chemical properties.

Chlorites are produced by various mineral reactions, including the decomposition of black mica. Chlorites are hydrated phyllosilicates. They contain medium sized cations. The cations often present are iron, magnesium and aluminium. The interplanar space is filled with a layer composed of Mg and OH. Al is locally replaced by Fe. Chlorites exist in larger crystals in magmatic rocks; they are also formed during the diagenesis of sedimentary rocks. They are found as detrital elements in soils with a mild climate [5].

(iii). Kaolin

Kaolins are white, brittle, refractory clays composed mainly of kaolinite, or aluminum silicates. Originally discovered in China, they are the basis of porcelain manufacture, but are also used in the paper, medical and cosmetics industries [11].

(iv). Paddy ball ash

The rice husk is the outer part covering the grain of rice (paddy). It produces many uses: cattle feed, fertilizer in agriculture, additive in cement or lime as a pozzolanic material, fuel, etc because of its treatment problem and its low cost. Its mass and composition depend on the variety of rice cultivated, the geographical area, the season, the cultivation methods, etc... The rice husk is composed of 70 to 80% organic matter (mainly cellulose, lignin, pentosan and a small amount of proteins and vitamins) and inorganic mineral

matter including silica. The latter is dispersed in the organic matter and concentrated on the outer part of the husk. If the rice husk is calcined at a defined temperature, it is transformed into an ash with a high content of reactive amorphous silica. The latter can thus be used as a pozzolan to enhance the durability and strength of cement-based (or lime-based) composites [7].

2.5. Sample Preparation

The basic operations we have adopted for the preparation of pozzolans are as follows [12]:

(i). Drying

Drying consists of drying the samples in ovens. The purpose of this operation is to remove by vaporization the liquid that impregnates a solid. The temperature of the oven is about 105°C and the drying time is 24 hours.

(ii). Manual crushing

Crushing is also called coarse crushing. In our case, it is carried out manually with a hammer to obtain pieces of more or less small size of about 3 mm. This step is necessary to facilitate the work of the crusher. Crushing is also called coarse crushing. In our case, it is carried out manually with a hammer to obtain pieces of more or less small size of about 3mm. This step is necessary to facilitate the work of the crusher.

(iii). Crushing

It consists in crushing the previously crushed sample manually with a jaw crusher to reduce the granulometry to 2.5 mm.

(iv). Grinding

This grinding operation brings the solids to dimensions of around 80 μm. Grinding is almost identical to the crushing operation, but it is the size of the products that differs. The grinding operation was carried out at the 'National mining Office and Strategic industries (OMNIS)'. It is carried out by balls whose mode of operation is by percussion or impact or wear by friction, or abrasion or attrition.

(v). Sieving

It is an operation of mechanical grading of grains of solid matter of various shapes and sizes by presenting these grains on surfaces provided with openings that allow fragments smaller than the openings to pass through and retain those that are too large. The devices used are called "Sieve" or "Automatic Vibrator". These sieves are made of fine square-meshed cloths or square openings. The part of the aggregate that has passed through the sieve is called a sieve or sieve board. And the part that remained on the sieve for this part of the aggregates is called reject. The total weight of the fractions remaining on each sieve after sieving allows the analysis of the product.

3. Results and Discussion

analyses of lime, pozzolan, mafefer, kaolinitic clay and calcined chlorite.

Tables 1, 2, 3, 4, 5 and 6 present the results of the chemical

Table 1. Chemical characteristics of lime (in % by mass).

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	P ₂ O ₅	Na ₂ O	MnO	PF
Percentage (%)	5.21	0.99	0.45	49.77	20.07	0.07	0.04	0.15	0.03	23.22

Table 2. Chemical Characteristics of Pozzolans (in % by mass).

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	P ₂ O ₅	Na ₂ O	K ₂ O	PF
Percentage (%)	41.54	13.63	11.92	11.82	10.15	3.16	0.22	0.15	1.88	5.53

Table 3. Chemical characteristics of slag (in % by mass).

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	P ₂ O ₅	Na ₂ O	K ₂ O	MnO	PF
Percentage (%)	37.28	12.22	15.97	14.91	7.46	5.81	1.94	0.92	1.02	0.31	2.16

Table 4. Chemical characteristics of kaolinitic clay (in % by weight).

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	PF
Percentage (%)	39.80	41.30	traces	1.40	1.20	14.60

Table 5. Chemical characteristics of chlorite (in % by mass).

Compounds	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	MgO
Percentage (%)	46.50	5.50	35.50	0.10	0.50	4.50

Table 6. Chemical characteristics of paddy ball ashes.

Compounds	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	PF
Percentage (%)	90.74	1.38	0.83	1.67	1.38	4.00

Table 7 gives the results on the optimization of pozzolan pseudo-cement lime content.

