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## Chemical, thermal and mineralogical characteristics of concretes in stabilized soil with sugar cane molasses

Nice Ngouallat Mfoutou<sup>1</sup>, Narcisse Malanda<sup>1</sup>, Erman Eloge Nzaba Madila<sup>2</sup>,  
Paul Louzolo-Kimbembe<sup>1,3</sup>

<sup>1</sup>Higher National Polytechnic School, Mechanics, Energy and Engineering Laboratory, Marien Ngouabi University, BP 69, Brazzaville, Congo

<sup>2</sup>Higher Institute of Architecture, Building Planning and Public Works, Denis SASSOU N'GUESSO University, Kintélé, Congo

<sup>3</sup>University of Quebec, Trois Rivieres, Hydrogen research institute, Quebec Canada

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**Abstract** This paper scrutinizes MEDDRX, TGA, IR, DTA's analyses performed on stabilized soil concrete with sugar cane molasses. It is important to underline that the soil remains the principal material in house construction in the Republic of the Congo. The use of sugar cane molasses as a stabilizing to bricks and soil roads appears as an alternative solution to valorise this agro-industrial by-product; moreover, sugar cane molasses has led to obtain soil-made materials with highly enhanced mechanical properties. Therefore, this study has enabled to determine the evolution of induced structure by the presence of molasses within the soil matrix. As a consequence, the final results clearly indicate that the molasses brings no alteration to kaolinite's structure. However, molasses spreads on basal and lateral surface of clay, and sugar groupings establish physical interactions with silanol and aluminol groupings of clay's external surface. Thereby, the interaction between molasses and clay of soil is essentially physical. Molasses' presence within stabilized soil matrix is ascertained by the appearance of thermal peaks attributed to sucrose pyrolysis, whereas the appearance of absorption bands is attributed to aromatic compounds responsible of the colouring. The thermal decomposition of stabilized soil with molasses takes place following four thermal peaks: 150-200 °C, 300 °C, 480-500 °C, and 700 °C.

**Keywords** Characteristics, chemical, thermal, mineralogical, soil concrete, stabilization, fine soil of stabilized concrete and caused by dyes presented in the clayey molasses, sugar cane molasses

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### 1. Introduction

The soil remains the principal material in house construction in the Republic of the Congo. As a matter of fact, the analysis, following the different departments throughout the country, illustrates that clay bricks construction prevails in the departments of Bouenza (76.3%) and Niari (60.6%) where these clayey soils seem the most adequate materials. Nevertheless, 52% of households in Cuvette Department, and 5% in Plateaux department have lodgings with precarious and dangerously fragile walls [1].

However, the techniques used in elaborating soil construction materials remained quite archaic. Nevertheless, constructions' sustainability and resistance at the factory and to the laundry due to the rain waters remain major problems in the sector of construction with soil. Consequent decisions for a sustainable development in this key sector are taken henceforth.

Sugar cane molasses is particularly used during the dry season to attenuate dust and stabilize soils on soil roads in the city of Nkayi (figure 1). This operation of technical nature proves a cohesive and quite noticeable reaction on soils' aggregates. In this connection, Malanda and al. (2017) observed an increased resistance of stabilized raw soil bricks with molasses [2].





Figure 1: Sugar cane molasses poured on a soil road in the city of Nkayi

As a consequence, the use of molasses as a stabilizing for soil bricks or for the stabilization of soils for soil roads appears as an alternative solution in the frame of sustainability of the above-mentioned materials. The aim of this study is to determine the evolution of implicated structure by the presence of molasses within the soil matrix. To do so, stabilized clay concretes with a certain quantity of molasses have been submitted to many analyses: Infrared Spectroscopy, Electronic Microscopy of sweeping (EMS). It analyses thermo gravimetric Analysis (ATG), and Differential Thermal Analysis (DTA). For, Differential Thermal Analyses (DTA) of sweeping and gravimetric Analyses (TGA) are used to evaluate fusion temperatures, of crystallization, of glass transition, and thermal decomposition.

## 2. Material and methods

### 2.1. Material

The molasses and soil, from the city of Nkayi in Bouenza Department (Republic of Congo), are basic materials of our study.

#### 2.1.1. Soil sampling site

The soil, is extracted from a depth of one meter (1m), so as to reduce in middle the presence of organic materials in this soil. The sampling zone of soil samples in the city of Nkayi, department of Bouenza (Republic of Congo) is shown on the figure 2.

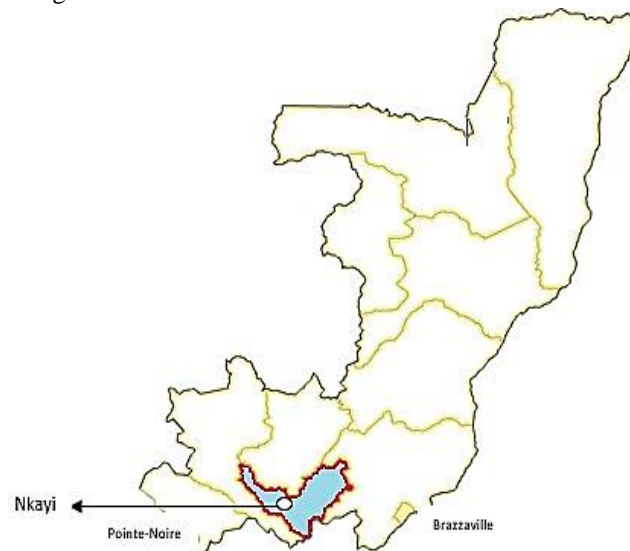


Figure 2: The sampling zone soil samples. Republic of Congo



In this way, in this operationalization, after the sampling on the site, the soil is brought to the Civil-Engineering Laboratory, National Higher Polytechnical College (ENSP) Marien Nguabi University, Brazzaville, for different analyses before being forwarded to the laboratory of the Hydrogen Institute of Research, university of Quebec at Trois Rivières, Quebec, Canada.



Figure 3: Yellow soil sample in the city of Nkayi



Figure 4: Powder of obtained soil from sieve 0.4mm, intended to the preparation of stabilized clay cakes

### 2.1.2. Geotechnical characteristics of the soil sample

The results of some geotechnical tests performed on the soil are presented in table 1. In accordance with the norm XP P 13-901 (picture 5), Nkayi's soil is optimal for bricks production. It presents an adapted plasticity for the BTC.

