Original Research Article

Laboratory Testing on the Promotion of Madagascar's Industrial Waste and Natural Materials as Clinker Mineralizers

ABSTRACT

This study presents laboratory tests on the effects of several mineralizers added to black raw materials, in the manufacture of cement. This manufacturing process is based on crushing quarry limestones with clays and fuels in order to be fired at 1450°C to obtain clinker, the main component of cement. In the case of the Ibity cement industry, the natural materials of Madagascar and the waste from local industries were studied. The main goal of this study was to find the best mineralizer that could reduce the thermal energy expended in the formation of clinker while improving its quality. In order to realize this, four different temperature values were applied namely 1250°C, 1350°C, 1400°C and 1450°C. In addition, it was added 1% and 4% of these mineralizers to the white raw materials used and three different qualities of the raw material, a, b and c were used respectively, as controls. The Lime Saturation Factor or LSC is the performance indicator that indicates the quality level of these raw materials.

With these evaluation criteria, the characteristics of each of these mineralizers also helped us to detect these own efficiencies. The glass comes from the waste of local industries. It is a material rich in amorphous silica that reacts easily under the effect of temperature. Industrial ash is rich in crystalline silica, which prevents its reactivity. Pozzolan is one of the most accessible materials at the plant but has poor thermal conductivity despite the presence of reactive silicas Sulfogyspes 1033 and 1034 are respectively rich in iron oxide and sulphur trioxide or SO3. They are responsible for the melting properties in the reaction of clinker formations.

At only 1350°C, our tests with Sulfogypses (1033 and 1034) gave us the best results. At the low temperature used in the furnaces, these additions of mineralizers allowed the vintages to surpass the quality in front of the control. They will later be able to optimize the compressive strength of the cement, given the high C_3S value observed in the experiments. As for the other mineralizers, their reactivity requires other conditions that will be the subject of another study.

Keywords: mineralization, clinker, C_3S, FSC, free lime, melting, firing, temperature.

1. INTRODUCTION

Currently, the cement industry is facing a significant expenditure of thermal energy in the operation of clinker manufacturing processes, which is the main component of cement. However, customers are demanding quality products at a lower cost. Thus, the competition in this field is based on controlling combustible costs, respect for the environment and production with a lower cost price [2, 8]. It is also world-renowned that this type of industry is responsible for air pollution through the emission of carbon dioxide (CO_2) [5]. It should be noted that the problems linked to the heterogeneity of raw materials, and the ecological degradation are associated with its frequent exploitation [8]. The effect of this deterioration directly impacts on the on the quality of the produced cement. However, the quality of cement is reflected in the choice of the best raw materials used and the careful management of combustibles.

To overcome this, research organizations in this field are working hard to improve these processes. Then various solutions are applied, such as the substitution of more economical combustibles and the practice of mineralization [5, 8]. That is the reason why a cemetery in Madagascar located in Ibity recycles and promotes the type of combustible waste such as petroleum coke. It is a fossil combustible which provides enough heat and energy used in these processes [5]. The choice of these raw materials is based on their reactivity and chemical composition but also on their accessibility to the factory. At our disposal, we possess as mineralizers, the pozzolans as natural materials and industrial wastes such as glass, ash called BOTTOM ASH or BA and FLY ASH or FA as well as Sulfogypses 1033 and 1034. In addition, industrial ash such as BA and FA are both waste from local industries and the reuse of Sulfogypses for other purposes will protect us from environmental hazards due to their release into the environment and storage. These wastes are known as residues containing significant impurities [4]. For Ibity factory, most of these raw materials are extracted locally in Madagascar except for the combustible. Cipolin is extracted directly from the open-pit quarry near the factory; pozzolans from the Tritriva quarries and clays from the Andranomanelatra quarries.

It should be remembered here that cement comes from the combination of pozzolan additions with the main material, which is called the clinker. In order to better understand the cement manufacturing process at Ibity (appendix 1). Therefore, the quality of cement depends on the best treatments and close monitoring of manufacturing processes (appendix 2). So, we can determine the quality of the mineralized clinker after testing different performance indicators such as free lime content, alite (an impure form of tricalcium silicate C_3S) and lime saturation factor or FSC.

Thus, three different types of crus will be formulated as controls to the experiments. They are named:" a" the low FSC control," b" the high FSC control and" c" with the average FSC. These controls correspond to the blends of crus similar to those produced in this factory. At the very beginning, our work concerns the studies of the efficiencies of each of these mineralizers in relation to the proportions of addition to these crus, the effects of temperature and the quality of the crus themselves. Then, we started testing for the proportion of mineralizer additions at 1% and 4%. According to the literature [10], this temperature is between 1200℃ and 1500℃.

In fact, we will discuss the influences of these mineralizers in the raw material mixture, looking for the main parameters necessary to improve the quality of the cement. We will insist in our research on finding the best clinker firing temperature and above all on fixing the best mineralizer content added to the chosen raw material. The main goal of this study was to find to find the best mineralizer that could reduce the thermal energy expended in the formation of clinker while improving its quality.

2. MATERIALS AND METHODS

The quality characteristics of the clinker are enhanced by the formation of the alite along with the other phases formed during clinkerization and the level of free lime remaining in these samples [6, 10]. The clinkerization reaction is said to be successful when all the oxides present in the mixture can be combined. The aim is to minimize the amount of free matter in the clinker, whether lime or silica. Thus, with reference to our performance indicators, the test efficiencies are based on criteria where the phases of the bed, referred to as C3S, are greater than 40%, and the free lime content is less than 1% [2, 10].

For this, three distinct qualities of white crus (a, b and c) were chosen as controls for the experiments (table 1). According to previous studies, the speed and efficiency of activation of natural materials is achieved with a significant increase in temperature [9]. The reactions of these mineralizers under the action of temperatures are then studied, from the following values: 1250℃, 1350℃ and 1450℃.

