Original Research Article

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

Affiliation 2: Ecole Supérieure Polytechnique d'Antananarivo, Campus Ambohitsaina, Antananarivo, Madagascar.

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ABSTRACT

This study presented laboratory tests on the effects of several mineralizers added to black raw materials, in the manufacture of cement. This manufacturing process is based on vintageshing quarry limestones with clays and fuels in order to be fired at 1450℃ 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℃, 1350℃, 1400℃ and 1450℃. 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 (LSF) 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 industry but possesses poor thermal conductivity despite the presence of reactive silicas while Sulfogypsum 1033 and 1034 are respectively rich in iron oxide and sulphur trioxide. They are responsible for the melting properties in the reaction of clinker formations.

At only 1350℃, our tests with Sulfogypsum (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 other mineralizers, their reactivity requires other conditions that will be the subject of another study.

Keywords: Mineralization, clinker, C_3S, LSF, 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 [1-2]. It is also world-renowned that this type of industry is responsible for air pollution through the emission of carbon dioxide (CO_2) [3]. It has to be noted that the problems linked to the heterogeneity of raw materials, and the ecological degradation are associated with its frequent exploitation [2]. 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 [2-3]. That is the reason why a cement industry 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 [3]. The choice of these raw materials was based on their reactivity and chemical composition but also on their accessibility to the industry. At our disposal, we had as mineralizers, the pozzolans as natural materials and industrial wastes such as glass, ash called BOTTOM ASH (BA) and FLY ASH (FA) as well as Sulfogypsum 1033 and 1034. In addition, industrial ash such as BA and FA are both waste from local industries and the reuse of Sulfogypsum for other purposes will protect the population from environmental hazards due to their release into the environment and storage. These wastes are known as residues containing significant impurities [4]. For Ibity industry, 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 industry; pozzolans from the Tritriva quarries and clays from the Andranomanelatra quarries.

It has to be noted that cement comes from the combination of pozzolan additions with the main material, called "clinker". The scheme below helps to better understand the cement manufacturing process at Ibity (see appendix 1) while the quality of cement depends on the best treatments and close monitoring of manufacturing processes (see appendix 2). Henceforth, the quality of the mineralized clinker after testing different performance indicators such as free lime content, alite (an impure form of tricalcium silicate or C_3S) and lime saturation factor can be determined.

Thus, three different types of vintagesvintages were formulated as controls for these experiments and they were named as follows:" a" the low LSF control, "b" the high LSF control and "c" with the average LSF. These controls correspond to the blends of vintages similar to those produced in this industry. At the very beginning, the aim was to study the efficiency of each mineralizers in relation to the addition proportion of these vintages, the effects of temperature and last the quality of vintages themselves. vintagesvintagesThen, the experiment was to test for the proportion of mineralizer additions at 1% and 4%, and following the literature, this temperature is between 1200 ℃ and 1500 ℃ [5].

In fact, the discussion would focused on the influences of these mineralizers in the raw material mixture, looking for the main parameters necessary to improve the cement quality. The main goal of this research was to find the best clinker, which could reduce the thermal energy expended in the formation of clinker while improving its quality. The emphasis was on the finding of the bestclinker firing temperature and on fixing the best mineralizer content added to the chosen raw material.

2. MATERIALS AND METHODS

2.1 Data Presentation

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 [5-6]. 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 of efficiencies are based on criteria where the phases of the bed, referred to as C_3S, are greater than 40%, and the free lime content is less than 1% [1, 5].

To achieve this, three distinct qualities of white vintages (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 [7]. The reactions of these mineralizers under the action of temperatures were then studied, from these values: 1250℃, 1350℃ and 1450℃ respectively.

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Table 1: Control analyses in mass percent

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI
a (LSF=90.91)	14.23	3.20	2.67	41.24	1.67	35.28
b (LSF=100.53)	13.31	2.81	2.32	42.33	1.63	35.35
c (LSF=95.54)	13.77	3.01	2.50	41.79	1.65	36.35

The basis of this study was to determine the reactivity of mineralizers to vintages 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 the used vintages was 1% and 4%.

Table 2 illustrates the results of chemical analyses performed on these mineralized materials.

Table 2: Chemical compositions of all mineralizers

	LOI	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 vintages 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.

2.2 Method Used

The different steps for the determination of a good clinker are represented in Figure 1 then constitute the analysis process used in the current study.

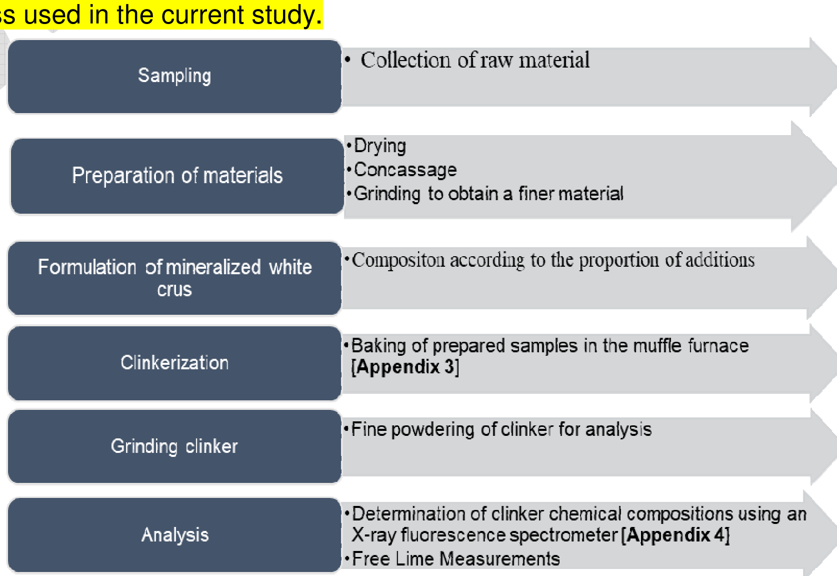

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Figure 1. Diagram of the laboratory test procedure

3. RESULTS AND DISCUSSION

3.1 Mineralizer

For a mineralizer to be efficient, it is sufficient to set all the conditions that allow it to react in the mixture. In the first trials, the proportion of addition of mineralizers added to controls a, b and c varied. First, 1% of the mineralizers are added to each control by setting the temperature at 1350°C. From each control, the results are presented below as shown by the following figures 2, 3 and 4.