Table 7. Optimization of pozzolan pseudo-cement lime content.

Physical characteristics						
Characteristics	P ₉₀ C ₅ G ₅	P ₈₀ C ₁₅ G ₅	P ₇₀ C ₂₅ G ₅	P ₆₀ C ₃₅ G ₅	P ₅₀ C ₄₅ G ₅	P ₄₀ C ₅₅ G ₅
Apparent density	0.989	0.985	0.955	0.921	0.903	0.835
Specific weight	2.85	2.81	2.78	2.72	2.71	2.33
Blaine specific surface area				3740		
Mixing water	27.7	29.0	31.8	37.5	41.2	46.2
Start of setting	04h31	04h00	02h36	01h16	58mn	45mn
End of catch	07h03	06h00	03h47	02h03	01h30	01h10
Mechanical characteristics						
Characteristics	P ₉₀ C ₅ G ₅	P ₈₀ C ₁₅ G ₅	P ₇₀ C ₂₅ G ₅	P ₆₀ C ₃₅ G ₅	P ₅₀ C ₄₅ G ₅	P ₄₀ C ₅₅ G ₅
Compression resistance						
2 days in MPa	1.2	1.4	2.1	2.7	2.0	1.4
7 days in MPa	1.2	2.4	3.5	4.8	3.0	2.6
28 days in MPa	0.5	2.1	3.7	5.0	3.9	3.2
Resistance to bending						
2 days in MPa	0.2	0.3	0.5	0.7	0.5	0.3
7 days in MPa	0.2	0.6	1.0	1.4	0.8	0.7
28 days in MPa	-	0.5	1.1	1.5	1.3	1.5

Table 7 revealed that, for optimum mixing, simple compressive strength reaches 5 MPa at 28 days. At this age, whatever the percentage of lime incorporated, depending on the moulding water content, the study of the compressive

strength shows that it is maximum for the water/solid ratio = 0.55. During the optimization of the mixing water we cannot go below the value water/solid = 0.50 because the mixer makes a deafening noise due to the decrease of the water quantity.

Table 8 displays the results on the optimization of macheder pseudo-cement lime content.

Table 8. Optimization results of macheder pseudo-cement lime content.

Physical characteristics						
Characteristics	M ₉₀ C ₅ G ₅	M ₈₀ C ₁₅ G ₅	M ₇₀ C ₂₅ G ₅	M ₆₀ C ₃₅ G ₅	M ₅₀ C ₄₅ G ₅	M ₄₀ C ₅₅ G ₅
Specific Weight	2.97	2.95	2.93	2.91	2.90	2.89
Blaine specific surface area			3664			
Mixing water	20.00	25.20	28.00	33.10	39.00	43.46
Start of setting	04h52	05h00	01h57	20mn	16mn	13mn
End of catch	07h50	07h40	04h15	01h30	50mn	34mn
Mechanical characteristics						
Characteristics	M ₉₀ C ₅ G ₅	M ₈₀ C ₁₅ G ₅	M ₇₀ C ₂₅ G ₅	M ₆₀ C ₃₅ G ₅	M ₅₀ C ₄₅ G ₅	M ₄₀ C ₅₅ G ₅
Compression resistance						
2 days in MPa	1.5	2.3	2.4	2.5	1.8	1.3
7 days in MPa	1.7	4.6	4.9	4.8	4.6	4.1
28 days in MPa	0.6	5.5	6.1	5.9	5.8	6.2
Resistance to bending						
2 days in MPa	0.4	0.4	0.5	0.5	-	-
7 days in MPa	0.5	1.3	1.3	1.3	1.1	1.3
28 days in MPa	-	1.4	1.5	1.4	1.1	2.1

As can be seen in Table 8, on the 28th day, the optimal proportion of lime that gives the maximum resistances is equal to 25% and 55%. For the optimum mix, the compressive strength reaches 6.1 MPa and 6.2MPa at 28 days. At this age, whatever the percentage of combined lime, depending on the moulding water content, the study of the compressive strength shows that it is maximum for the Water/Solid ratio = 0.49. We have also noted that quicklime

brings an improvement on the mechanical resistance of the pseudo-macheder cement, 5% in lime corresponds to a resistance of 0.6 MPa on the 28th day while 55% in lime, the compressive resistance becomes 6.2 MPa.

The present research work made it possible to optimize the quantity of lime to be incorporated into the metakaolin and led to the results summarized in Table 9.

Table 9. Lime content optimization results of pseudo-metakaolin cement.

