Characterization of mahogany bark ash for its use as supplementary cementitious material and its behavior in a cement paste at its earlier age

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ABSTRACT
The cement demand is constantly increasing in Africa while the production of clinker is still not the most environmentally friendly process. Besides, the agriculture is this the backbone of the economy many African countries. Based on these two observations, more studies are now focused on the use of waste from agriculture in concrete technology. In this framework, the ashes of the bark of Mahogany tree were studied to be used as a supplementary cementitious material (SCM). This article presents the characterization of ashes produced by different process and the behaviour of Mahogany bark ash in a cement paste. The results show that the calcination of Mahogany bark induces ashes with a high content of calcium oxide. The composition of the ashes is not affected by the calcination mode. Moreover, the substitution of cement with the Mahogany bark ash increases the heat of hydration of the cement paste and this also affects the rheology of the modified cement paste.

Keywords: Mahogany bark ash, SCM, characterization, calcination temperature, cement paste.

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ISSN No.: 2521-8263

CEMENT & CONCRETE SA

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The cement demand is constantly increasing in Africa while the production of clinker is still not the most environmentally friendly process. Besides, the agriculture is this the backbone of the economy many African countries. Based on these two observations, more studies are now focused on the use of waste from agriculture in concrete technology. In this framework, the ashes of the bark of Mahogany tree were studied to be used as a supplementary cementitious material (SCM). This article presents the characterization of ashes produced by different process and the behaviour of Mahogany bark ash in a cement paste. The results show that the calcination of Mahogany bark induces ashes with a high content of calcium oxide. The composition of the ashes is not affected by the calcination mode. Moreover, the substitution of cement with the Mahogany bark ash increases the heat of hydration of the cement paste and this also affects the rheology of the modified cement paste.

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1. INTRODUCTION

The demand of cement is in constant increase all over the globe but mainly in developing countries. This is due to the economic growth in these countries that lead to the development of infrastructures. This is the case for almost all the sub-Saharan African countries. Besides, it is in this region that the cost of the cement is still high compared to the rest of the continent.

Moreover, it is clearly known that the production of clinker is not the most environmentally friendly technology in construction field, even though concrete is one of the most used materials on the earth. Indeed, the cement industry highly pollutes the environment since it produces 900 kg of CO^2 per ton of cement [1].

In the case of African sub-Saharan regions, this observation is more blatant since this region hardly produces cement replacement like GGBFS or fly ash, and not even concrete chemical admixtures. Moreover, most of the sub-Saharan country economies are still based mainly on the agriculture. Indeed, this region is known for its extreme diverse agricultural products. Therefore, it is easy to imagine the huge amount of agricultural waste which is most of the time not used. Though some agro-waste materials have already started to be used in the formulation of cements, such as rice husk ash and cassava peels [2,3], the majority remains unexploited.

The Adaptation of systemic infrastructural concrete structures to environmental challenges and risks (INFRACOST) project aims to develop adequate materials for infrastructure rehabilitations in Sub-Saharan region and to promote more waste materials by using them in concrete technology. It was in the framework that some agro-waste were selected based on their availability to their possibility to be used as supplementary cementitious materials (SCMs). This was the case for the Mahogany bark. Mahogany is ranked as one of the best-known and most valuable tropical timbers on the international market [4]. Mahoganies are distributed across Africa in Benin, Ghana, Ivory Coast, Sudan, Togo, D.R Congo and Uganda. 327,119 m^3 of Mahogany wood were exported from Ghana alone from 2000 to 2015 [4], not including locally used wood. This shows that the waste from the Mahogany wood production is abundant enough for it to a good source of economical SCMs.

This article focuses on the calcination of the Mahogany bark to obtain ashes and on the impact of Mahogany ash on a cement paste. The ashes were produced at different calcination temperatures, then they were characterized to select the one with the highest potential alkali-reactivity. The ash with the highest potential alkali-reactivity was used to substitute the cement and the properties of the modified cement paste was analysed.

2. MATERIALS AND TECHNIQUES

2.1 Calcination

To determine the optimal calcination temperature, a part of the Mahogany bark powder was calcinated at the following temperatures: 600, 700, 800, 900 and 1000 °C for an hour with a pre-firing of 20 min in an open flame to burn the organic phase that induces smoke. These calcinations were done in platinum crucibles. After the selection of the optimum temperature, the remaining Mahogany bark powder was calcinated in an electric furnace for 12 hours at this temperature. These second calcinations were done in ceramic crucibles.