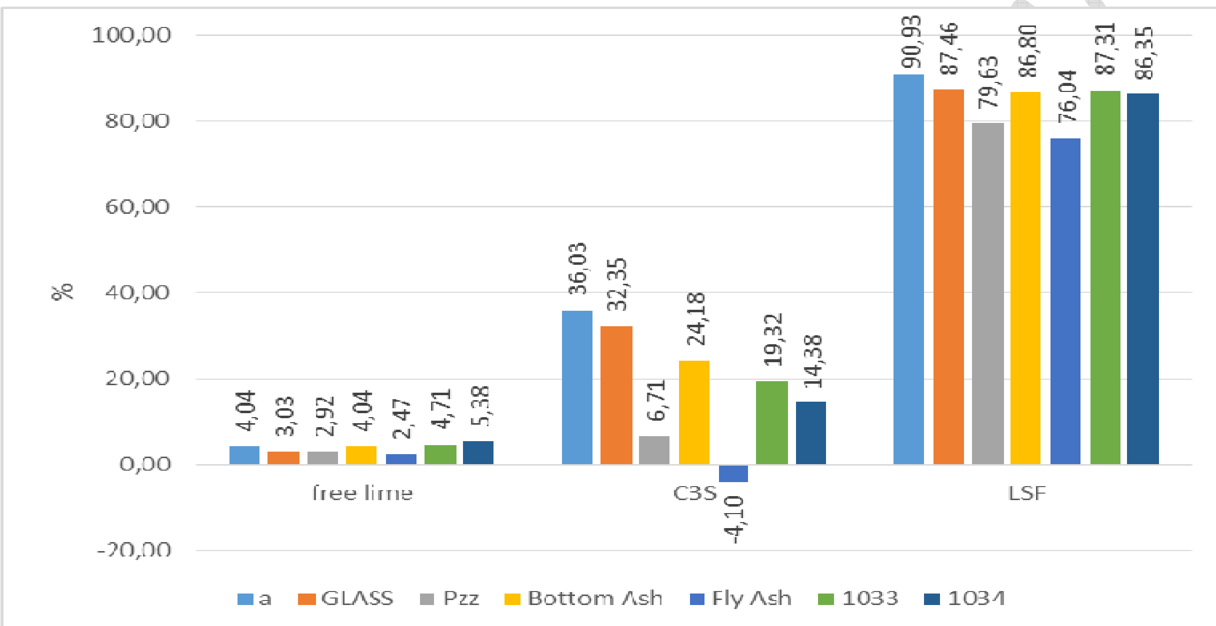

Figure 2: Mineralizers effects at 1% with control "a"

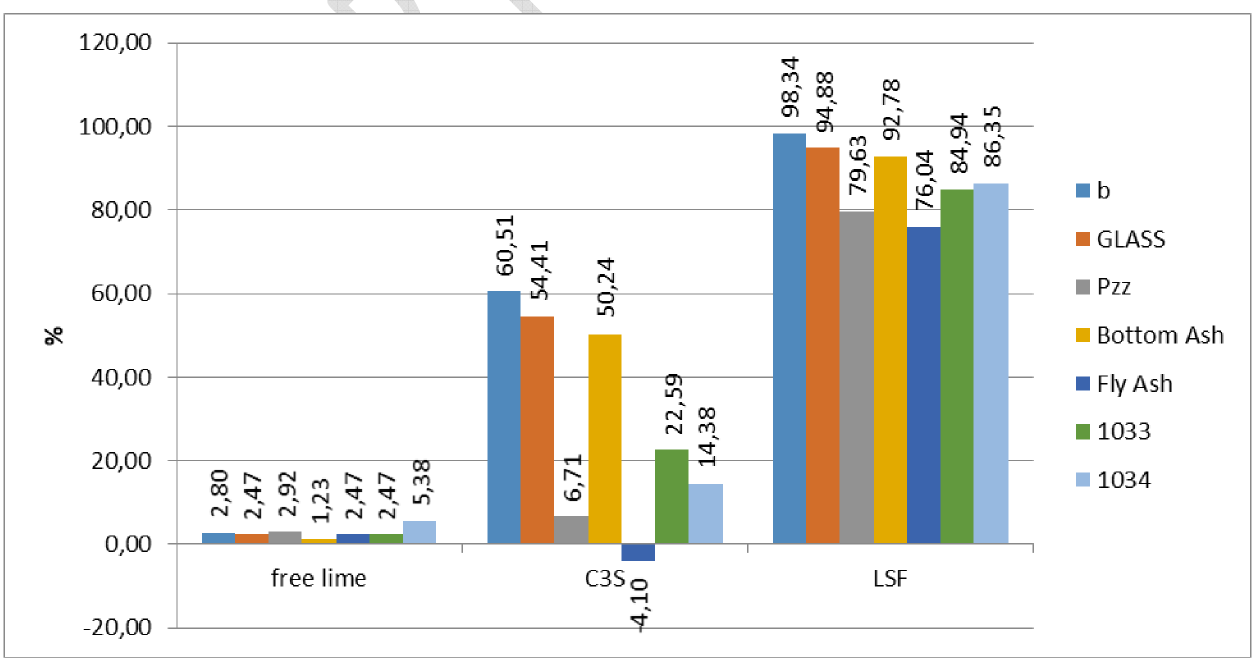

Figure 3: Mineralizers effects at 1% with control "b"