Physical characteristics						
Characteristics	MK ₉₀ C ₅ G ₅	MK ₈₀ C ₁₅ G ₅	MK ₇₀ C ₂₅ G ₅	MK ₆₀ C ₃₅ G ₅	MK ₅₀ C ₄₅ G ₅	MK ₄₀ C ₅₅ G ₅
Specific Weight	2.42	2.44	2.47	2.51	2.53	2.57
Blaine specific surface area					3889	
Mixing water	58.10	55.92	53.67	56.30	51.10	49.20
Start of setting	07h05	08h13	07h27	04h15	03h50	02h38
End of catch	12h54	11h48	10h13	06h20	05h47	04h10
Mechanical characteristics						
Characteristics	MK ₉₀ C ₅ G ₅	MK ₈₀ C ₁₅ G ₅	MK ₇₀ C ₂₅ G ₅	MK ₆₀ C ₃₅ G ₅	MK ₅₀ C ₄₅ G ₅	MK ₄₀ C ₅₅ G ₅
Compression resistance						
2 days in MPa	1.2	3.5	3.5	3.8	3.2	2.2
7 days in MPa	1.3	9.2	11.4	10.7	10.9	10.4
28 days in MPa	1.5	10.0	14.2	13.3	16.3	10.8
Resistance to bending						
2 days in MPa	-	0.9	0.9	0.8	0.9	0.5
7 days in MPa	-	2.3	2.0	2.0	2.4	1.9
28 days in MPa	-	1.8	2.4	2.1	3.1	2.4

Table 9 revealed that, on the 28th day, the optimal quantity of lime that gives the optimal resistances is equal to 45%. For the optimum mix, the compressive strength reaches 16.3 MPa on day 28. At this age, whatever the percentage of lime incorporated, according to the moulding water content, the

study of the compressive strength shows that it is maximum for the Water/Solid ratio = 0.64.

The results of mechanical tests on mixtures of calcined chlorite and rice husk ashes are gathered in Table 10.

Table 10. Results of mechanical tests on mixtures of calcined chlorite and rice husk ashes.

		Manufactured binders				Control binders	
Compression resistance (MPa)		CC-CBR10		CC-CBR20		CC-CBR30	
Ages of the test tubes (MPa)		CC-CBR10	CC-CBR20	CC-CBR30	CC-CBR40	Natural cement	MC 12.5
2 days	Without addition	1.00	4.00	4.35	3.00	-	-
	With addition	3.50	1.75	2.10	1.60	-	-
7 days	Without addition	11.00	12.00	13.85	9.00	-	-

		Manufactured binders				Control binders	
Compression resistance (MPa)							
Ages of the test tubes (MPa)		CC-CBR10	CC-CBR20	CC-CBR30	CC-CBR40	Natural cement	MC 12.5
28 days	With addition	9.50	11.50	12.00	8.00	-	-
	Without addition	19.25	20.00	21.75	16.25	19.00	12.50
	With addition	18.00	19.10	20.50	16.75	-	-
Resistance to bending (MPa)							
2 days	Without addition	2.50	2.00	2.13	0.98	-	-
	With addition		1.50	1.63	0.40	-	-
7 days	Without addition	3.00	4.00	4.25	2.00	-	-
	With addition	2.75	3.50	4.00	1.50	-	-
28 days	Without addition	3.75	4.50	4.80	2.25	-	-
	With addition	3.50	4.00	4.75	2.00	-	-

For these mixes, the mortar resistance at day 28, at young ages on binders without and with addition varies from 16.45 to 21.75 MPa depending on the amount of addition. We have obtained natural cement and a masonry cement: The CC-CBR40 binder with 5% addition is of masonry cement class MC12.5. The binders CC-CBR10, CC-CBR20, CC-CBR30 without additive are of the natural cement class. The optimum quantity of the mixture of calcined chlorite and rice

husk ash is in the ratio (70-30) to obtain a good binder. The values obtained for mixtures with gypsum are small compared to mixtures without additions, since free lime does not react with silica and iron oxide in chlorite. The addition of CBR 10%, 20%, 30% increases the compressive strength of the binder but at 40% it decreases the compressive strength of the binder. The temperature evolution of different materials is given in Table 11.

Table 11. Temperature evolution as a function of mechanical resistance.