2.2 X-ray diffraction (XRD)

X-ray diffraction was done on all ash samples from the initial burning process and the final burning process. All samples were grinded and compacted in the holder to ensure accuracy. The device used was made by Rigaku incorporating the Ultima IV X-ray diffraction (XRD) systems. The program used for XRD results analysis was Match! 3 version 3.8.3.151 64-bit. The reference database was Crystallography Open Database (COD).

2.3 Chemical analysis and loss of ignition

The chemical analysis and the loss of ignition of the ashes were realised in accordance to the European standard EN 196 [5].

2.4 Consistency

The device used for this test was a CT3 Texture Analyzer made by Bookfield. The program used to collect the data was TexturePro CT V1.9 Build 35. The machine was set up to use a spherical probe of 12.7 mm of diameter that was lowered at a rate 1mm/s into the cement mix sample. The device measures the resistance exerted by the cement mix during the lowering of the probe. The samples were prepared in cylinder containers with the height of 32mm and a diameter of 34mm. The samples were measured at 6 different time intervals after mixing: 0, 0.5, 1, 1.5, 2 and 3h.

2.5 Heat of hydration test

The evolution of heat during hydration was measured for the control mix and all the mixes. A Thermometric TAM Air calorimeter was used to measure all the samples. The calorimeter was calibrated for 3g samples at 20°C. The samples were prepared in accordance with EN 196-11 [5].

3. RESULTS

3.1 Influence of the temperature on the calcination yield and on the composition of the Mahogany bark ashes

The Table 1 shows that the loss of the matter increased with the calcination temperature. At 600°C, only 13% of the bark ash was collected at the end of the calcination, while it was remaining only 7% of the matter at the end of the calcination at 1000°C. however, this yield seems to become constant from 900°C. These results are similar the one obtained with the rice husk that are also calcinated to be used as SCMs [2,3,6].

Table 1: Lost yield after the calcination of Mahogany bark at different temperatures

Temperature	600°C	700°C	800°C	900°C	1000°C
Lost yield	86.80%	87.40%	81.60%	93.24%	93.82%

Table 2: Composition of the Mahogany bark ashes

%		T 600	T 700	T800	T 900	T 1000
Silicium	**SiO_2**	12.02	12.51	13.22	13.05	17.69
Aluminium	**Al_2O_3**	0.08	0.10	0.14	0.45	0.18
Iron	**Fe_2O_3**	0.07	0.07	0.22	0.20	0.22
Titan	**TiO_2**	0.01	0.02	0.01	0.02	0.02
Calcium	**CaO**	2.76	4.12	32.55	58.99	2.26
Magnesium	**MgO**	0.29	0.37	1.42	3.15	0.17
Natriumoxid	**Na_2O**	0.20	0.33	0.13	0.11	0.30
Kaliumoxid	**K_2O**	7.02	7.42	4.02	5.12	4.50
Sulfat	**SO_3**	3.76	3.50	1.49	2.86	4.71
Phosphat	**P_2O_5**	1.14	1.11	0.33	1.00	1.57
Rest		72.65	70.45	46.47	15.05	68.38