Table 1: Control analyses in mass percent

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	FSC
a	14.23	3.20	2.67	41.24	1.67	90.91
b	13.31	2.81	2.32	42.33	1.63	100.53
c	13.77	3.01	2.50	41.79	1.65	95.54

The basis of this study was to determine the reactivity of mineralizers to crus mixtures. They derived from chemical compositions and physico-chemical properties. In order to start with these tests, the variation in the percentage of additions of natural materials and industrial waste chosen to our crus was 1% and 4%. Table 2 illustrates the results of chemical analyses performed on these mineralized materials.

Table 2: Chemical compositions of all mineralizers

	Paf	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
BOTTOM ASH	2.09	64.94	14.42	4.96	9.3	1.54	0.01
Glass	0	68.48	1.75	0.33	13.72	1.09	-
1033	13.41	4.38	5.27	38.96	12.01	0.22	14.75
1034	28.88	3.5	10.11	2.18	23.4	0	36.06
POUZZOLAN	6.18	41.31	13.64	11.61	12.32	9.74	0.41
FLY ASH	9.82	46.98	27.56	3.14	6.18	1.1	-

We first compared the effects of each mineralizer on our different crus at the same temperature of 1350℃. Then, small-scale tests were carried out in a muffle furnace in order to determine their effects on the different variations in clinkerization temperature. Therefore, the following method was adopted as described in the diagram as follows:

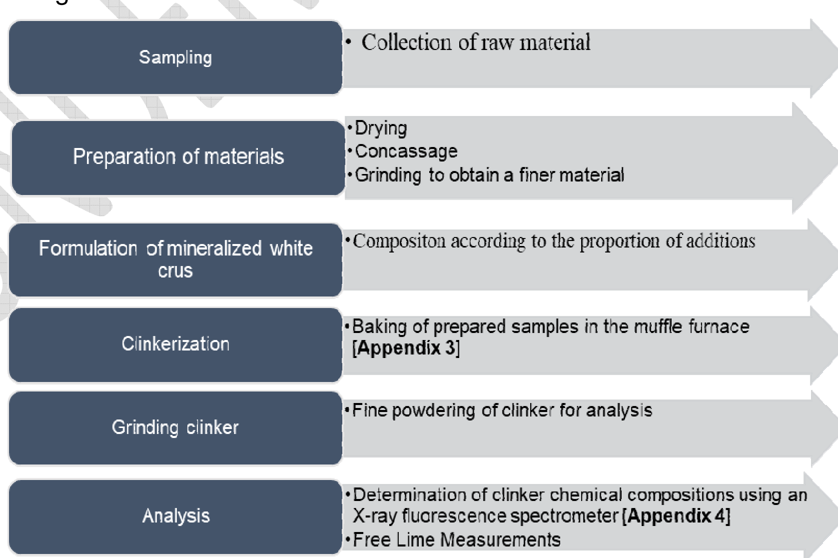


Figure 1. Diagram of the laboratory test procedure

3. RESULTS AND DISCUSSION

3.1 Mineralizer

For a mineralizer to be efficient, it is sufficient to install all the conditions that allow it to react in the mixture. In the first trials, we varied the proportion of addition of mineralizers added to controls a, b and c. First, 1% of the mineralizers are added to each control by setting the temperature at 1350℃. From each control, we obtained the following:

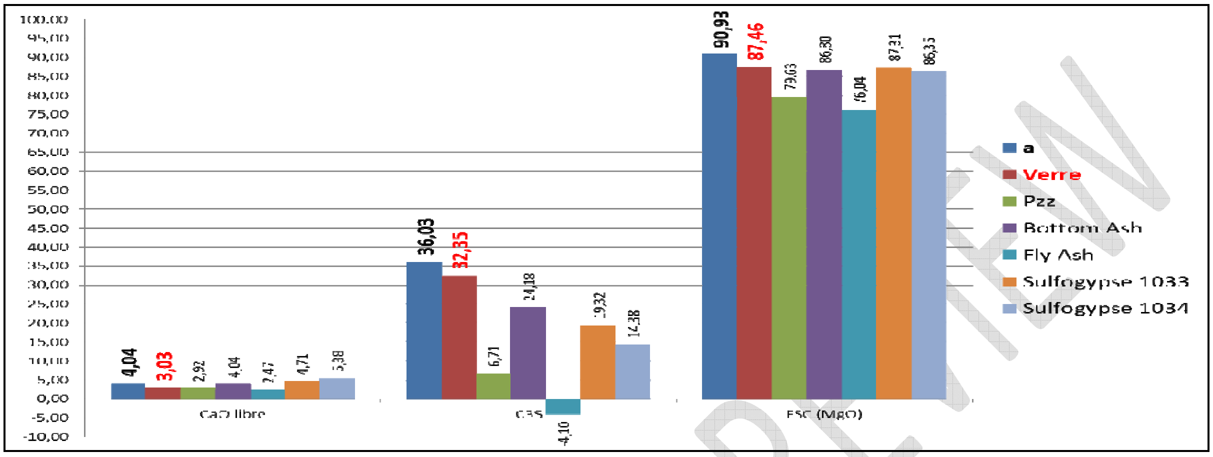


Figure 2: Mineralizers effects at 1% with control "a"