Temperature (°C)		0	25	55	Observation
Pozzolan	Rt (MPa)	1.4	1.5	1.3	P ₆₀ C ₃₅ G ₅
	Rc (MPa)	4.8	4.9	4.6	
Machefer	Rt (MPa)	2.0	2.1	1.5	M ₄₀ C ₅₅ G ₅
	Rc (MPa)	6.1	6.2	5.7	
Metakaolin	Rt (MPa)	2.8	3.2	2.6	MK ₅₀ C ₄₅ G ₅
	Rc (MPa)	15.9	16.4	15.1	
Calcined Chlorite	Rt (MPa)	3.6	4.7	4.5	CC ₃₀ C ₇₀
	Rc (MPa)	18.0	21.3	19.2	

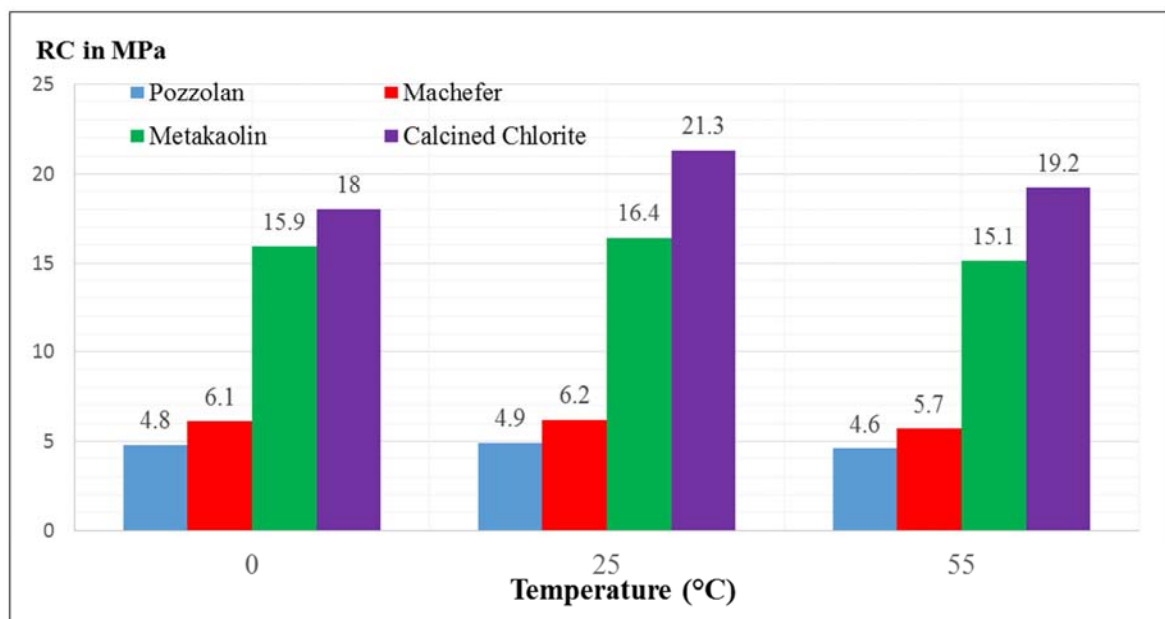


Figure 12. Temperature variation as a function of the mechanical resistance of the binders.

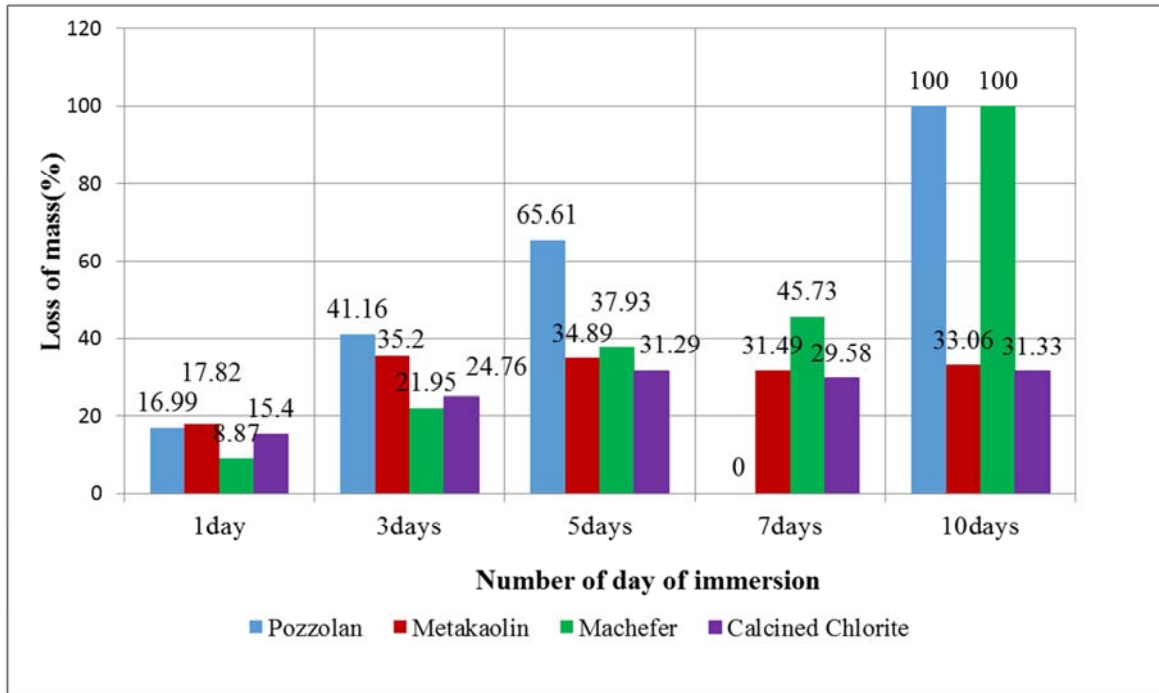


Figure 13. Variation of mass loss as a function of the number of days of immersion in the 5% pozzolanic cement HCl solution.