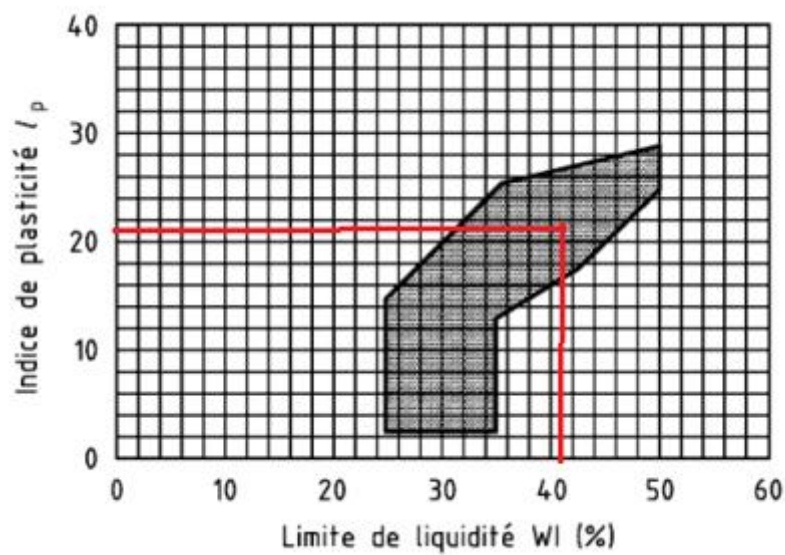


Figure 5: Plasticity diagram (the norm XP P 13-901) of Nkayi's soil



**Table 1:** Geotechnical characteristics of the soil [2,3]

Materials	particle size distribution				Atterberg Limits			Compatibility		Methylene Blue
	% fines (<80 $\mu\text{m}$ )	Clay < 2 $\mu\text{m}$	Silt between 2 $\mu\text{m}$ et 63 $\mu\text{m}$	Sand between 63 $\mu\text{m}$ et 2mm	W <sub>L</sub> (%)	W <sub>p</sub> (%)	I <sub>p</sub> (%)	$\gamma_d$ (g/cm <sup>3</sup> )	W (%) (OPM)	VBS (g/100g)
Soil extracted at 1 meter depth	88	54	34	12	42	21	21	1,68	15	0,34

### 2.1.3. Preparation of the stabilized soil with the molasses

The sample of the extracted soil at the depth of 1, 00 m contains clump of soil (picture 3). It is manually crushed brought to a granulometric inferior to 400 micrometres (or 0.4 mm) (picture 4), thanks to granulometric analysis. Thereafter, a mixture of this soil and of water at the height of 1.5 times the limit of liquidity of soil is prepared, at the saturated paste (initial water content:  $w_i=1.5 w_L$ ). Afterwards, molasses is added according to the wish quantity, and the components are mixed up with an electrical mixer during 15 minutes. The homogeneous paste from that operation is placed in test tubes and dried up in open-air. The obtained clay cakes (picture 7) are intended to different tests:

- Samples stabilized at 0% of molasses, that is to say without molasses (reference sample);
- Samples stabilized at 8% of molasses;
- Samples stabilized at 12% of molasses;
- Samples stabilized at 16% of molasses.

Table 2 displays indications on the making of soil concretes to be analysed.

**Table 2:** Making of used materials [3]

	Soil quantity (in masse) to put into the mixer
Masse of dry soil sample	80g
Masse of water (% water=1.5W <sub>L</sub> )	50.4g
0% molasses	X
4% molasses	3.2g
8% molasses	6.4g
12% molasses	9.6g
16% molasses	12.8g



Figure 7: (a) Dry soil powder obtained with a 0.4 mm sieve, intended for the preparation of patties. (b) Dry clay patty, stabilized with molasses, after one week of drying.





### 2.1.5. Sugar cane molasses

The used molasses displays the following characteristics: Brix value is (82.95), which represents a content in sugar of 82.85%. Thus, the corresponding polarity is of 29.07%, and purity of 35.09%.

The infrared chemical analysis of sugar cane molasses is shown in Picture 6.

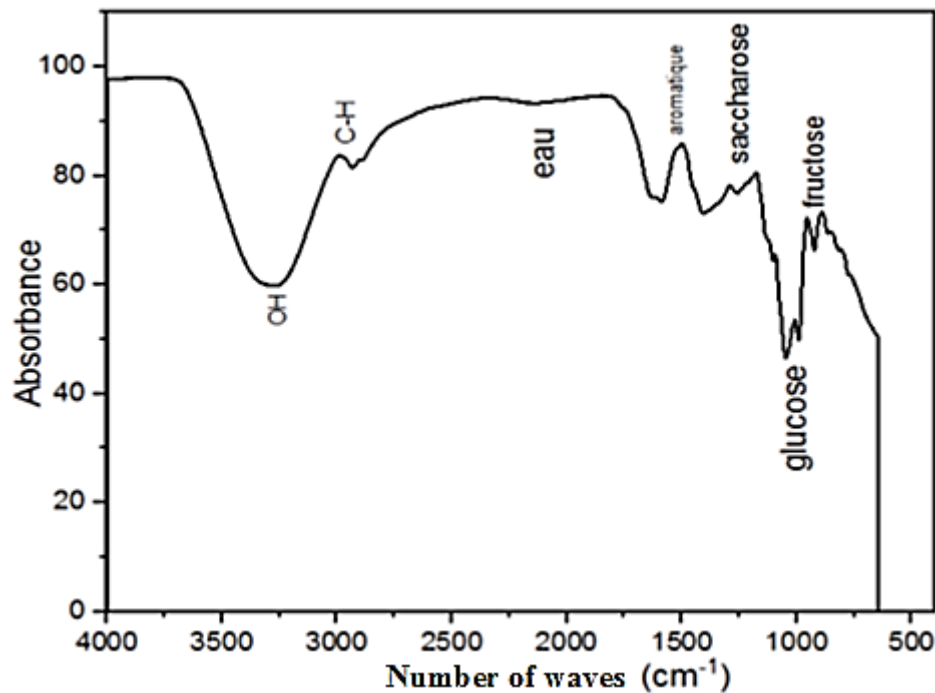


Figure 6: Infrared spectrum of sugar cane molasses

The region between 1200 and 1000  $\text{cm}^{-1}$  is a characteristic of glycosidic bonds (C-O-C) in combination with other modes such as: (C-O-H), (C-C), (C-H) of polysaccharides, of sucrose indeed. The region between 950 and 1200  $\text{cm}^{-1}$  is characteristic of glucoses. The region between 950 and 400  $\text{cm}^{-1}$  is characteristic of fructose. The peak at 1582  $\text{cm}^{-1}$  is characteristic of the vibration of C=C bond of aromatic compound responsible for the colouring of sugar cane molasses like maltol and furaneol. The considered sugarcane molasses is made of sucrose, glucose, fructose, water and colouring compound such as maltol and furaneol (Ashori et al. (2012); Mathlouthi, 1998; Janekarn et al. (2020); Belghiti, 1993) [4, 5, 6, 7] came to make the same observation.

## 2.2. Material and Methods

### 2.2.1. Electronic Microscopy of Sweeping (EMS)

For microstructural characterization, stabilized soil concrete at 8%, 12%, 16% and a witness sample (0%) (Without molasses) dried have been analysed. Microstructures of soil and molasses' aggregate matrixes have been inspected under Electronic Microscopy of sweeping (SEM, JEOL JSM-6084LV to 10 kV) for the study of agglomeration reaction.

### 2.2.2. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermogravimetric Analysis (TGA) has been realized on all samples with an appliance of analysis Diamond Pyris thermogravimetric 6000 TGA/DTA of Pekin-Elmer in the range of temperature between 30°C and 850°C, using aluminium crucibles under the flow of  $\text{N}_2$  to a speed of heating of 20°C/min. The precision of the temperature of the appliance is of  $\pm 0.5^\circ\text{C}$ . The Differential Thermal Analysis (DTA), has been used to measure the difference in temperature between a sample and a reference according to the temperature. In fact, thermogravimetric analysis (TGA) enables monitoring mass variation of a sample according to the temperature.