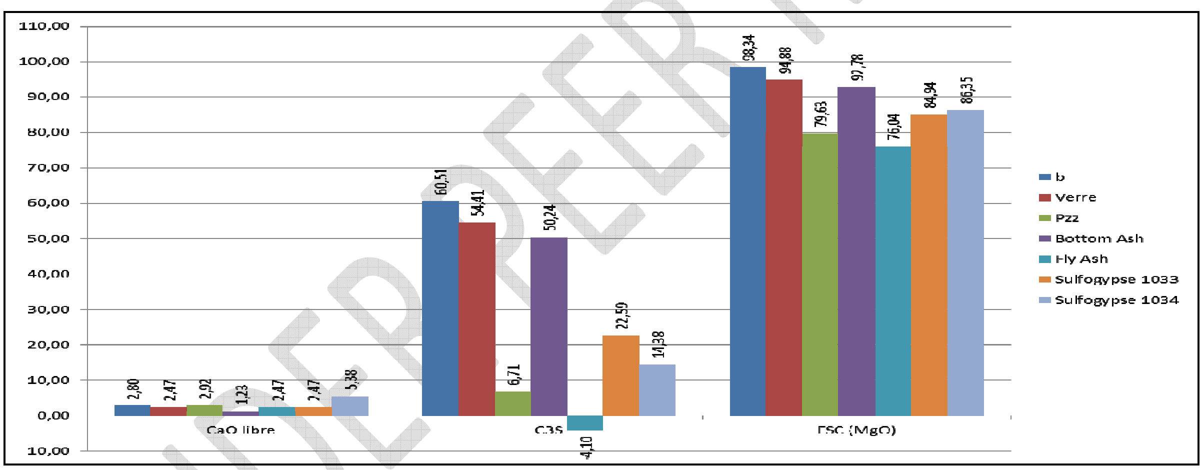


Figure 3: Mineralizers effects at 1% with control "b"

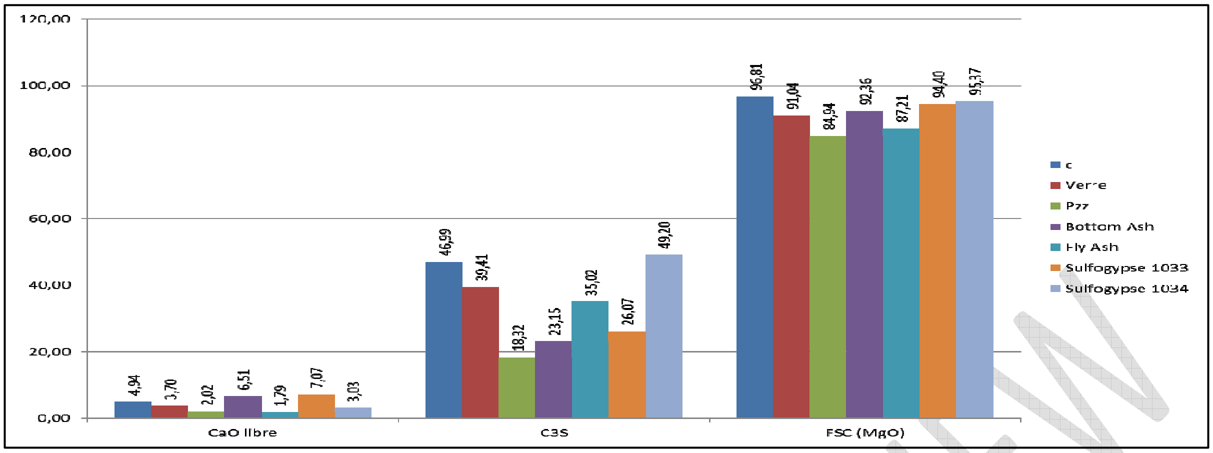


Figure 4: Mineralizers effects at 1% with control “c”

Considering the above figures, it should be stated that a mineralizer is conclusive if the C_3S of the black mineralized cru exceeds that of the control. This was not observed for mineralizers 1% mixed with control “a”. At 1% addition to the mixture, it may be deduced that industrial ashes (BA and FA) considerably reduce the free lime rate only to 1350°C along with the three controls due to high Silicon oxide content in its chemical composition. This phenomenon can be explained by the presence of alumina as fluxes in industrial ashes and causes oxides to combine with each other [3, 13].

With control "b" (Figure 2), the glass can form more alite than the other mineralizers but not exceeding the control. The high amount of silicon oxides in the glass satisfies the combination with all the lime present in the mixture and facilitates the formation of the alite. But it is still ineffective in this case and it requires other conditions to make it react better. Only Sulfogypsum 1034 can improve the quality of non-mineralized crus (Figure 3). The “1034" is obtained from an industrial desulphurization. This explains its high content of SO_3; which is a main flux in the cru mixture [9, 12, 18]. The proportions of calcium oxides increased its reactivity with the medium lime saturated cru. All these conditions together considerably produce the formation of alite and push this mineralizer to improve the control cru.

For the same temperature than the previous cases, the proportion of addition was increased at 4% and the findings are given in the figures below.

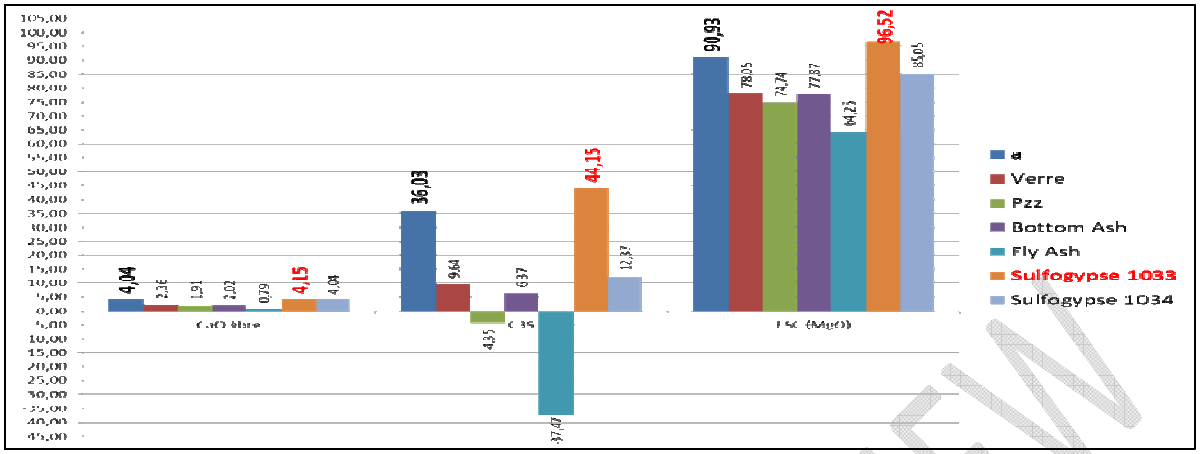


Figure 5: Mineralizers effects at 4% with control “a”