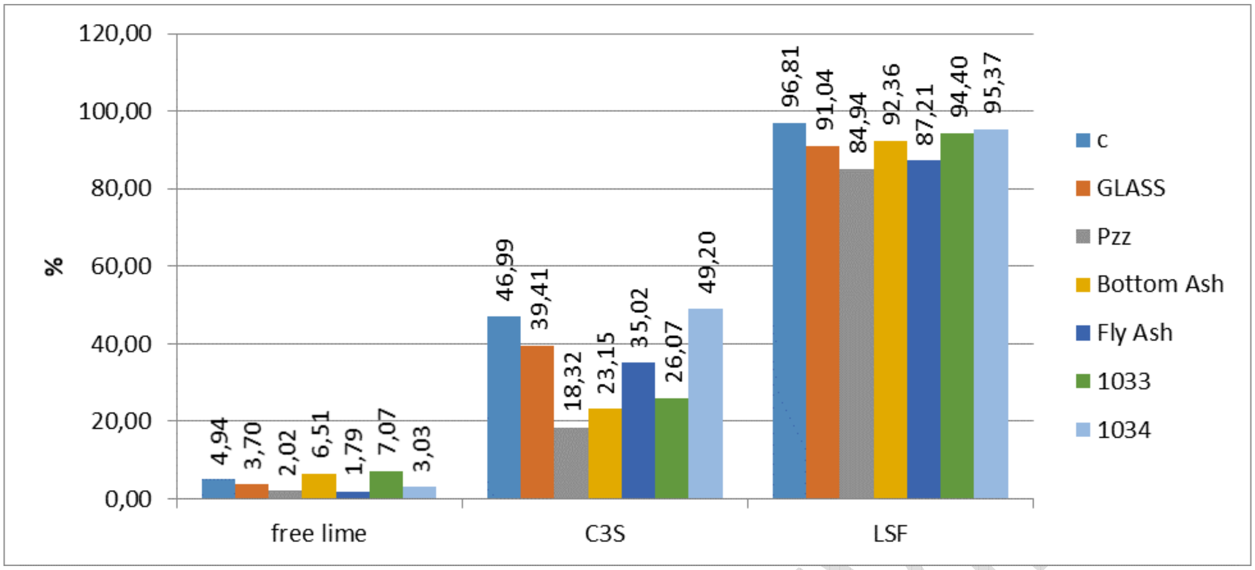

Figure 4: Mineralizers effects at 1% with control "c"

Considering the above figures, it should be stated that a mineralizer is conclusive if the C_3S of the black mineralized vintage exceeds that of the control. This is not observed for the case of 1% mineralizers with the indicator "a" which is illustrated in Figure 2. At 1% addition to the mixture, it may be deduced that industrial ashes (BA and FA) considerably reduce the free lime rate only at 1350℃ along with the three controls due to high Silicon oxide content in its chemical composition. FA reduces free lime to 2.47% when added with control "a" (Figure 2) and 1.79 % with control "c" (Figure 4) while the BA reduces this rate at 1.23 % when it is added with the indicator "b" (Figure 3). This phenomenon can be explained because of the presence of alumina as fluxes in industrial ashes and causes oxides to combine with each other [8-9].
With control "b" (Figure 1), the glass is able to form more alite than the other mineralizers which is 32.35% but does not exceed the control with 36.03%. 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 vintages (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 vintage mixture [7, 10]. The proportions of calcium oxides increased its reactivity with the medium lime saturated vintage. All these conditions together considerably produce the formation of alite and push this mineralizer to improve the control vintage because it was observed that the rate of C_3S increased from 46.99% to 49.20% (figure 3).

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.

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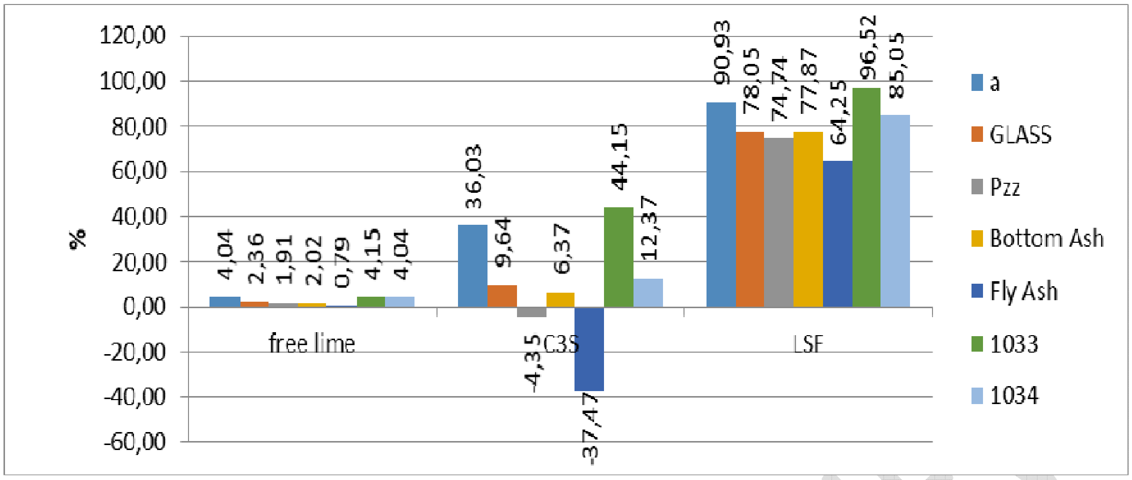