### 2.2.3. X-Ray Diffraction (XRD)

X-ray diffraction diagrams have been acquired on D8 Bruker diffractometer (Cu-K $\alpha$  radiation,  $\Theta$ -2 $\Theta$  geometry, back monochromator) with a mode of sweeping step-by-step on a space 2 $\Theta$  of 10°-70°, using Cu-K $\alpha$  radiation (1.5406 Å), under a voltage and an electric current of 40kV and 100mA, respectively, and during a total duration of measure of 2 hours, with a step of about 0.006° and a crack of fix difference of 0.3°.

### 2.3.4. The Infrared absorption

Infrared absorption enables to determine, in this particular case, the variations of structure of stabilized soils according to the rate of the considered molasses. The transformed infrared absorption of Fourier (TIAF) has been recorded with a FT-IR Nicolet iS 10 Smart spectrometers in the range from 4000 to 400 cm<sup>-1</sup>.

## 3. Results and Discussion

### 3.1. Infrared Analysis of stabilized soil with molasses

Figure 8 displays infrared spectrum of stabilized soil samples:

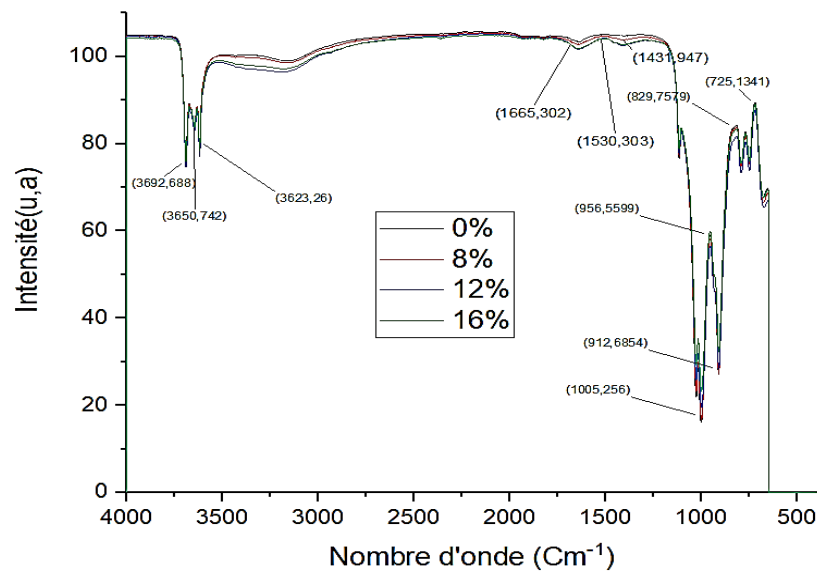


Figure 8: Infrared spectrums of stabilized soil samples at 8%, 12%, and 16% of sugar cane molasses

A deep observation and analysis of picture 8 reveals that infrared spectrum is divided into two main zones. The first one is related to high frequency bands ranged between 3700 and 3400 cm<sup>-1</sup>. The second one is related to weaker frequencies ranged in the zone of 1500-400 cm<sup>-1</sup>. The High frequencies concern H-O hydroxyls vibrations, on the other hand, low frequency bands (right side) concern connections Al-OH, Si-O, Si-O-Si and Si-OAl [8]. Vibrations of valence groups OH made of the elementary stitch of kaolinite are perceived through three vibration bands adjusted on frequencies 3695, 3650 cm<sup>-1</sup> (external hydroxyls) and 3620 cm<sup>-1</sup> (internal hydroxyls). A lack of the vibration band centered on the frequency 3667 cm<sup>-1</sup> (external hydroxyl) means that this kaolinite has a disordered structure [8, 9]. The presence of vibration OH to 3181 cm<sup>-1</sup> characterizes the presence of goethite [8; 9]. The wave number 1661 cm<sup>-1</sup> corresponds to the vibration of H-O-H connections of water. The absorption band ranged between 1006-950 cm<sup>-1</sup> corresponds to the pulled muscle of the connection Si-O and to the Si-O-Si [9] antisymmetric stretching connection. Bands observed in regions 913 cm<sup>-1</sup> are attributed to the distortion of connections of Al<sub>2</sub>O-H (OH free internal and OH in external). Vibrations around 840 cm<sup>-1</sup> and 808 cm<sup>-1</sup> characterize the presence of quartz SiO<sub>2</sub>. According to Russel and Fraser, the intensity band situated at 750 cm<sup>-1</sup> indicates a presence of kaolinite. On the other hand, Millogo Younoussa (2008) [9], Farmer (1974) [10], Madejova J. (2001) [11] have obtained kaolinite bands at (3700, 3668, 3620, 1090, 1050, 920, 696, 520, 470 cm<sup>-1</sup>). This kaolinite displays an unbalanced structure because of the lack of its characteristic band 3650 cm<sup>-1</sup> [10, 11]. Similarly, Bich (2005) has obtained the infrared bands of three kaolinites: The Kita kaolin (Kaolin from Brazil) presents only three hydroxyls bands ranged between 3800 cm<sup>-1</sup> and 3500 cm<sup>-1</sup> (OH<sup>-</sup> hydroxyls at 3699, 3645, 3622 cm<sup>-1</sup>); whereas Klpi kaolins (Kaolin from Brazil) (OH<sup>-</sup> hydroxyls at 3695, 3669, 3652, 3619 cm<sup>-1</sup>); and KSia (kaolin from Great Britain) (OH<sup>-</sup> hydroxyls at 3696, 3669, 3653, 3619 cm<sup>-1</sup>) have four bands [12]. This observation clearly indicates that Klpi and KSia kaolins are better crystallised in



comparison with Kita Kaolin [13]. However, Millogo (2008) [9], Farmer (1974) [10], and Madejova J. (2001) [11] have attributed in *hygroscopic* water the band ( $1640\text{ cm}^{-1}$ ). Bich (2005), has obtained for the three Kaolinites: For the Kita kaolin ( $\text{H}_2\text{O}$  at  $1634\text{ cm}^{-1}$ ), for the KIpi kaolin ( $\text{H}_2\text{O}$  at  $1637\text{ cm}^{-1}$ ), and for the KSia ( $\text{H}_2\text{O}$  at  $1630\text{ cm}^{-1}$ ) [12]. Wetshondo Osomba (2012) has attributed to the large absorption band of weak intensity centered on  $1626\text{ cm}^{-1}$  to water molecules [13].

Infrared spectrums of stabilized soils with molasses (picture 8) displays no difference, no new peak compared to soil without molasses (picture 8). The infrared spectrums of stabilized soils with sugar cane molasses and soil without molasses exactly show the same peaks with the same positioning, as if molasses was inexistent in the soil (picture 8). This situation well corroborates to the idea that the molasses does not bring any alteration to kaolinite structure, because only the kaolinite spectrum is displayed. This observation also attests that, the molasses is either present in a very small quantity; it is therefore quite minority in the soil to be detected in the near-infrared. Nevertheless, the appearance of a peak around  $1500\text{ cm}^{-1}$  on all stabilized concretes with molasses characterizes the presence of aromatic compounds responsible of colouring the stabilized concretes, thanks for the coloring presence in the molasses.