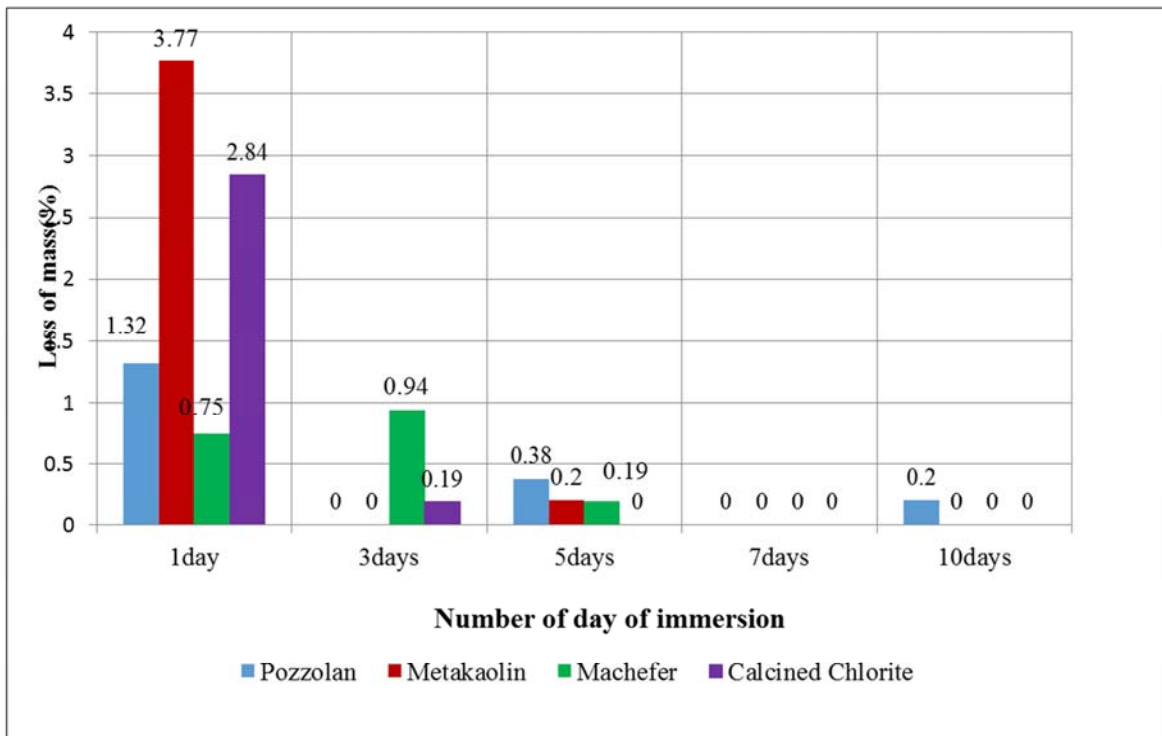


Figure 14. Variation of mass loss as a function of the number of days of immersion in the 5% pozzolanic cement NaOH solution.

The results obtained in this study revealed that the importance of the degree of aggressiveness of the acidic environment on the durability of mortars. Also, a total alteration of the specimens in the case of pozzolan and machefer on the 10th day and a small loss of mass in the case of metakaolin and calcined chlorite were observed. The loss of mass of pseudo-cement is due to the fact that, after

hydration, the pseudo-cement gives part of the free calcium hydroxide $Ca(OH)_2$ which can be leached out internally when subjected to acid. These soluble calcium salts are easily removed from the mortar and thus weaken the structure of the whole. The chemical attack for specimens immersed in hydrochloric acid is much more significant compared to that in sodium hydroxide solution,

The consequences of acid attack can be very significant. First of all, the formation of expansive products often leads to problems of cracking and alteration of the coating, then the dissolution of these products, which affects the resistance of

the coating.

The analyses carried out on water absorption tests on pozzolan samples show that they retain little water (Figure 15).