Figure 5: Mineralizers effects at 4% with control "a"

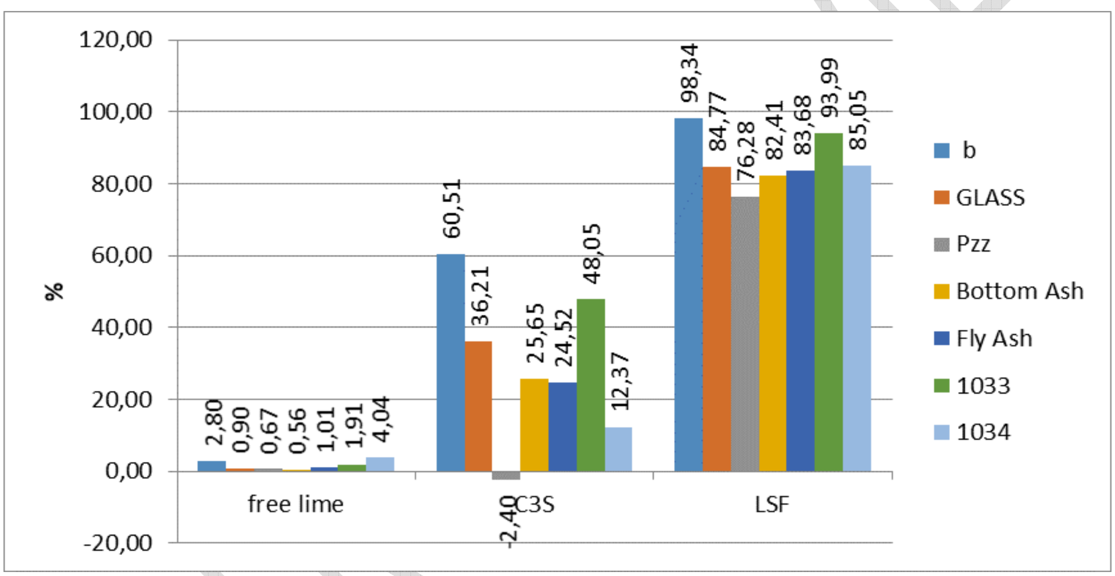

Figure 6: Mineralizers effects at 4% with control "b"

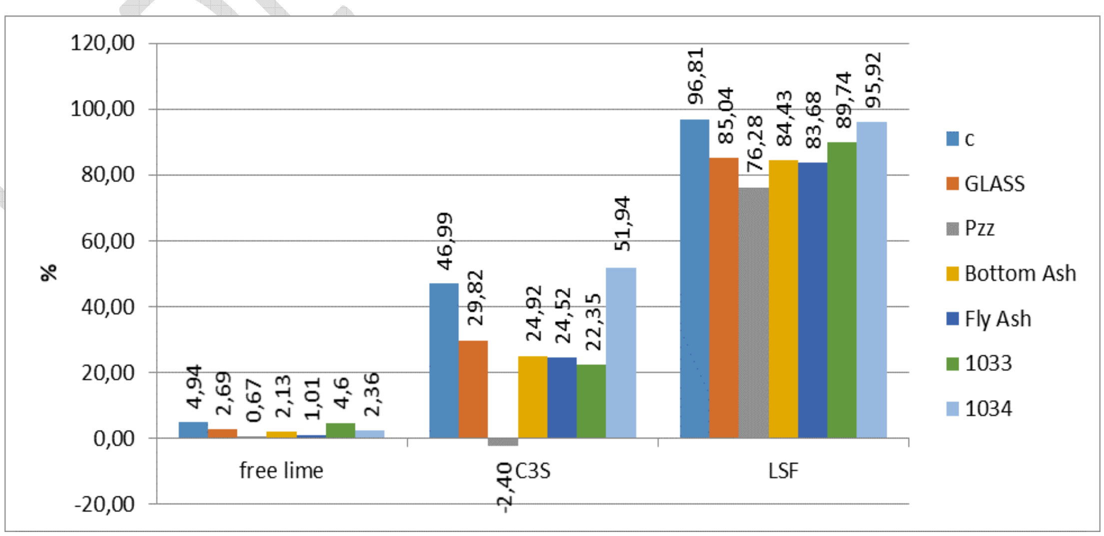

Figure 7: Mineralizers effects at 4% with control "c"

It was observed that the mineralizer addition at 4% increased the rate of C_3SSulfogypsum 1033 reacts distinctly with controls "a" and "b" with the vintage having a low lime saturation factor (LSF), meanwhile the "1033" forms more C_3S levels than the control which is 44.15% (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 C_3A and C_4AF 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 vintage (Figure 6). As observed in the figure 6 above, the control "b" mineralized with 1033 gives a C_3S of 48.05% which is lower than those of the control. Thus, there are still lime not combined with oxides.

On the other hand, the "1034" still only reacts with the control "c" (Figure 7). This mineralizer does not require a high lime saturation vintage 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, the pozzolan reduces this rate by less than 1% with the control "b" because it has the ability to bind with calcium oxides at low temperatures thanks to its melting temperature of 1140℃ [7, 11].

3.2 Effect of firing temperature

Different tests presented in section 3.1 highlight the role of temperature on the evolution of the clinker quality for the same temperature at 1350 ℃. This process would consist of detecting the effects of different minerals present in the vintage mixtures with the temperature variation between 1250℃ and 1450℃.