Janekarn Intuorn and al. (2020) have found for the CSC (carbonate silicate composite drugged of molasses) carbonized at  $800^\circ\text{C}$ , a band at  $1582\text{ cm}^{-1}$  which is characteristic to aromatic micro-vibrations  $\text{C}=\text{C}$  [6]; this would suggest that aromatic structures have been formed during the carbonization at high temperature. Finally, these findings enable to conclude that the molasses does not bring any change to the kaolinite structure. The interaction between the molasses and soil clay is essentially physical. Some more scientists, such as Guckert, Chone and Jacquin (1975), Hassan, Moavad, Guzev, Bab'yeva and Zvyagintsev (1974), quoted by Bachelier (1978) [14] have shown that polysaccharide absorption on kaolinite is essentially physical.

Table 3: characteristic Absorption bands of radicals of stabilized soils with sugar cane molasses

Radical	Wave number	Minerals
OH	$3600\text{-}3700\text{ cm}^{-1}$	Kaolinite
	$3141\text{ cm}^{-1}$	Goethite
$\text{H}_2\text{O}$	$1651\text{ cm}^{-1}$	Amorphous Aluminosilicate
$\text{SiO}_4$	$993\text{ cm}^{-1}$ et $949\text{ cm}^{-1}$	Kaolinite
Al-OH	$913\text{ cm}^{-1}$	Kaolinite
$\text{SiO}_4$	$828\text{ cm}^{-1}$ and $774\text{ cm}^{-1}$	Quartz

### 2.3. Mineralogical Analysis by X-ray of stabilized soil with sugar cane molasses

Diffraction patterns of stabilized samples at 0%, 8%, 12% and 16% of molasses are displayed in picture 9. The diffraction pattern of sample without molasses (0%) shows that it is composed of quartz, kaolinite, aluminosilicates, and goethite. Similarly, the diffraction patterns of stabilized samples at 8%, 12% 16% of molasses show the same mineralogical composition that the sample without molasses (0%).

As a matter of fact, the molasses is essentially made up of organic components, such as saccharose, glucose, and fructose, the molasses added into soil has little influence over soil mineralogical. Nevertheless, it is observed that the intensity of peaks increases with the quantity of sugar cane molasses.

The molasses does not bring any change to kaolinite structure, for only the peaks attributed to kaolinite have been detected by X-ray spectrums. This has led us to suggest that the interaction between clay fine soil and the molasses is essentially physical. On the contrary, Abidallah (2008) has examined changes brought by polystyrenes within kaolinite' structure. IR spectrums from these samples have shown apart from kaolin absorption bands, typical bands to the exploited organic molecules. X-ray diffraction spectrums indicate that the space of kaolin leaves increases at  $3.85\text{ \AA}$  in comparison with the initial clay sample [15]. Indeed, this finding evidenced an insertion of organic molecules in the inter-foliar space of kaolin.



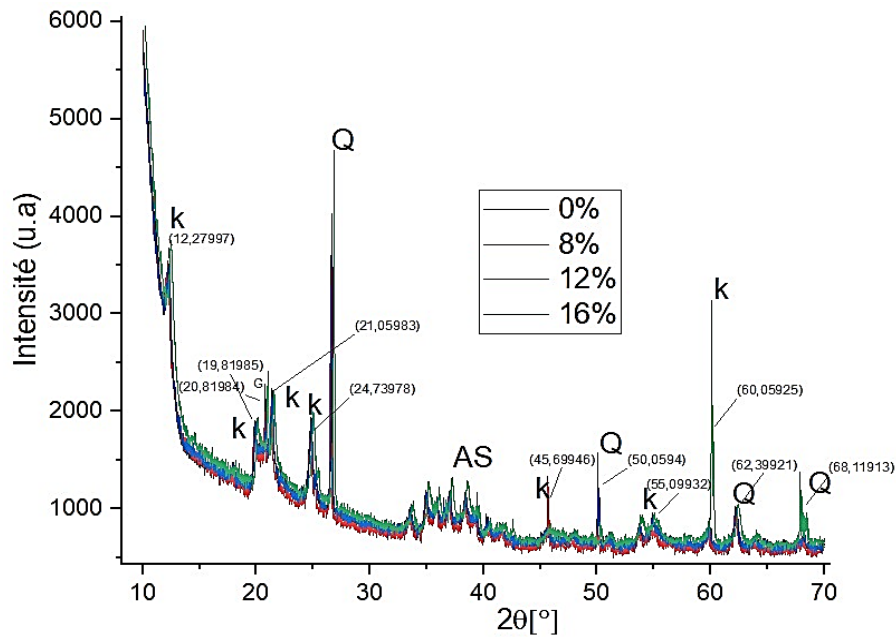


Figure 9: Superposition of X-ray diffractograms

**K:** Kaolinite, **Q:** Quartz, **G:** Goethite, **AS:** Aluminosilicate.

The table 4 sums up mineralogical characteristics of stabilized soil with sugar cane molasses. In our particular case of the infrared spectrums, as for x-ray spectrums of stabilized concretes with the molasses indicated neither structure modification nor appearance of attributed bands to major constituent organics of the molasses (saccharose, glucose, and fructose). Only bands attributed to kaolinite have appeared in addition to attributed bands to coloring compounds present in the sugar cane molasses on the infrared spectrum. It is quite obvious that the sugar cane molasses did not alter kaolinite' structure. This observation brings further evidence that there is no chemical interaction between by clay soil and the major organic constituents of the molasses. For, chemical interaction necessarily induces a structural modification noticeable through X-ray and infrared. In this connection, Allan and al. (2005) explained that the improvement of mechanical properties is due to the formation of hydrogenous connections between hydroxyls groups from sugar and those from cellulosic slats within cell walls [16]. Alireza Ashori and al. (2012) made the same finding: the saccharose main constituent of the molasses is linked via hydrogenous connections with cell walls of paper's pores [4]. In fact, aluminol groupings (Al-OH) and silanol groupings (Si-OH) groupings at the edges of kaolinite leaves and many hydroxyl groupings of sucrose establish hydrogenous as well as electrostatic connections which do not cause any assortment in the structure of soil kaolinite.

**Table 4:** X-ray characteristics of minerals of stabilized concretes with sugar cane molasses

$2\theta [^\circ]$	Minerals
11	Kaolinite
20	Kaolinite
21	Goethite
25	Kaolinite
26	Quartz
30-40	Aluminosilicate
45	Quartz
50	Quartz
55	Kaolinite
60	Kaolinite
62	Quartz
68	Quartz





**2.4. Crystallinity of the kaolinite of stabilized soil with sugar cane molasses:**

The obtained crystallinity indications by X-ray diffractograms (Hinckley’s indication), by infrared spectrum ( $P_0$  and  $P_2$ ) [picture 11], and by thermal curves (slope ratio) [picture 10] are presented in the table 5.