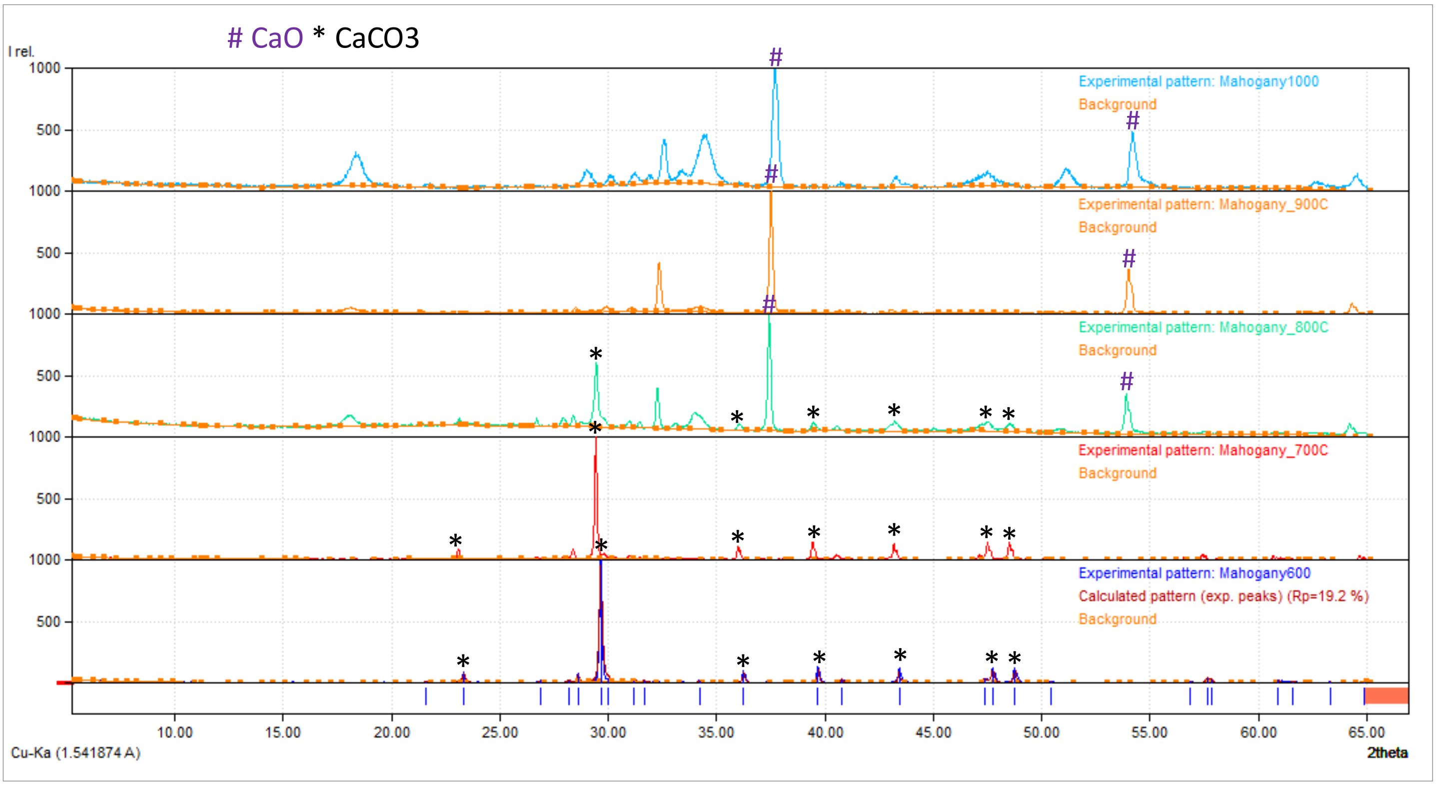

Figure 1: X-Ray spectra of Mahogany bark ashes

The composition of each of these ashes was found with the combination of their X-ray spectrum (Figure 2), and results of their chemical analysis (Table 2). The major observation is the presence of calcium carbonate (CaCO3) between 600°C and 800°C, which is transform into calcium oxide (CaO) above 800°C (1).

$CaCO_3 \rightarrow CaO + CO_2$ Equation (1)