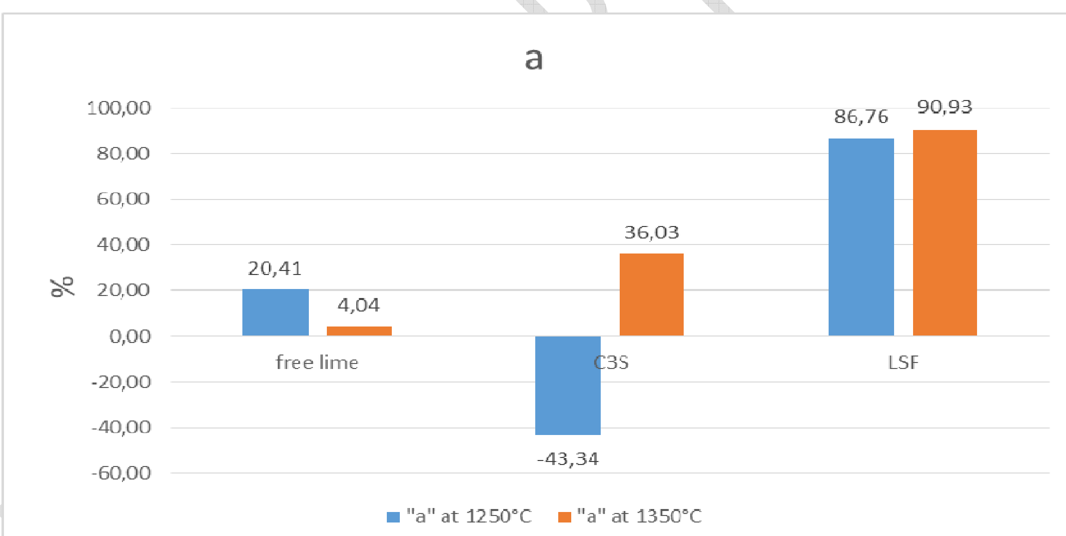

Figure 8: Evolution of temperature with control “a”

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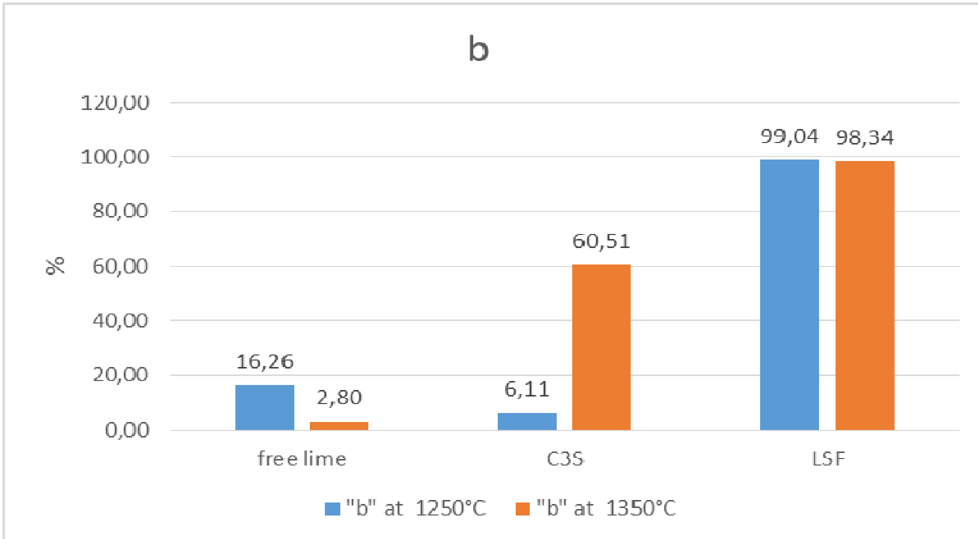

Figure 9: Evolution of temperature with control "b"

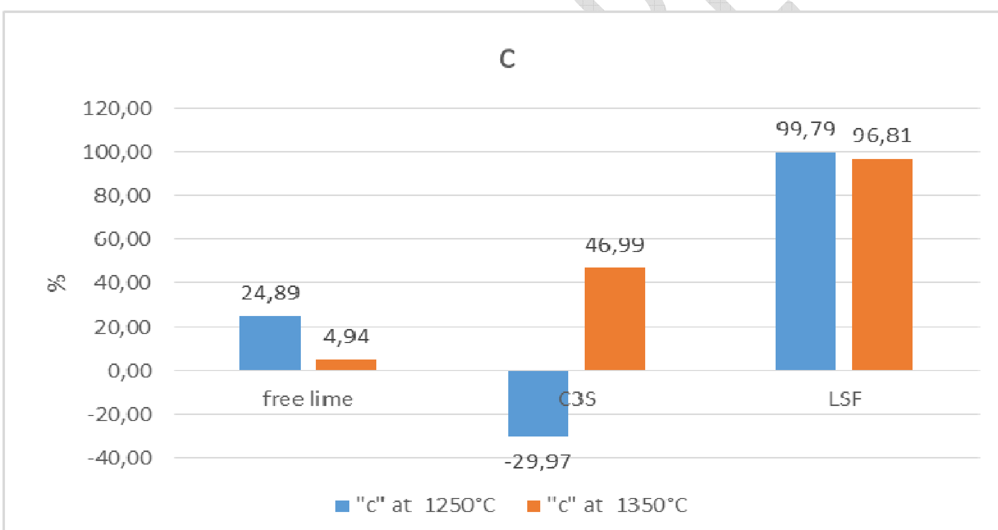

Figure 10: Evolution of temperature with control "c"

With the control tests a, b and c, the C_3S values increased remarkably with the increase in clinker firing temperature between 1250℃ and 1350℃. Figure 9 shows this important evolution of C_3S from 6.11% to 60.51%. This remarkable increase in these indicators is seen in the figures above (8-10). However, the free lime rate drops sharply up to 2.80%, especially with the vintage "b". This efficiency is due to the high lime content of this flour. The mineralizers demonstrated their ability to react under the influence of temperature i.e. the efficiency of C_3S 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 C_3A and C_4AF knowing that these mineral reactivities require an optimum temperature.