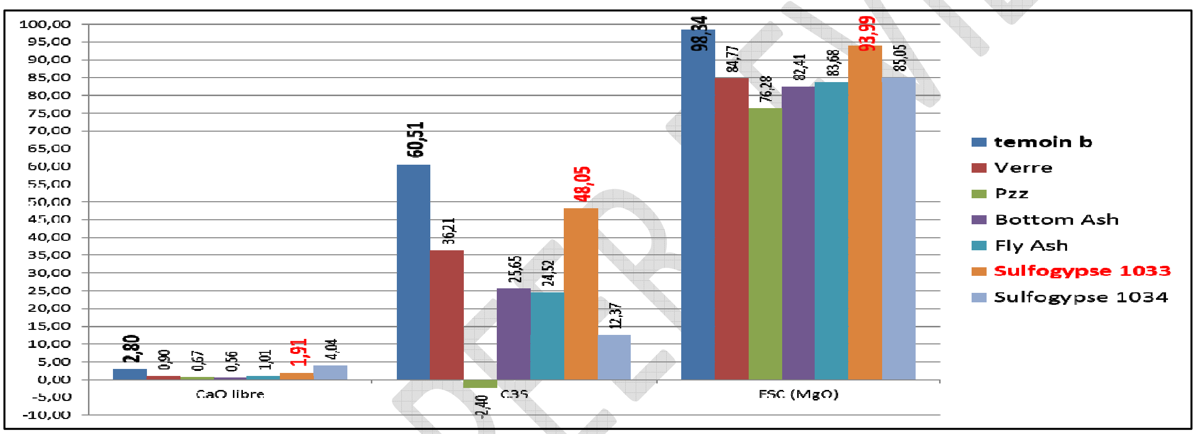


Figure 6: Mineralizers effects at 4% with control “b”

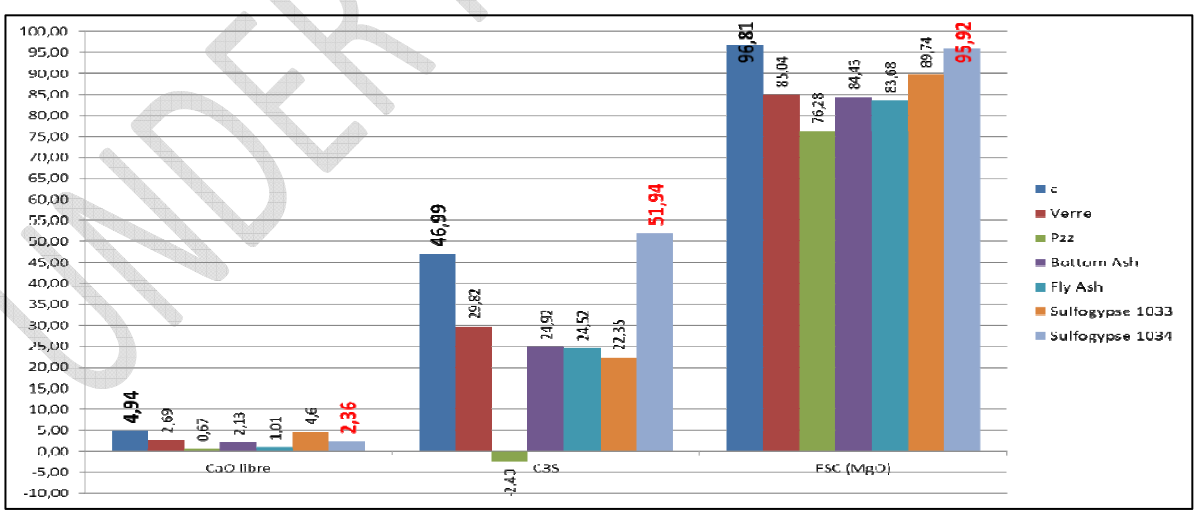


Figure 7: Mineralizers effects at 4% with control “c”

It was observed that with the increase in the addition of mineralizers to 4%, Sulfogypsum 1033 reacts distinctly with the controls "a" and "b". With the cru having a low lime saturation, the "1033" forms more C3S levels than the control (Figure 5). It is a mineralizer from the treatment of bauxite, which explains the enormous proportion of iron oxides in its chemical composition. In addition to the melting properties of sulphur trioxide, which pushes other oxides to consume calcium oxides, iron oxides reinforce the formation of liquid phases or the formation of C3A and C4AF ores. This would then help to obtain more alite in the clinker. Its mixture with "b" reduced its reactivity due to the rise of lime in this cru (Figure 6). Thus, there are still lime not combined with oxides.

On the other hand, the "1034" still only reacts with the "c" indicator (Figure 7). This mineralizer does not require a high lime saturation cru to react because of the high calcium oxide content in its chemical composition. As a result, its C_3S content increases by 51.94% depending on the addition rates. Industrial ashes always remarkably reduce the free lime rate, especially by increasing its quantity to 4%. In addition, pozzolana reduces this rate by less than 1% with raw "b" because it has the ability to bind with calcium oxides at low temperatures thanks to its melting temperature of 1140℃ [9, 11].

3.2 Effect of firing temperature

Different tests presented above highlighted the role of temperature on the evolution of clinker quality for the same temperature at 1350℃. The following process would consist of detecting the effects of different minerals present in the cru mixtures with the temperature variation from 1250℃ to 1450℃.