**Table 5:** Crystallinity indication according to content in sugar cane molasses

Cristallinity indication \ Molasses content	Molasses at 0%	Molasses at 8%	Molasses at 12%	Molasses at 16%
	$P_0$	1.025	1.032	1.037
$P_2$	0	0	0	0
HI	1.33	1.43	1.56	1.28
Slope ratio	1.59	1.72	1.35	1.32

Whatever method the kaolinite of our soil presents a bad crystallinity. The values of crystallinity indication  $P_0$  increase with the added molasses at 12% and decrease at 16% in the same order with the sample without molasses. The variation of crystallinity indication  $P_0$  with the adding of the molasses means that the sugar cane molasses contributes to improve the structural disorder in the crystalline network. Yet, at the content of 16% of molasses the disorder is the same for the sample without molasses. In fact, the crystallin disorder of network is principally due to the absence of external hydroxyl (OH) centered at the frequency of  $3667\text{ cm}^{-1}$  of infrared spectrum. Yet, cane molasses is essentially made up of saccharose and sucrose, rich in hydroxyl groupings. The sugar cane molasses present in the surface of clay getting into the gaps, and provides to network with the missing hydroxyls; thereafter, the crystallinity indication increases with the adding molasses. Still, at 16% of the crystallinity decreases, the disorder is identic with the sample without molasses. As a matter of fact, the stabilized sample at 16%, absorbs less molasses molecules on the specific surface than the stabilized at 8% and 12%.

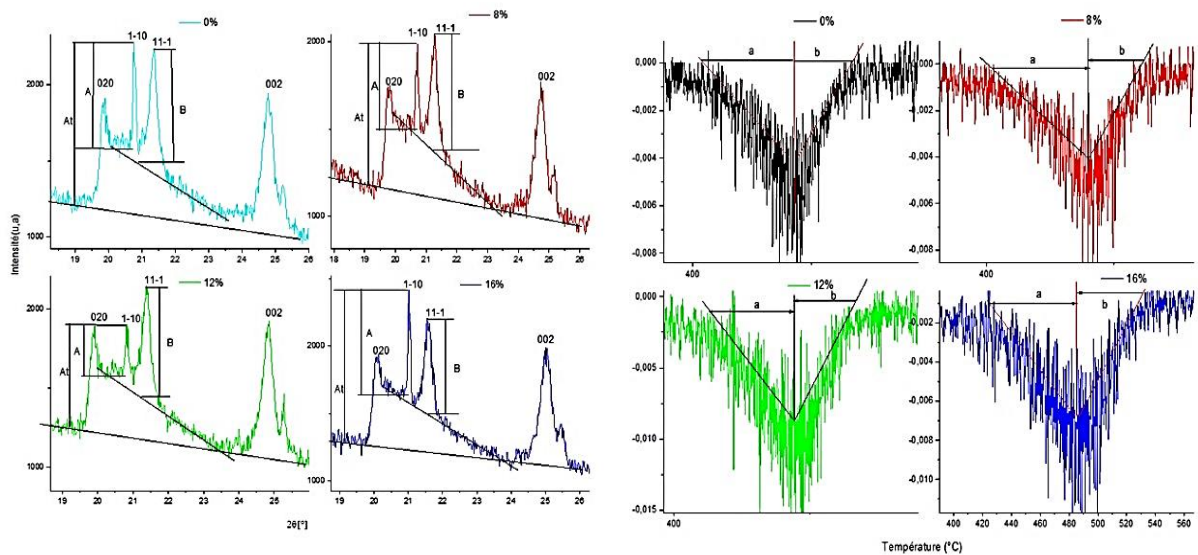


Figure 10: Determination of Hinckley indication, of slope ratio of the stabilised soil with molasses

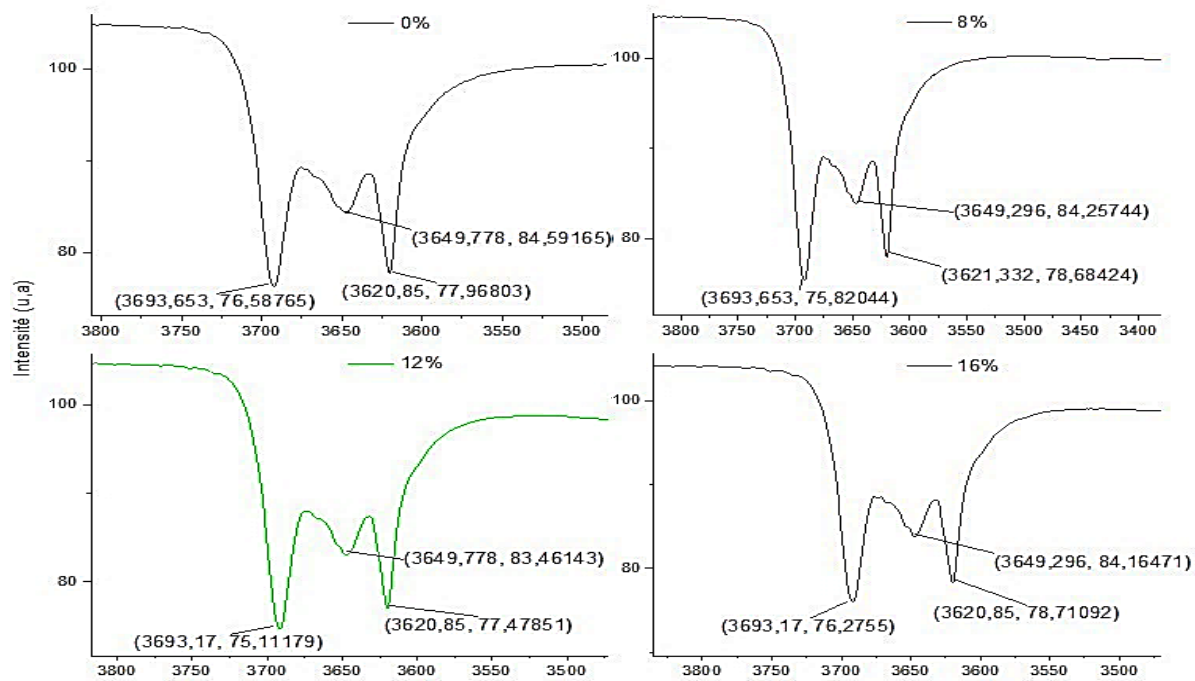


Figure 11: Determination of the  $p_0$  and  $p_2$  report of the stabilised soil with molasses

The kaolinite studied presents a density of surface defect (defect in the OH layer) increased, for its slope ration is estimated at 2 (sample at 0%). The density of defects of surface decreases with the adding of the molasses: The sample without molasses has a defect density of the higher surface than the stabilized samples at 12% and 16%. The stabilized sample at 12% has a density of defects of surface higher than the stabilized at 16%. The molasses reduces the defects of surface. Nevertheless, the stabilized sample at 8% contains a density of defects of surface higher than all samples. This might be due to electrostatic repulsions associated to the associative interactions of type hydrogen bonds between hydroxyls of molecules constituting the molasses. In fact, the stabilized sample at 8% adsorb more molecules constituting sugar cane molasses than other samples (12% and 16%).

- At the position  $2\theta = 20^\circ$ ,  $2\theta = 21^\circ$  and  $2\theta = 25^\circ$  (picture 12), the sample without sugar cane molasses presents the highest peaks, followed by the stabilized sample at 16%, and the stabilized sample at 12%, and finally the stabilized sample at 8%. The intensity of peaks to these positions increases with the adding of cane molasses. This means that the crystallin disorder increases with the adding of sugar cane molasses on (hk0) bands of plans (A and B) or lateral plan of clay. The sites situated on the crystal borders being hydroxyl groupings of type silanol (Si-OH) and aluminol (Al-OH) [Errais E. (2011)]. This might be due to physical interactions between hydroxyl groupings of lateral plan border of clay and those from sugar cane molasses constituents which forms connections to Hydrogen Bridge. According to Wetschondo D. (2012), the decrease of crystallinity observed in x diffraction, of the starch matrix with the adding of kaolinite is due to the interferences of reactions clay-starch on interactions chain-chain [13].