Among these 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 figures above. The C_3S rate increases according to the saturation rate of lime present in the vintage. Some minerals in the vintage then require a temperature rise of 100 ℃ to combine all the oxides with lime and at the same time decreasing the free lime content of 4.04% with the control "a" (Figure 8), 2.8% (Figure 9) with the control "b" and 4.94% for the control "c" (Figure 10).

Figures 10-12 illustrate the importance of the role of temperature in the current study. For the next step, we chose “glass” as one of the mineralizers in our tests for a good understanding of its efficiency in relation to the temperature changes. “Glass” was taken as one of the mineralizers to be studied; it is because of its ability to melt at low temperature [2, 12].

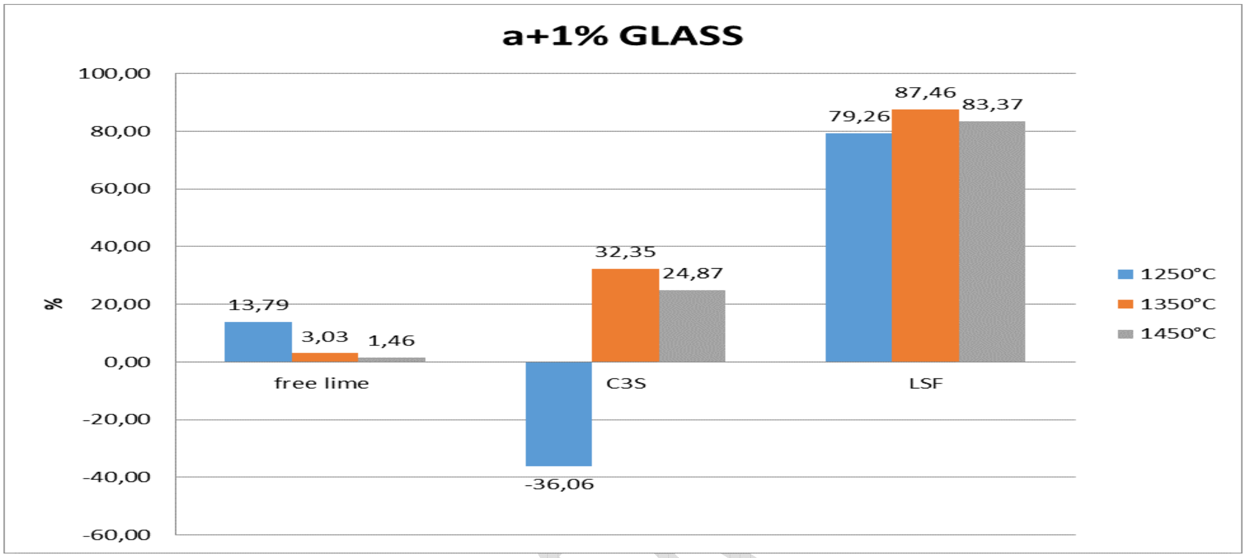

Figure 11: Evolution of temperature of glass at 1% with control “a”

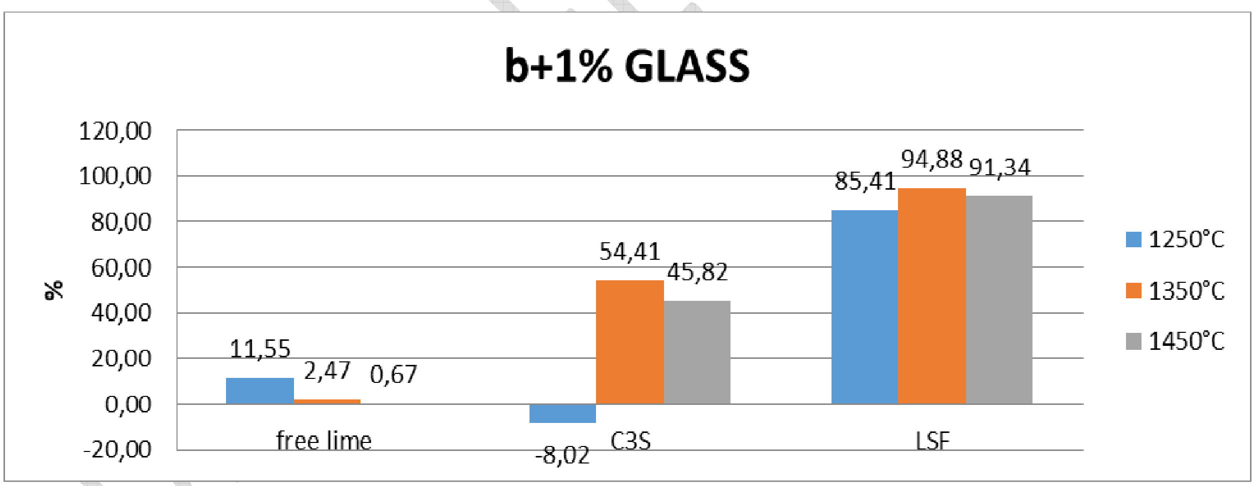

Figure 12: Evolution of temperature of glass at 1% with control “b”