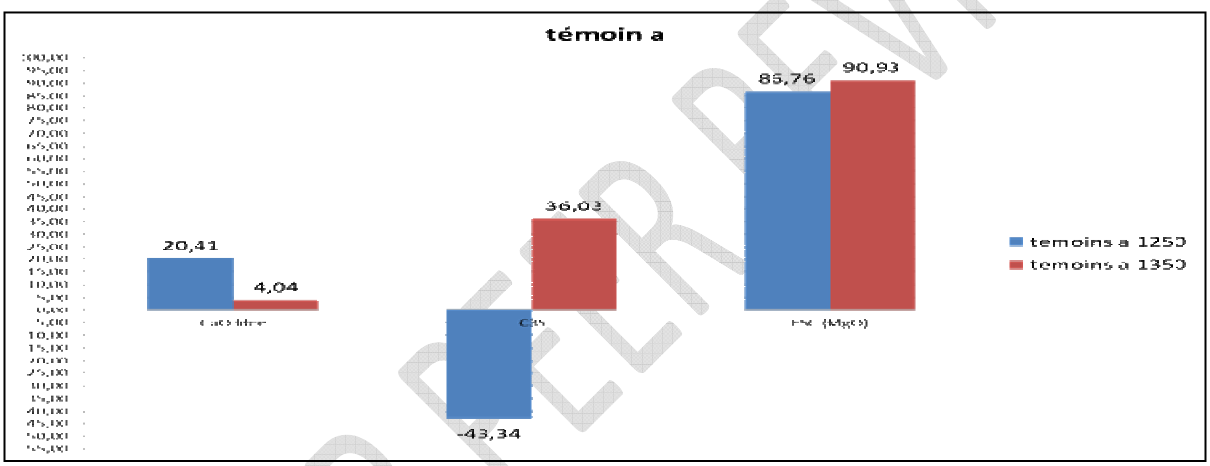


Figure 8: Evolution of temperature with control "a"

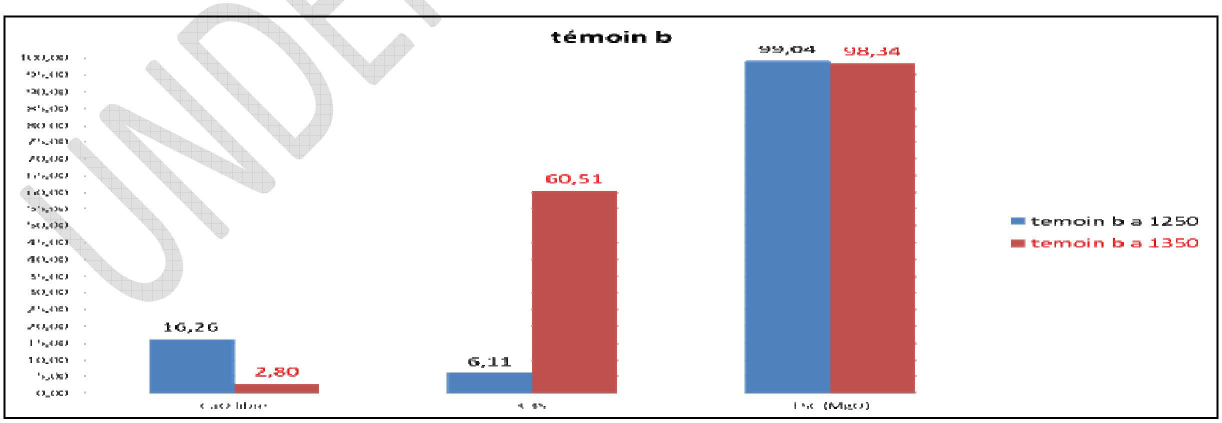


Figure 9: Evolution of temperature with control "b"

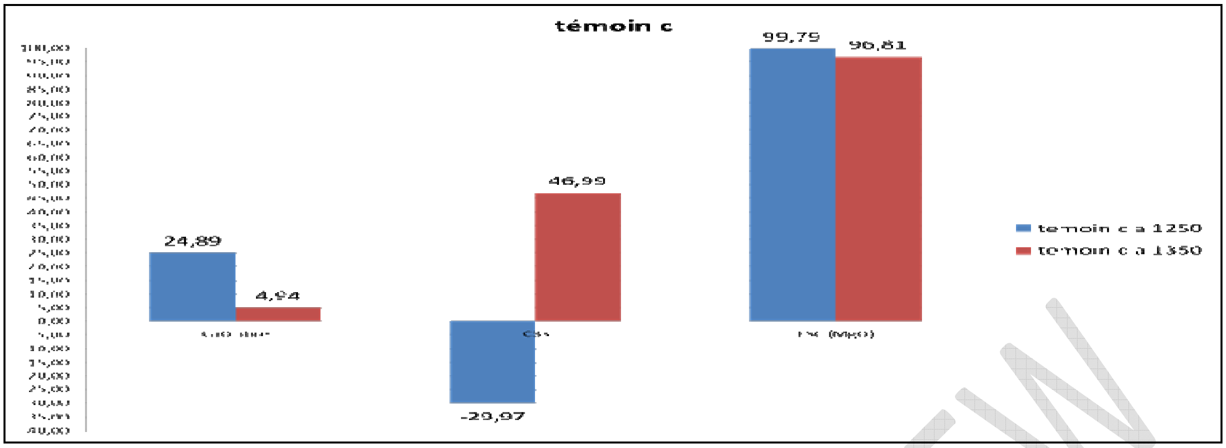


Figure 10: Evolution of temperature with control "c"

With the control tests a, b and c, the C_3S values increased remarkably with the increase in clinker firing temperature from 1250℃ to 1350℃. On the other hand, the free lime rate drops sharply, especially with the cru "b". This efficiency is due to the high lime content of this flour. The mineralizers have been demonstrated for their ability to react under the influence of temperature. Then, the efficiency depends on those with a high oxide content. They also improve fusion in clinkerization, especially with a higher addition rate, by promoting the combination of lime with oxides and increasing the formation of C3A and C4AF. In addition, these mineral reactivities require an optimum temperature.