- At the position  $2\theta = 60^\circ$  (picture 12), the intensity of peaks increases with the adding of the molasses, however the intensity of peak at 0% is higher than the stabilized samples at 8% and 12%. This shows that, the crystalline imbalance decreases on the plan (001) or basal. Yet, this crystallin imbalance of network of the kaolinite of the studied soil is due to the lack of external hydroxyl (OH) centered on the frequency  $3667\text{ cm}^{-1}$  of infrared spectrum. This justifies the presence of gaps or positive charges (aluminous basal surface) on basal surface. The contribution by the sugar cane molasses of the additional hydroxyl groupings on the basal surface, fills in the gaps or the deficit of charge to crystallin network. Thereafter, sugar cane molasses improves the stability of the crystalline network.



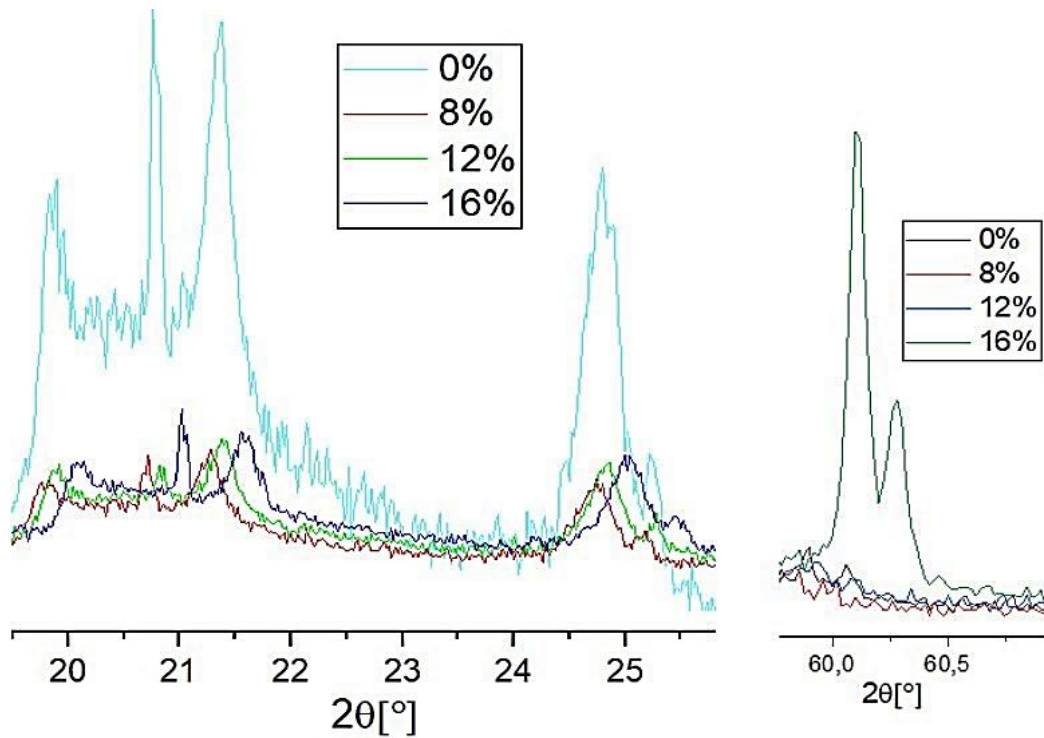


Figure 12: DRX diffractograms enlarged to positions  $2\theta = 20^\circ$ ,  $2\theta = 25^\circ$  and  $2\theta = 60^\circ$  of the stabilized soil with the molasses

**Table 6:** Interplanar spacing to positions  $2\theta = 12^\circ$ ,  $2\theta = 20^\circ$ ,  $2\theta = 25^\circ$  and  $2\theta = 60^\circ$  according to the content in sugar molasses

Molasses content	0% of molasses	8 % of molasses	12% of molasses	16% of molasses
<b>Interplanar distance (Å)</b>				
$2\theta=12^\circ$ ( $d_{001}$ )	7.25	7.29	7.29	7.25
$2\theta=20^\circ$ ( $d_{020}$ )	4.49	4.49	4.48	4.48
$2\theta=25^\circ$ ( $d_{002}$ )	3.6	3.6	3.6	3.6
$2\theta=60^\circ$	1.5	1.6	1.5	1.5

After several tests, it is attested that the adding of sugar cane molasses to the soil has no influence on interplanar distances within the kaolinite (table 6), as no important variation is observed on distances ( $d_{001}$ ,  $d_{020}$ , and  $d_{002}$ ). Nonetheless, the basal distance of the kaolinite is of  $7.15 \text{ \AA}$  in an ordinated kaolinite, the increasing at  $7.25 \text{ \AA}$  for our kaolinite (0%) means that there is a series of stacking faults, and our kaolinite is an unbalanced structure. This also means that molecules constituting cane molasses do not penetrate into the kaolinite. Accordingly, the intensity variations of observed peaks on the X-ray curves (picture 12) essentially results to interactions that took place in external surfaces of the kaolinite (basal and lateral surfaces) with molecules of the sugar cane molasses.

## 2.5. Analysis thermogravimetry (TG) and its derivative Thermogravimetric Decomposition (TGD)

### 2.5.1. TG and TGD results of soil without sugar cane molasses

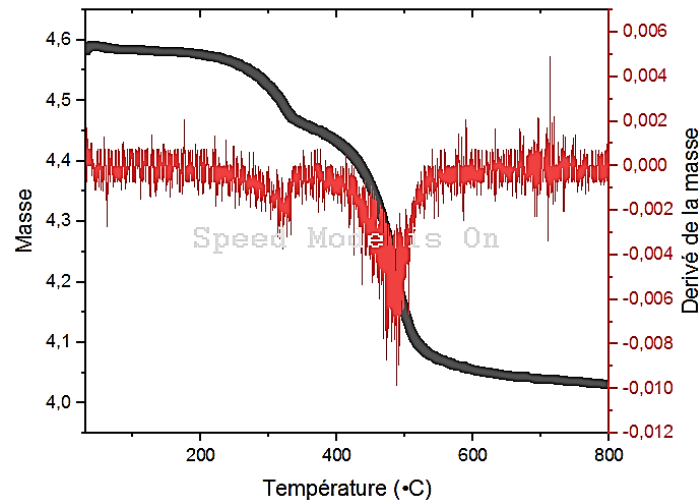


Figure 13: TG curve of the sample without sugar cane molasses

The curve TG (picture 13) shows that the thermal decomposition of the sample occurs following two stages. The central sections of mass diminution of samples and their related temperatures are clearly displayed on the derive curve of the thermogravimetric curve (TDG). At this level, two peaks are observed on the curve DTG and show the inflexion points of the TGA curve that is characterized by:

- Around 300, a mass loss corresponding to the composition of the goethite into hematite [9].
- Around 480-500°C, the significant mass loss linked to the departure of water of constitution and to the kaolinite decomposition and its transformation into metakaolin [9, 17, 18]. As a recall, the dihydroxylation temperature in a balanced kaolinite is around 600°C but those an unbalanced kaolinite is weak [9]. The dihydroxylation temperature of the kaolinite of our sample being of 480-500°C, this kaolinite would be unbalanced. The unbalanced structure of the kaolinite would be justified by the replacement of the aluminium in the octahedral leaf by trivalent iron engendering gaps within the structure [9].