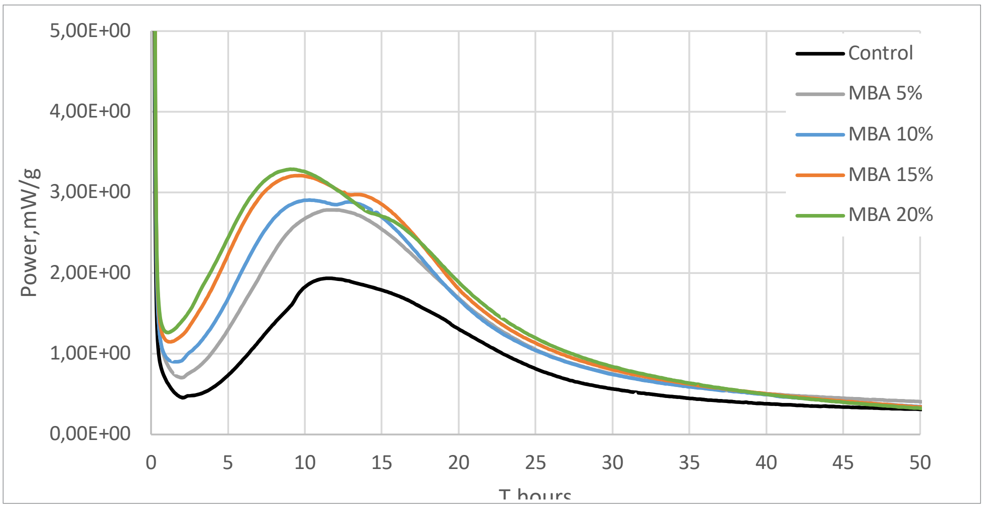

Figure 2: Heat of hydration of cement pastes modified with Mahogany bark ash

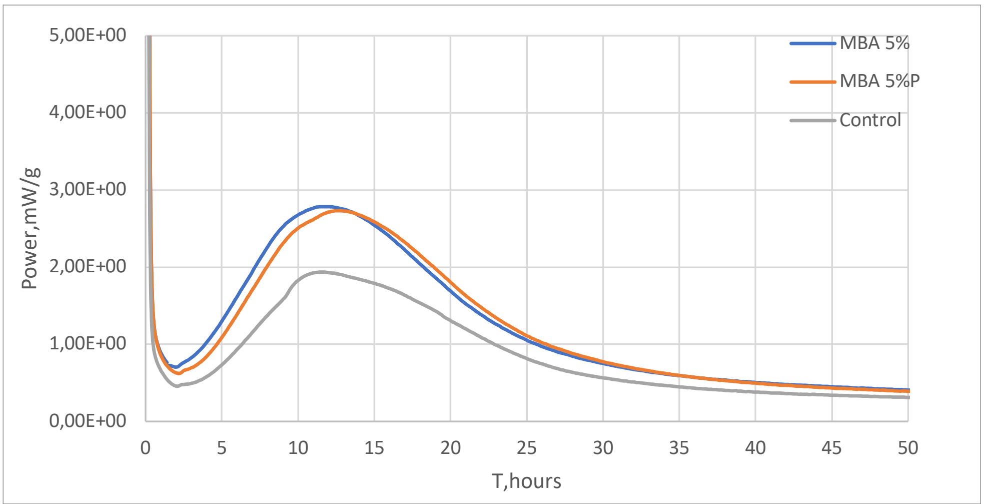

Figure 3: Evolution of the heat of hydration of cement pastes modified with Mahogany bark ash with a superplasticizer

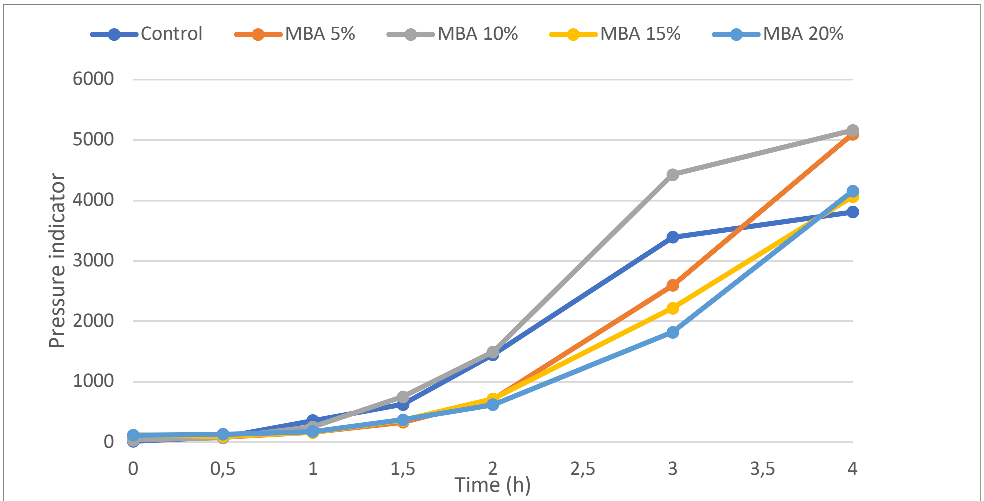

Figure 4: Consistency of the cement pastes modified with Mahogany bark ash

The other minerals found during the chemical analysis appeared on a very low amount (lower than 5%), except for the phosphor oxide that has a percentage of around 7% before 800°C and around 4% from 800°C. Therefore, the choice for the optimum calcination temperature was made based only on the amounts of silica and calcium oxide. Thus, the optimum temperature was 900°C, since the calcium oxide is at its highest percentage (58,99%) and the percentage of silica is similar the one at 800°C (13,35%).

3.2 Substitution of cement with Mahogany bark ash on a cement paste

3.2.1 Evolution of the hydration

The Figure 2 presents the evolution of the heat of hydration in function of the percentage of substitution of the cement by of the Mahogany bark ash. This heat increases and appears earlier with the increase of the substitution rate. This is due to the rapid and exothermic reaction of calcium oxide with water (2).

$CaO + H_2O \rightarrow Ca(OH)_2$ Equation (2)

This acceleration of the hydration induced by the Mahogany bark ash may be an asset for the cement paste in the case of the elaboration cementitious materials that aim to set quickly. However, this acceleration can also play against the durability of cementitious materials by creating extra-internal heat that can lead to microcracking [7]. Furthermore, the rapid hydration of the CaO can reduce water in the system, available for the cement hydration.