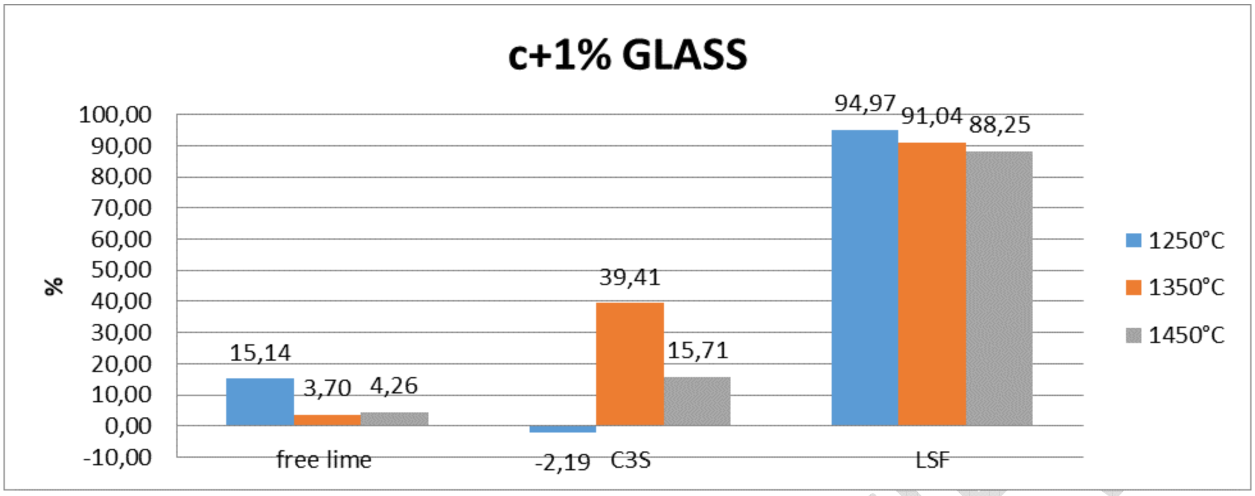

Figure 13: Evolution of temperature of glass at 1% with control “c”

The reactivity of glass with 1% of addition to the three controls “a”, “b” and “c” was compared and the above figures show that the mixture remains unchanged at 1250℃. This poorly cooked character is presented by the high values of free lime, which are 13.79% with "a", 11.55% with "b" and 15.14% with "c". But with the three different vintages, the glass remarkably reduced the free lime content when the temperature increased. This rate was reduced to 0.67% when mixed with control "b" (Figure 12) and the formation of C_3S is more favored with this increase in lime saturation in the vintage. All silica thus succeeds in filling all the maximum lime present in the vintage "b" and reduces the number of non-combined lime. This phenomenon is shown in the above figures whereby there was an increased clinkerization temperature to an optimum temperature of 1350 ℃, as it is the case at 1450 ℃, the C_3S decreases to 45.82%. The abundance of amorphous silicas in the chemical composition of the glass helps to better react considerably. So, its melting characteristic 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 [1]. On the other hand, it was observed that "a" containing very little lime does not react efficiently with the glass even if we increased the firing temperature; the C_3S cannot exceed 40% (figure 11) and we had only 24.87% at 1450 ° C. Similarly, for the "c" tests, only 15.73% of C_3S was obtained at 1450℃ (figure 13). The effectiveness of the glass is seen only when it is mixed with a vintage of good quality.

The rate of addition provided that all the silica in the mineralizer is combined with the lime in the vintages meanwhile non-combined lime and silica become free lime and silica respectively. These conditions later in the process would probably harm the quality of cement produced [2, 5, 7, 10].

4. CONCLUSION

The mineralization was considered as one of the best solutions for a good production in quantity and quality of cement. The main aim of this study was to find the best mineralizers that can improve the clinker quality while reducing the clinkerization temperature to improve processes. These various facts led us to value natural materials and transform industrial wastes into a clinker mineralizer.

The findings of this study showed that not all mineralizers reacted at a low temperature of 1250 ℃. The Pozzolan is one of the raw materials used in the Ibity cement industry. Its mixture with the vintage "b" had the effect of reducing the clinker firing temperature while remarkably reducing the free lime content to less than 1% but it lacks 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.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 SO_3 content in the mixture to further promote

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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 vintages. These experiments then allowed to prove that the glass can react well under the clinkerization temperature of 1350℃ and with the type of raw material with a high FSC level.

Moreover, at a clinker temperature of 1350 ℃, It was found that the sulphate 1033 as mineralizer was added if the quality of the type "a" and sulphogypsum 1034 was improved in case where if a vintagevintage of type "c" is received. These mineralizers then make us benefit from a temperature decrease of 100℃ during the formation of the clinker, which represents a significant thermal energy gain. Following the findings presented, the sulphogypsum 1034 were the best mineralizers because the improvement in the clinkerization process met our expectations.