### 2.5.2. TG and TGD results of stabilized soil at 8% of sugar cane molasses

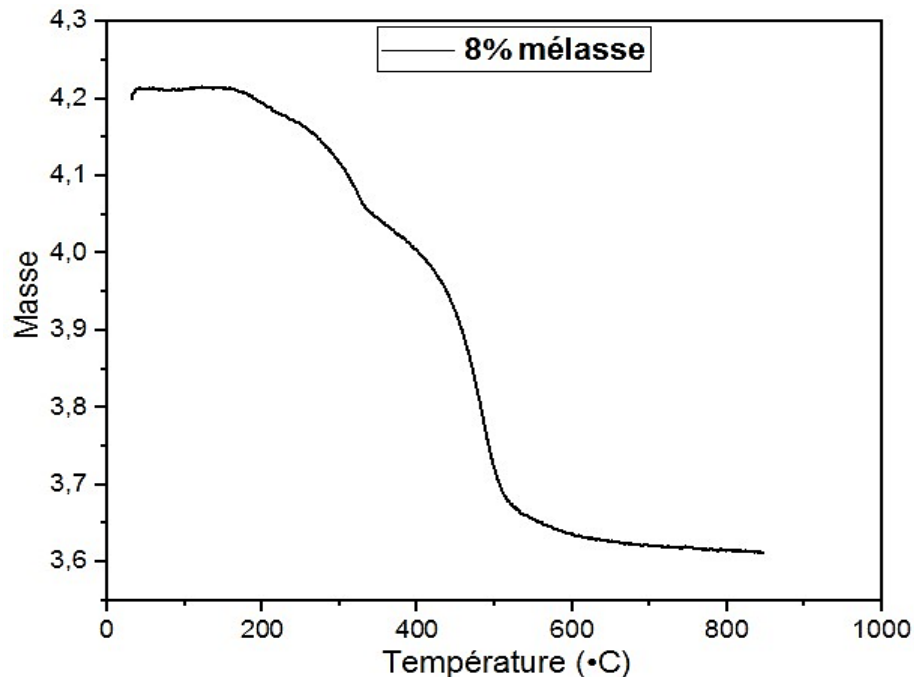


Figure 14: TG curve of the stabilized sample at 8% of sugar cane molasses



The curve TG above (picture 14) shows that the thermal decomposition of the sample occurs following three stages.

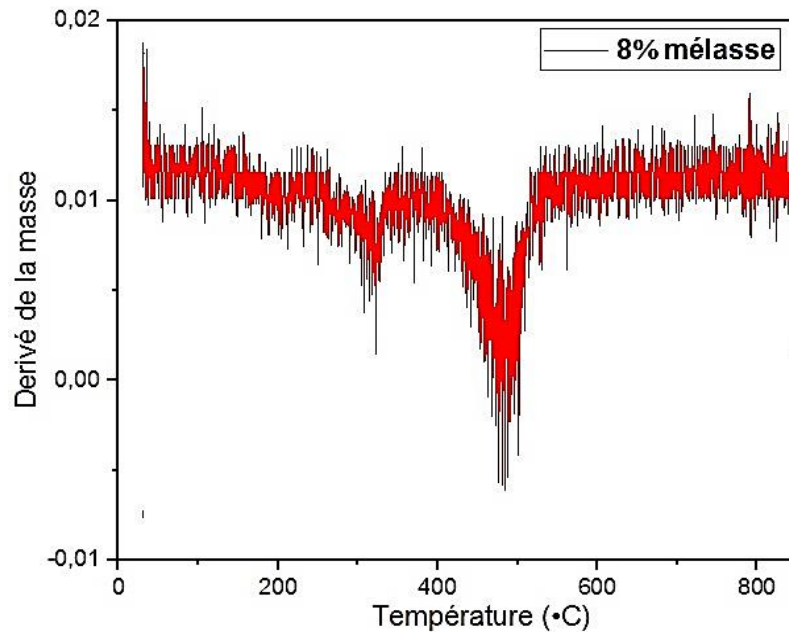


Figure 15: TGD curve of stabilized sample at 8% of sugar cane molasses

The TDG curve of the sample (picture 15) shows highlights the temperatures or have taken place the major mass losses. Those show three peaks of inflexion:

- Around 200°C, we observed an endothermic peak linked to the thermal degradation of the saccharose (19).
- Around 300°C, we observed another endothermic peak with the light mass loss of the corresponding mass to the decomposition of the goethite in hematite (9).
- Around 450-500°C, we observed endothermic peak with a diminution of mass linked to water departure of constitution, kaolinite decomposition and its transformation into metakaolin [9, 17, 18].

### 2.5.3. TG and TGD results of stabilized at 12% of sugar cane molasses

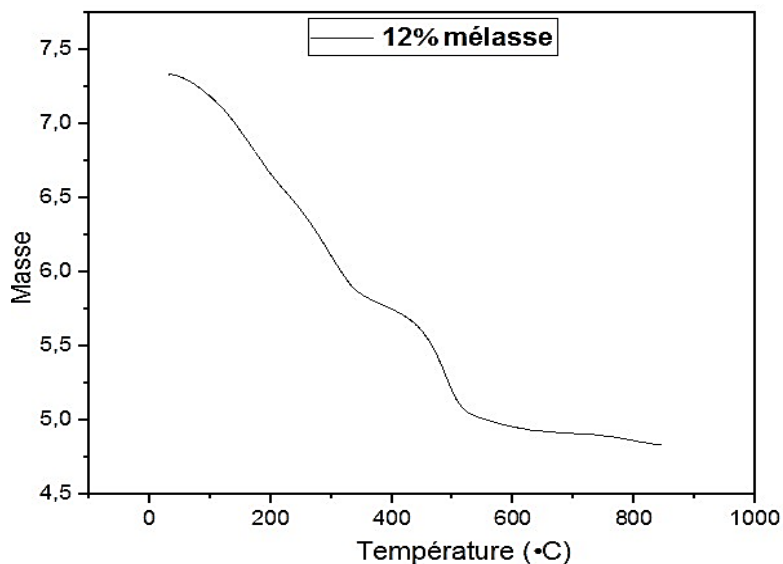


Figure 16: TG curve of the stabilized sample at 12% of sugar cane molasses

The TG curve above (picture 16) shows that the thermal decomposition of the sample occurs in the following three stages, thereby three temperature levels define the thermal stability.