3.2.3 Effect on the paste consistency

The results of the evolution of the consistency were presented on the Figure 4. Globally, the pressure applied on the samples started to increase after an hour, and the differences of pressure clearly appeared after 1,5h. Between 1h and 3h, the pressures of the cement paste without ash (control) and the one with 10% (MBA 10%) of ash were the highest, meaning they were the paste with the fastest setting. On the same period, the pressure of the three other modified cement pastes (MBA 5%, MBA 15%, and MBA 20%) were decreasing with the increase of the amount of ash. After 4h, the unmodified cement paste and the one with 15 and 20% of Mahogany bark ash were presenting the lowest pressures, while the one with 5 and 10% one had the highest pressures.

3.2.4 Effect on the paste consistency in presence of superplasticizer

The Figure 5 shows that the cement paste that contains both the ash and the superplasticizer (MBA 5%P) had the lowest pressure between 0,5h and 3h, while the unmodified cement paste had the highest pressure on that same interval. But at 4h, the modified pastes had similar pressures and higher than for the control one. According to these results, the superplasticizer tends to slow the settling of the modified cement paste.

4. DISCUSSION

Regarding the composition of the Mahogany bark ashes in function of the calcination temperature, the XRD spectra showed that there were some pics that were not able to be identified. This observation is aligned with the chemical analysis results. Indeed, for almost all the calcination more than the half of the samples could not be identified by this method. These results can be explained by the fact that the measurement methods used for the characterization of this bio-ash are the same commonly used for classic cementitious materials. Indeed, there was a limitation in the type of elements that can be analysed with the chemical analysis, for instance the carbon that could not be analysed. Therefore, these results could be questionable, and they should be confirmed by other methods of characterisation, more appropriate to bio-based materials.

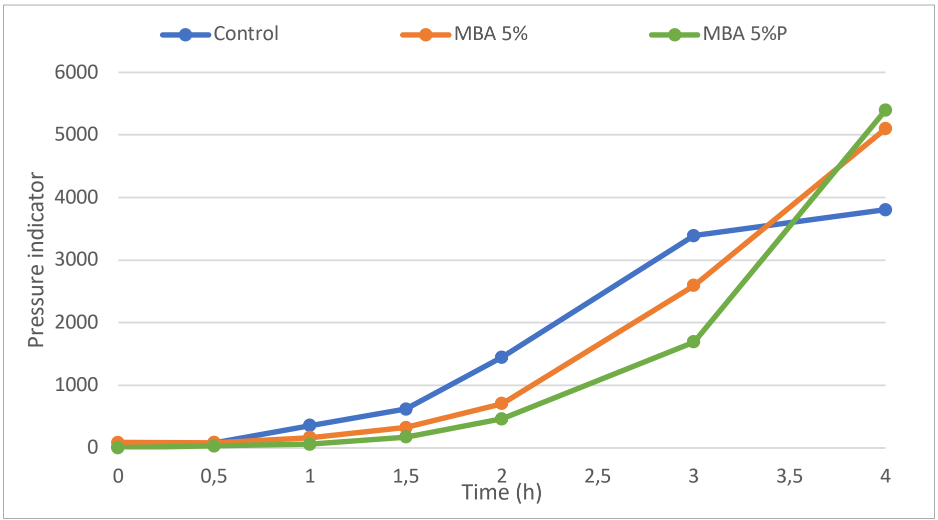

Figure 5: Consistency of a cement paste modified with Mahogany bark ash with a superplasticizer

In the same line, the outcomes on the consistency can also be doubtful. Indeed, it was showed that the almost all the cement pastes modified with the Mahogany bark ash slowly settled, compared to the unmodified cement paste. However, the Mahogany bark ash contained in majority the calcium oxide, according to the results of their characterization. This was also illustrated with the increase of the temperature and the heat of the hydration observed with the calorimetry measurements because of the hydration of the calcium oxide. Therefore, it was expected that the modified pastes settle faster than the unmodified paste.

Finally, there was no difference in the results when a superplasticizer was added to the modified cement paste.

4. CONCLUSION

This article deals with the influence of the temperature on the composition of the Mahogany bark ashes and their potential to be used as a SCM. The characterisation of these ashes showed that the classic methods and techniques used for the characterisation of cementitious materials might not be the most adequate for this bio-waste materials. Indeed, there was a huge part of the samples which could not be identified. Moreover, the behaviour of cement pastes, in which a percentage of cement was substituted with the Mahogany bark ash, tended to delay the settling. This result was not expected since the ash contained a high amount of calcium oxide which hardens rapidly with water. To sum up, it will be interesting to look for adequate methods and techniques for the bio-waste materials. CB

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