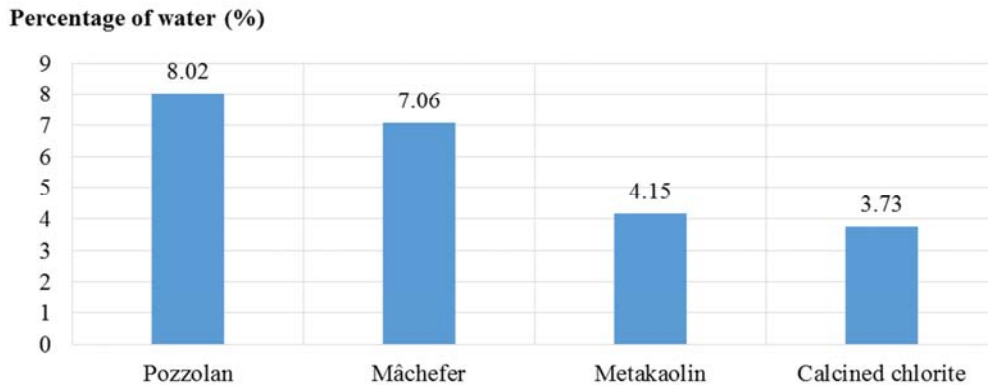


Figure 15. Water absorption of pseudo-cement.

Cement is an essential material for construction, which is one of the world's leading industries and one of the largest employers. Of vital importance for housing and basic infrastructure, the cement industry plays a key role in economic development and poverty reduction in emerging and developing countries. Cement production remains fundamentally local, except for some fragmented markets such as those in sub-Saharan Africa. It requires heavy investments that require financing and long-term profitability that are difficult to access in developing countries. There is therefore a need to promote new local materials for the construction of basic infrastructures in Africa. Developing our local resources is an essential phase for the economic take-off of the African continent. Indeed, countries of sub-Saharan Africa are characterized by low human development

and by a high incidence of poverty. Most of these countries are failing to develop an efficient supply of local resources that would contribute to rapid poverty reduction. This study therefore proposes the valorization of local resources (pozzolanic materials) as substitute materials for clinker for the production of cement. To do so, the quality of the raw material resources must be evaluated before beginning this cement manufacturing process. The chemical analysis of all raw materials used in this study reveals the presence of oxides such as SiO_2 , Al_2O_3 , CaO , Fe_2O_3 , MgO , etc in good proportion, suggesting their use as substitution materials of Portland cement clinker. The oxide found in very large quantities in all raw materials is SiO_2 (90.74% in paddy ball ashes).

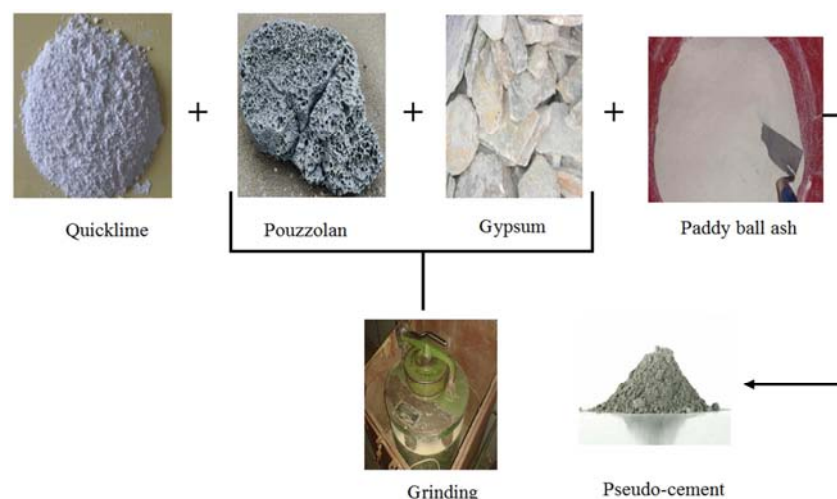


Figure 16. Cement manufacturing process of Pseudo-cement.

However, the use of alternative raw materials brings other additional impurities such as the oxides of phosphorus,

titanium, sodium or manganese. These impurities have been evaluated and their small values range from 0.31 to 5.81% do not make these substitution materials poor [13-16]. TiO_2 is

the very largest impurity in all of these raw materials. The foundation of the clinkerization process is largely determined by the chemistry (chemical analysis) and the process engineering. This latter concerns the physical characteristics and the mechanical characteristics (i.e. compression resistance and resistance to bending) of the raw materials. The decrease in mechanical resistance in raw material is generally due to P₂O₅ mass percentages greater than 1% [17-19]. The results obtained for all raw materials investigated

suggest their use as clinker in the cement production, except for slag where P₂O₅ is evaluated at 1.94%.