Among these following series of tests, we were able to demonstrate the effects of temperature in clinker firing with changes in free lime and C_3S content. The evolution of the clinker without addition, with the variation of the temperature is shown in the following figures. The C_3S rate increases according to the saturation rate of lime present in the cru. Some minerals in the crus then require a temperature increase of 100℃ to combine all oxides with lime and at the same time decrease the free lime content (Figure 9).

The figures above illustrate the importance of the role of temperature in our studies. For the next step, we chose glass as one of the mineralizers in our tests to better understand its efficiency in relation to temperature changes. The reason for this choice is because of its ability to melt at low temperatures [7-8].

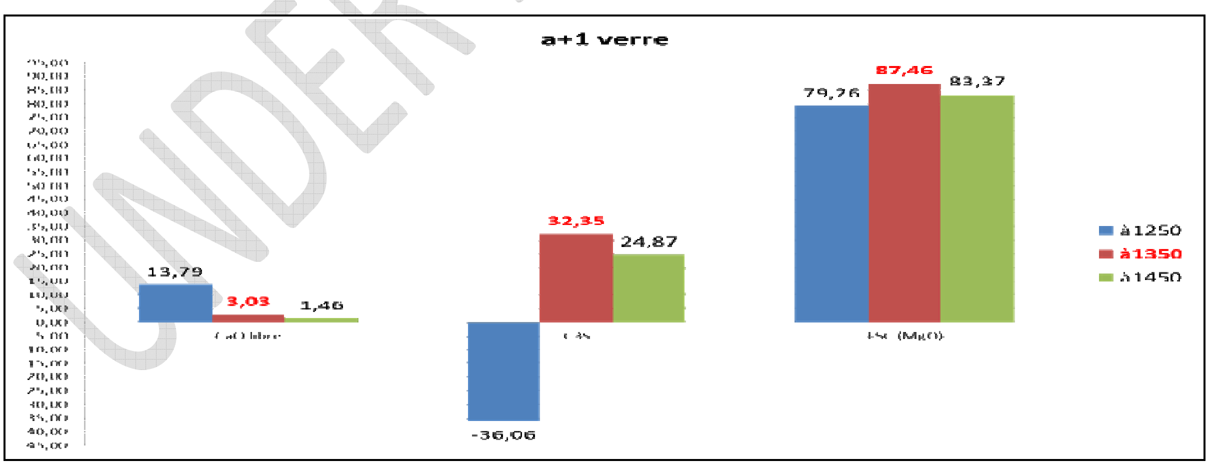


Figure 11: Evolution of temperature of glass at 1% with control "a"

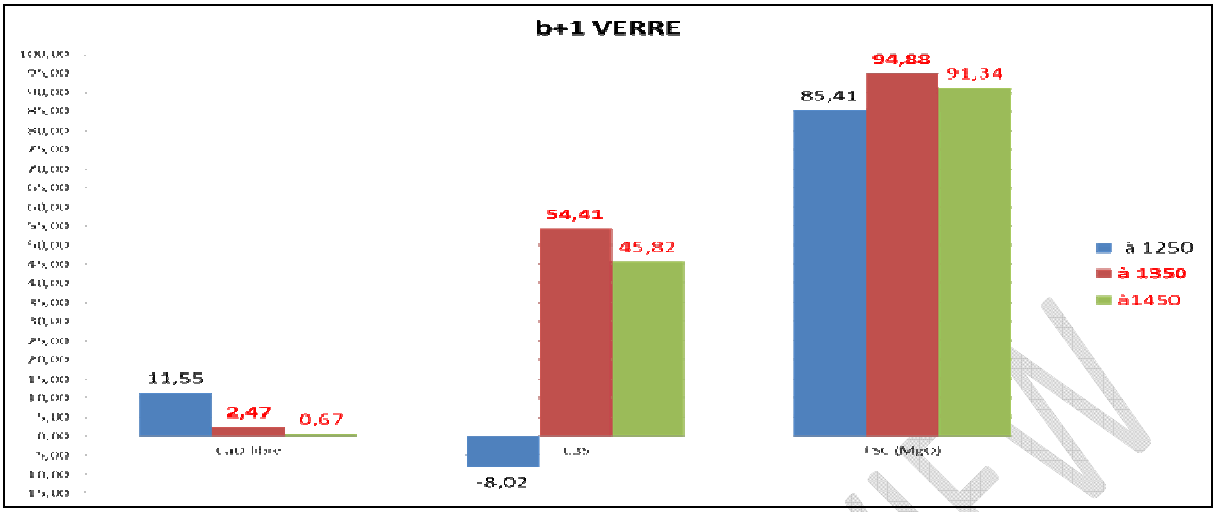


Figure 12: Evolution of temperature of glass at 1% with control "b"

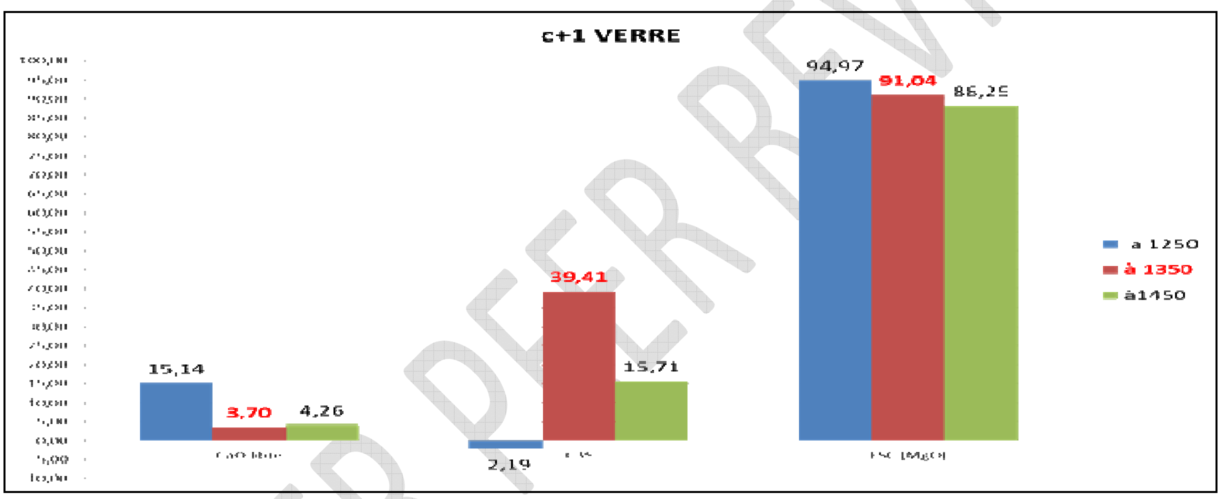


Figure 13: Evolution of temperature of glass at 1% with control "c"