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

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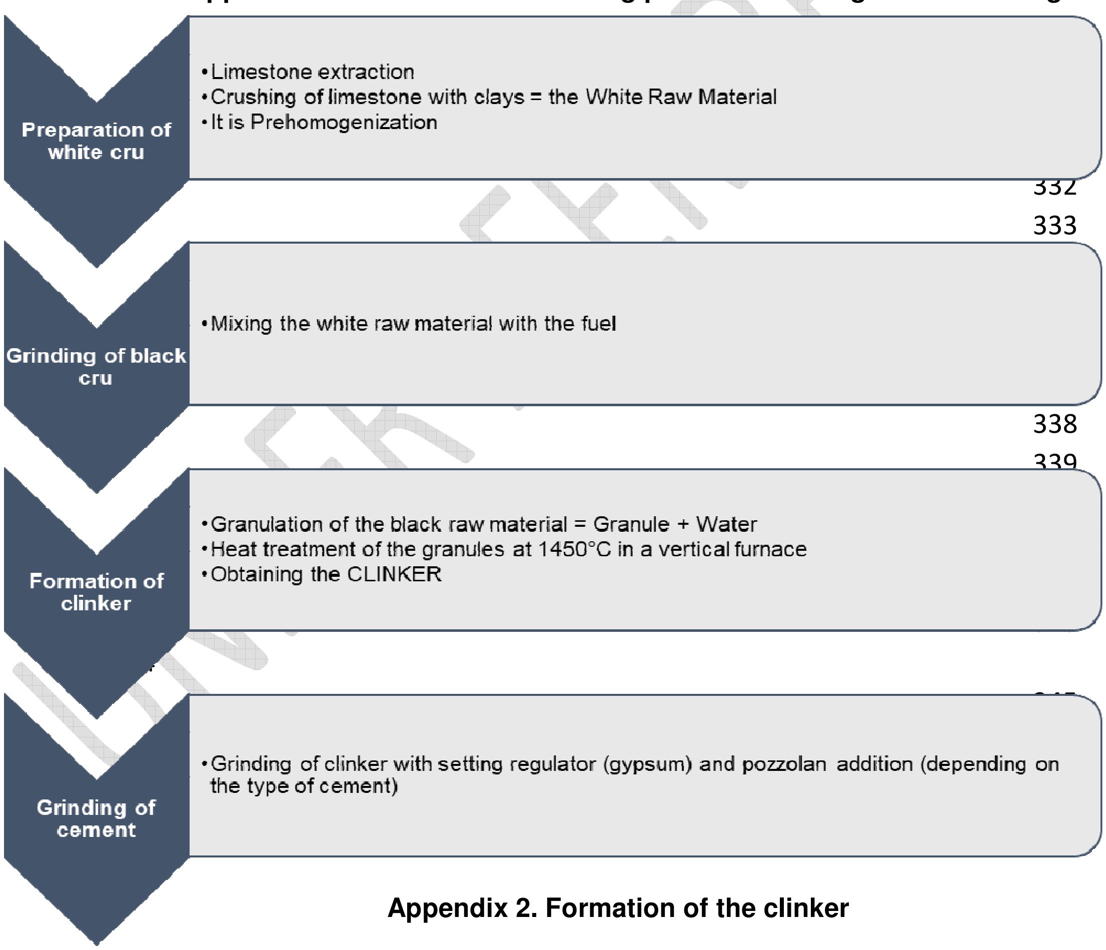
Appendix 1. Cement manufacturing process at LafargeHolcim Madagascar



Appendix 2. Formation of the clinker

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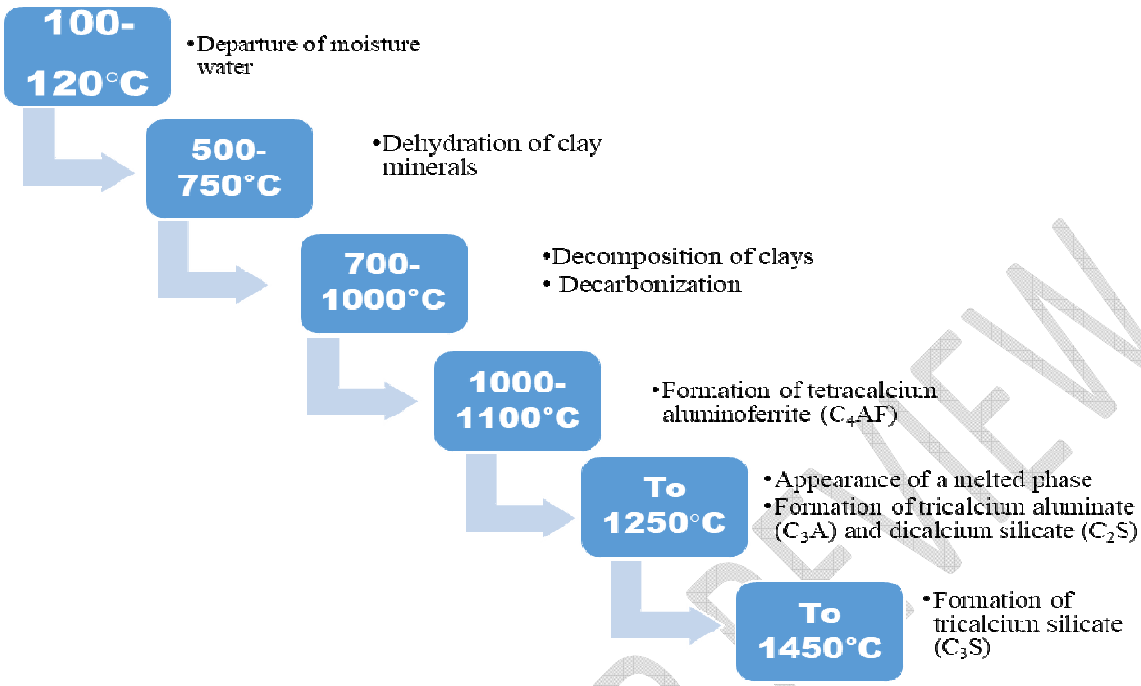

Appendix 3: Clinkerization method in the laboratory under the muffle furnace

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 vintagecible 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

ABBREVIATIONS

- **BA:** Bottom Ash or heavy ash
- **C_2S:** Bi-calcium silicate or (belite), its chemical formula is 2CaO, SiO2.
- **C_3A:** Tricalcium aluminates or (Celite), its chemical formula is 3CaO, Al2O3.
- **C_3S:** named tricalcium silicate (alite), its chemical formula is 3CaO, SiO2.
- **C_4AF:** Tetra-calcic ferroaluminates, of chemical formula is 4CaO, Al2O3, Fe2O3.
- **FA:** Fly Ash or flying ash
- **LSF :** Lime Saturation Factor
- **LOI:** Loss on Ignition
- **Pzz:** Pozzolan
- **SO_3:** Sulfur trioxide

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