1) Comparison between the classic cement manufacturing process and that of pseudo-cement

The manufacturing process of the pseudo-cement can be schematized as follows:

While for the classic cement, the manufacturing can be represented by the following scheme:

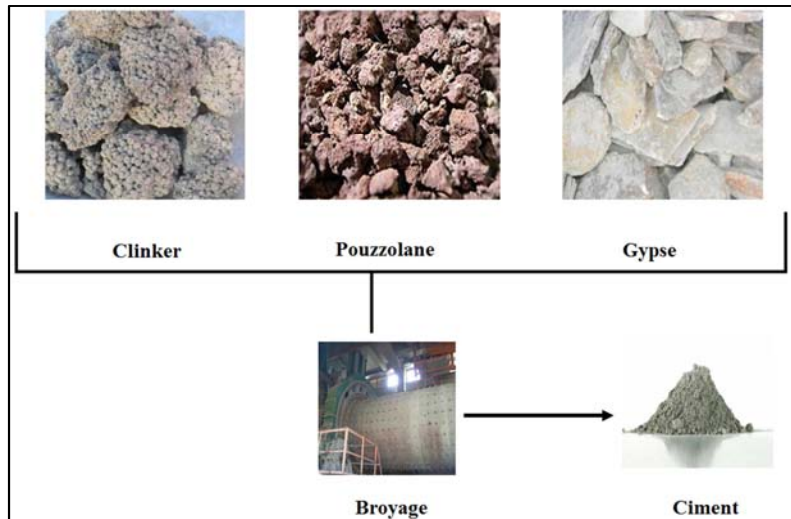


Figure 17. Cement manufacturing process of classic cement.

2) Comparison between Portland cement and our pseudo-cement

The following table summarizes and compares Portland cement with our new pseudo-cement binder based on quicklime + pozzolan + paddy hull ash. The comparison is based on the technical, economic and environmental characteristics.

Table 12. Comparison between Portland cement and pseudo-cement.

Characteristics	Pouzzolan	Machefer	Kaolinitic clay	Calcined chlorite	Portland cement
Raw material	Pouzzolan, Lime, gypsum	Machefer, lime gypsum	Clay, Lime, gypsum	Chlorite, Lime, gypsum, paddy husk ash	Limestone, clay, gypsum
Cooking temperature	850°C	850°C	750°C	850°C	1450°C
Specific weight	2.72	2.93	2.53	-	2.94
Blaine specific surface	3740	3664	3889	-	4377
Mixing water	37.5	28.0	51.1	42.0	35.8
Start of setting	01h16	01h57	03h50	-	03h53
End of setting	02h03	04h15	05h47	<24h	-
Compression resistances					
2 days in MPa	2.7	2.4	3.2	4.4	6.0
7 days in MPa	4.8	4.9	10.9	13.9	15.3
28 days in MPa	5.0	6.1	16.3	21.8	24.8
Resistance to flexion					
2 days in MPa	0.7	0.5	0.9	2.13	-
7 days in MPa	1.4	1.3	2.4	4.3	-
28 days in MPa	1.5	1.5	3.1	4.8	-
Fire resistance	Resists at 700°C	Resists at 700°C	Resists at 800°C	Resists at 800°C	Resists at 800°C
Corrosion resistance	Mortars are dissolved in an acidic environment	Mortars are dissolved in an acidic environment	Mortars are dissolved in an acidic environment	Mortars are dissolved in an acidic environment	Mortars are dissolved in an acidic environment
Durability or longevity	Mortars remain stable over time	Mortars remain stable over time	Mortars remain stable over time	Mortars remain stable over time	Mortars remain stable over time
Technology	Use of techniques under simple conditions	Use of techniques under simple conditions	Use of techniques under simple conditions	Use of techniques under simple conditions	Cement factories use modern and sophisticated technologies
CO ₂ emissions	Low level of CO ₂	Low level of CO ₂	Low level of CO ₂	Low level of CO ₂	High level of CO ₂

Making pozzolan based pseudo-cement solves environmental problem and reduces CO₂ emissions in the cement plant. Like all research, the realization of the pseudo-cement manufacturing plant required techniques under simple conditions, that is to say, it does not require sophisticated technologies. The results obtained in this study show that the pseudo-cement has similar qualities to the control cement.

In terms of energy, the manufacture of pseudo-cement consumes less energy (850°C) compared to conventional cement (1450°C).