We compared the reactivity of the glass with 1% of addition to the three controls. Thus, it was found that the mixture remains unfired at 1250℃. But with the three different crus, the glass remarkably reduced the free lime content when the temperature increased. This rate was reduced to 0.67% when mixed with control "b" and the formation of C_3S is more favored with this increase in lime saturation in the cru. All silica thus succeeds in filling all the maximum lime present in the cru "b" and reduces the number of non-combined lime. The abundance of amorphous silicas in the chemical composition of the glass then helps it considerably to react better. Its melting characteristic thus participates in the formation of liquid phases with the presence of C_3A and C_4AF elements, which is what represents the proportion of liquid phases in clinkerization [2].

The rate of addition would therefore be effective provided that all the silica in the mineralizer is combined with the lime in the crus. Non-combined lime and silica become free lime and silica respectively. Later in the process, this would harm the quality of the cement [9-10, 12].

4. CONCLUSIONS

Competition has become increasingly fierce in the cement production market. Since then, mineralization was considered as one of the best solutions for a good production in quantity and quality. The objectives of these experiments are to find the best mineralizers that can improve clinker quality while reducing the clinkerization temperature to improve processes. These various facts then lead us to value these natural materials and transform this industrial waste into a clinker mineralizer.

The findings of this study showed that not all mineralizers react at a low temperature of 1250°C. The Pozzolana is one of the raw materials used in the Ibity cement firm. Its mixture with the cru "b" has the effect of reducing the clinker firing temperature while remarkably reducing the free lime content to less than 1%. But it does not have the ability to form alite, due to its low content of aluminum oxide and iron. Meanwhile, Industrial ashes are materials that are difficult to react with when they are used as mineralizers. This is due to the presence of crystalline silicas in its chemical composition. The sulogypses that succeeded in meeting our expectations. Sulphogypsum called 1033 is a residue resulting from the handling of bauxites and 1034 comes from flue gas desulphurization in industries. These efficiencies are therefore due to its high S03 content in the mixture to further promote the formation of melting phases in clinkerization.

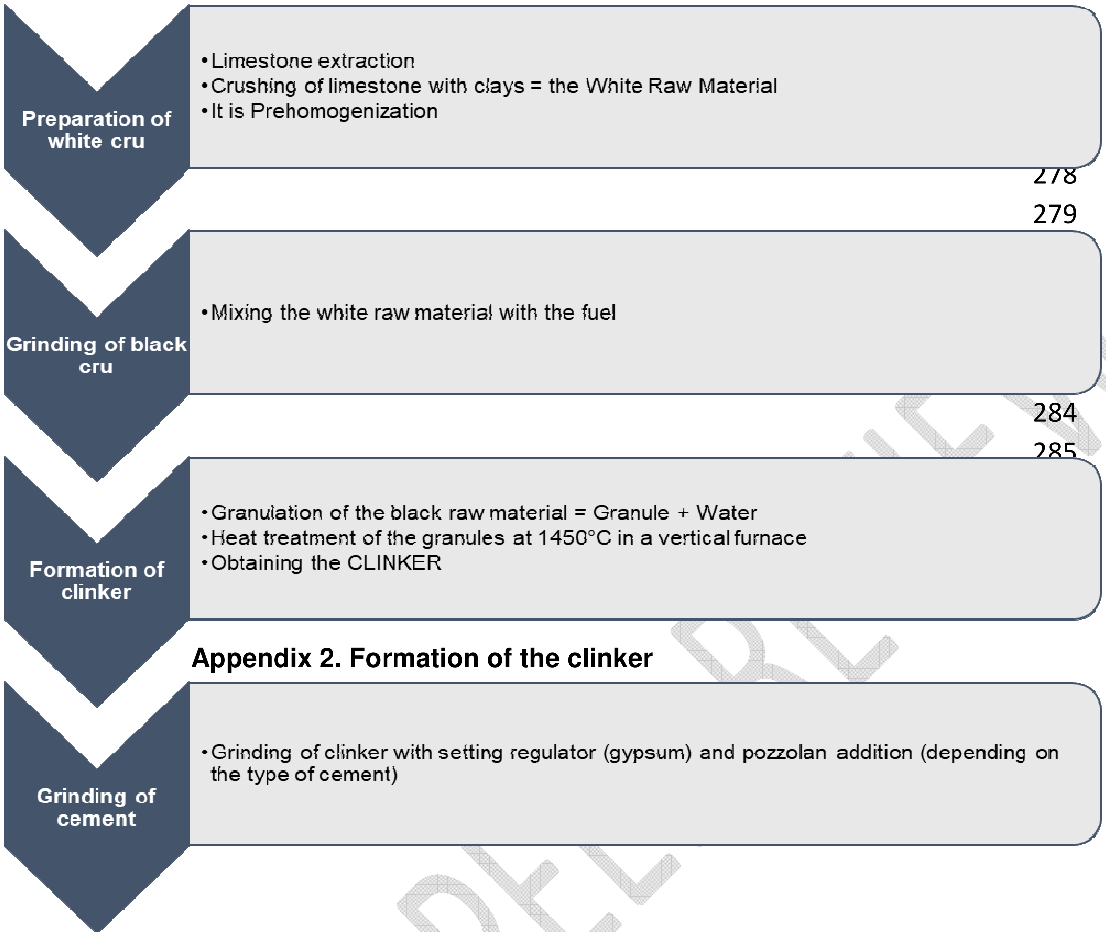
Glass is perceived as a little special because it requires some conditions to be able to react better in the blends of crus. These experiments then allowed to prove that the glass can react well under the clinkerization temperature of 1350°C and with the type of raw material with a high FSC level.

Further studies are required in order to find the benefits of mineralizers in the manufacturing process of clinker and its main reactions on an industrial scale.

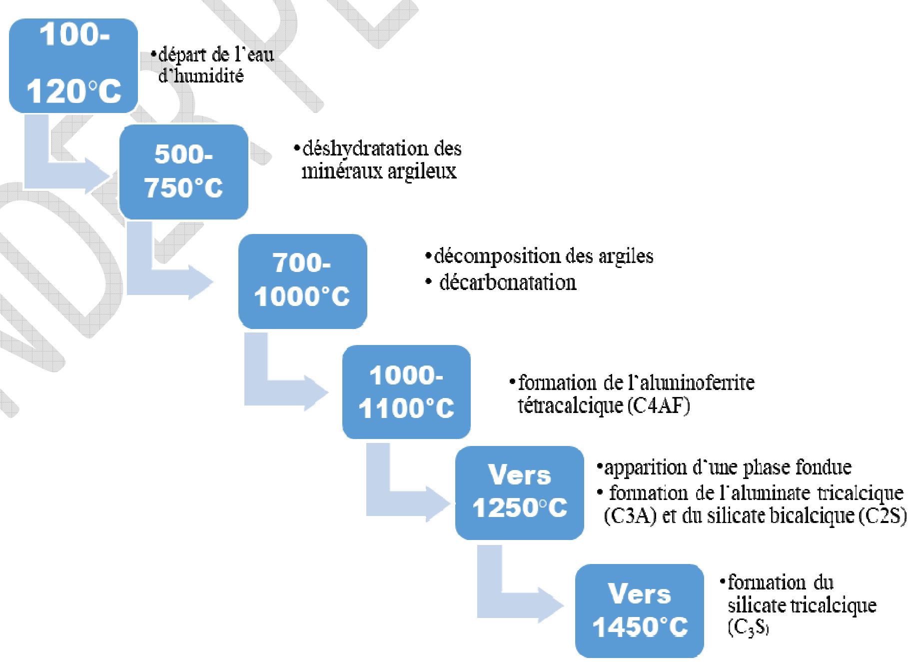
REFERENCES

[1]. Wittmann A, Willay G, Seffer R, Préparation de perles pour l'analyse par fluorescence X, Rapport final, IRSID, Saint-Germain-en-Laye, 1979, 13 pp.
[2]. Engelsen CJ, Effect of mineralizers in cement production, SINTEF Report, 2007, 25 pp.
[3]. Confederation of European Waste-to-Energy Plants, Bottom Ash fact sheet, Brussels, May 2016, 2 pp.
[4]. Karim F, Waqif M, Saâdi L. Caractérisation Physico-Chimique du Gypse Synthétisé et du Phosphogypse, Verres, Céramiques & Composites, 2011, 2(2) :19-31.
[5]. Schorcht F, Kourti I, Scalet BM, Roudier S, Sancho LD, Best Available Techniques (BAT), reference document for the production of cement, lime and magnesium oxide, JRC reference reports, 2013, 480 pp. ISBN 978-92-79-32944-9.
[6]. Mebarki H. Etude comparative des clinkers de l'ouest Algérien : Analyse Physico-chimique et Applications, Mémoire du Master Académique en Chimie, Faculté des Sciences, Université Abou Bakr Belkaïd de Tlemcen-Algérie, Septembre 2013, 99 pp.
[7]. Barton J and Guillemet C. Le Verre, Science et Technologies, EDP Sciences, 2005, 461 pp.
[8]. Meric J. Formation d'un clinker consommant peu d'énergie, 8èmes congrès internationaux de la chimie des ciments, Rio de Janeiro, Brasil, 1986, pp. 121-122.
[9]. Kacimi L, Ghomar A, Salem S and Derriche Z. Obtention d'un clinker portland consommant peu d'énergie, Université Mentouri, Constantine, Algérie, 2007, pp. 49-54.
[10]. Abdellah MM. Synthèse et caractérisation d'un ciment bélitique riche en AL-C2S et de haute réactivité hydraulique, Mémoire de Magister, Université des Sciences et de la Technologie d'Oran « Mohamed Boudiaf », Faculté des Sciences, 2009, 107p.
[11]. Rocher P. La pouzzolane, BRGM Auvergne, 2012, 4p.
[12]. Horkoss S. Influence du SO_3 dans le clinker sur la durabilité du béton : Attaque Sulfatique, Thèse, Faculté des sciences – Département de Chimie, Université Saint Joseph De Beyrouth, 2011, 67p.
[13]. Veli S, Kirli L, Alyuz B, Durmusoglu E. Characterization of Bottom Ash, Fly Ash, and Filter Cake Produced from Hazardous Waste Incineration. Polish J. of Environ. Stud., 2008, 17(1):139-145.

Appendix 1. Cement manufacturing process at LafargeHolcim Madagascar



Appendix 2. Formation of the clinker



Appendix 3: Clinkerization method in the laboratory under the muffle furnace

This is the determination of the behavior of the mineralizers and its mineralogical compositions, the process of which is the calcination of the samples by introducing the mixture into a platinum crucible in a muffle furnace for a period of 45 minutes at a defined temperature. By rapid cooling, the clinker is then obtained.

Appendix 4: Analysis under X-ray fluorescence spectrometer

The samples to be analyzed are presented in the form of beads made by melting at 1060°C, with Lithium Tetraborate and Lithium Bromide used as flux in the muffle furnace