4. Conclusion and Suggestions

The present work has shown that it is possible to produce from local materials (pozzolan, kaolinitic clay; calcined chlorite) a binder with sufficient mechanical strength for use in construction. The use can range from plaster to tiles. The test carried out on the natural pozzolan sample (5 MPa) incorporated with lime shows a lower compressive strength at 28 days compared to the artificial pozzolan (21.75 MPa) mixed with paddy ball centre. The experiments revealed that the calcined chlorite mixture with paddy ball ash provided the best industrially exploitable result, given its compressive strength meeting the desired requirements for plaster binder. This improvement is favoured by the paddy husk ash containing 90.74% active silica which has a high pozzolanic content. When pseudo-cement is used in construction as a wall, its main enemy remains water, mainly of meteoric origin. Analyses carried out on water absorption tests on pozzolan samples show that they retain little water. The manufacture of this binder by cooking at medium temperature (750-850°C) of the raw materials for the most part local is interesting for Madagascar. It now remains to develop these partial results by studying other chemical activators, determining the influence of mineralogical composition (role of secondary constituents) on pozzolanicity and researching applications of the synthetic binder in the habitat in order to prove its economic interest.

Acknowledgements

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References

- [1] László S., Ignacio H., Juan C. C., Antonio S., Peter R., 2003. Energy consumption and CO₂ emission from the world cement industry. Joint Research Centre.
- [2] Bisulandu B-J., Marias F., 2019. Modeling of cement clinker chemistry and engineering of cement manufacturing process: State of the art. *International Journal of Innovation and Applied Studies* 25 (2): 528-551.
- [3] Chatterjee A. K., 2011. Chemistry and engineering of the clinkerization process — Incremental advances and lack of breakthroughs, *Cem. Concr. Res.* 41: 624–641. doi: 10.1016/j.cemconres.2011.03.020.
- [4] Ishak S. A., Hashim H., Ting T. S., 2016. Eco-innovation strategies for promoting cleaner cement manufacturing, *J. Clean. Prod.* 136: 133–149. doi: 10.1016/j.jclepro.2016.06.022.
- [5] Sorrentino F., 2011. Chemistry and engineering of the production process: State of the art, *Cem. Concr. Res.* 41: 616–623. doi: 10.1016/j.cemconres.2011.03.020.
- [6] Despujols J., 1952. Application de la spectrométrie des rayons X au dosage des faibles teneurs de métaux dans les minerais, *Le Journal de physique et le radium. Physique appliquée*, 13.
- [7] ATILH, 1998. Guide pratique pour l'emploi des ciments, Eyrolles.
- [8] Protocole des essais au Laboratoire National des Travaux Publics et des Bâtiments, Antananarivo, Madagascar.
- [9] Frache B. J., 1965. Contribution à l'étude de quelque pouzzolane naturelle et artificielle en vue de la fabrication des ciments de pouzzolanes. Thèse de doctorat, Ecole Polytechnique de l'Université de Lausanne.
- [10] Rocher P., 1992. Memento roches et minéraux industriels: Ponces et pouzzolanes, BRGM, R 36447.
- [11] Sustrac G., 2011. *Vive la Terre*, Tome III, Atlantica.
- [12] Della V. P., Kühn I., Hotza D., 2002. Rice Husk Ash as an alternative source for active silica production. *Materials Letters* 57: 818-821.
- [13] Ngbolua K. N., Falanga C. M., Djoza R. D., Masengo C. A., Gamo A. N., Bongo G. N., Gbolo B. Z., Virima M., Mpiana P. T., 2019. Socio-economic and Environmental Impacts of Clay Brick Manufacturing in Gbado-Lite City (Nord Ubangi Province, DR Congo). *Journal of Environment Protection and Sustainable Development* 5 (3): 126-131.
- [14] Rakotoarison S., Rasolomanana E. H., Baholy R. R., Ngbolua K. N., 2016. Bemolanga tar sand: A local raw material for tarring roads in Madagascar. *International Journal of Innovation and Scientific Research* 24 (2): 397-406.
- [15] Rakotoarison S., Rasolomanana E. H., Baholy R. R., Ngbolua K. N., 2016. Physicochemical characterization of the non-conventional petroleum oil fossil products from Bemolanga and Tsimiroro, Madagascar. *International Journal of Innovation and Scientific Research* 24 (2): 423-427.

- [16] Razafindramanga A. W., Ngbolua K. N., Bongo G. N, Baholy R. R., 2019. Laboratory Testing on the Promotion of Madagascar's Industrial Waste and Natural Materials as Clinker Mineralizers. *Asian Journal of Geological Research* 2 (2): 1-13.
- [17] Girod-Labianca C., Noirfontaine M. N., Tusseau-Nenez S., Signes-Frehel M., Gasecki G., 2006. Combustibles de substitution dans les fours de cimenteries: Effet du phosphore sur la phase majoritaire du ciment Portland. *Matériaux* 13: 1-11.
- [18] Salge H., Thormann P., 1973. Effect of phosphorus pentoxide on the constitution of Portland cement clinker. *Zement-Kalk-Gips* 21 (11): 532-539.
- [19] Halicz L., Nathan Y., Ben-Dor L., 1983. The influence of P_2O_5 on clinker reactions. *Cem. Concr. Res.* 14: 11-18.