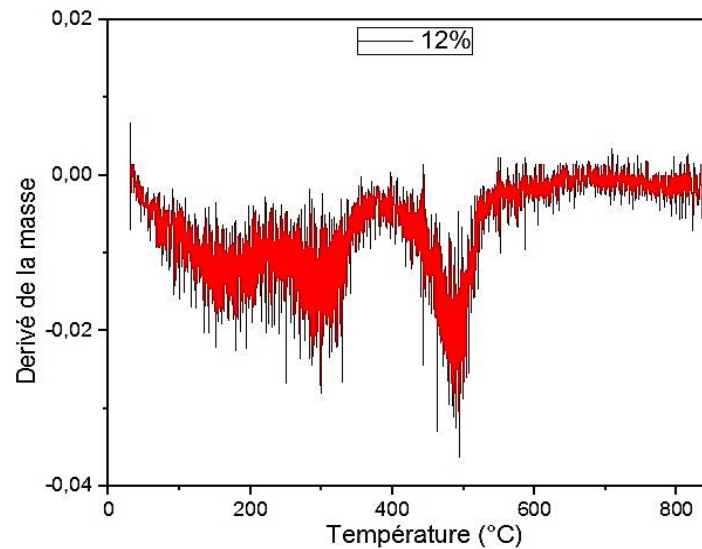


Figure 17: TGD curve of the stabilized sample at 12% of sugar cane molasses

The TGD curve of the sample (picture 17) shows that the mass loss increases with the temperature. Those curves show three important peaks.

- At the temperature of 150-200°C, the sample loses its mass, this is due mainly to the change of the saccharose structure which is transformed into glucose and fructose, carboxylic acid [6, 19];
- Around 300°C, an additional mass loss is recorded, linked to a decomposition of the goethite into hematite, and to a saccharose deterioration with the departure of the absorbed water, carbon dioxide and monoxide [6, 19];
- Around 480-500°C, the adding of mass loss is observed. The origin of that diminution is linked to the departure of the water constitution, and the kaolinite deterioration and its transformation into metakaolin.

#### 2.5.4. TG and TGD results of the stabilized soil at 16% of sugar cane molasses

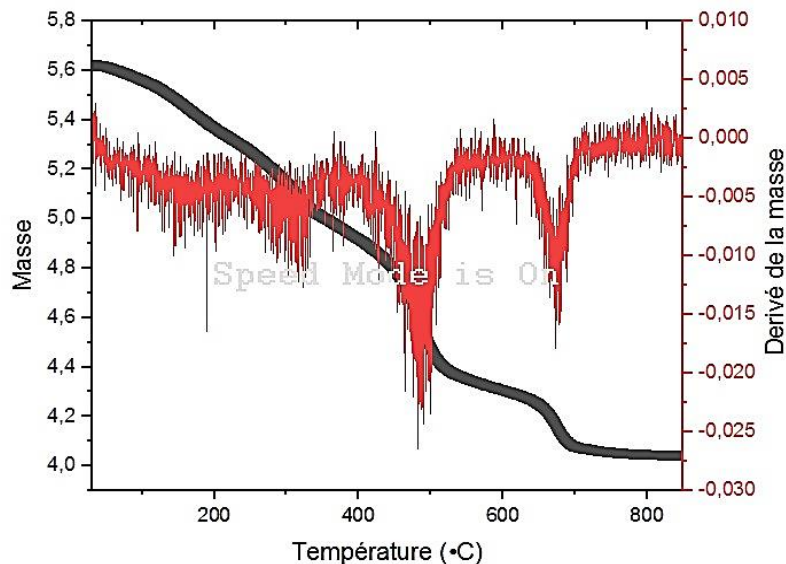


Figure 18: TG and TGD superposition curves of the stabilized sample at 16% of sugar cane molasses

The derive superposition of the thermogravimetric curve (DTG) and the TG curve (picture 18) shows four limited peaks:

- At the temperature of 150-200°C, the sample losses its initial mass. This is also due to the change of saccharose structure which is decomposed into glucose, fructose or carboxylic acid [6; 19];



- Around 300°C, a loss of the adding mass is observed corresponding to the departure of absorbed water, of the carbon monoxide and dioxide, of dihydrogen, and the decomposition of goethite into hematite, as well as glucose and fructose degradation [6; 9; 19].
- Around 480-500°C, a loss of the adding mass is noticed. The origin of this reduction is linked to the departure of the constitution water, kaolinite deterioration and its transformation into metakaolin.
- Around 680-700°C, a loss of the adding mass is noticed linked to the product degradation of saccharose decomposition in volatile substance [6; 9; 19].

## 2.6. Differential Thermal Analysis (DTA) of stabilized soil with sugar cane molasses

The differential curves (DTA) of stabilized soils (8%, 12%, and 16%) with molasses and of soil without molasses (8%) are presented in the picture 19.

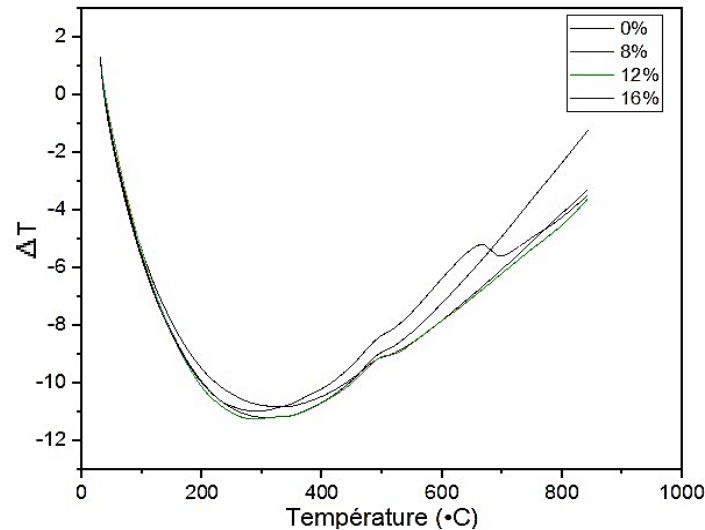


Figure 19: DTA curves of samples

The endothermic peak around 300°C indicates the OH expulsion to the change of the goethite into hematite, to the dihydroxylation of the kaolinite and to the sucroses dihydroxylation. The glass transition around 480°C due to the transformation of kaolinite into metakaolinite. And, the minor exothermic peak around 680°C for the stabilized sample at 16% is linked to a decomposition in sucrose and their decomposition products, the endothermic peak at 700°C, however, is linked to the fusion (as there is no mass loss associated on TG, picture 20) of microcrystallites of the sucrose decomposition into aromatic compounds.

The thermal decomposition of stabilized soil with molasses occurs following five thermal peaks: 150-200°C, 300°C, 480-500°C, 680°C, and 700°C.

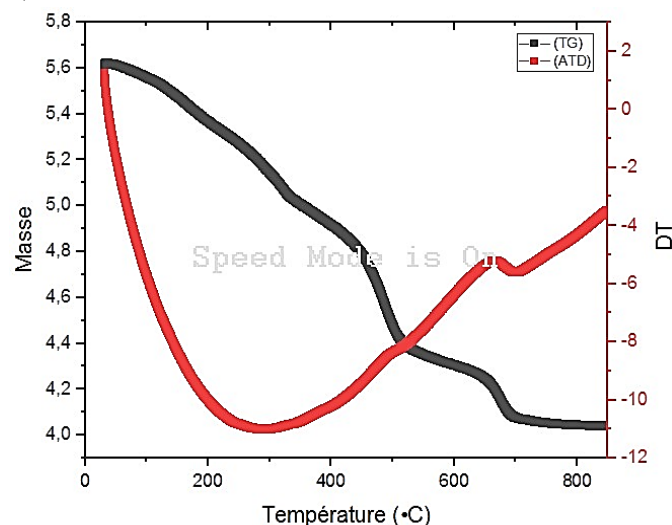


Figure 20: TG and TGD curves of stabilized sample at 16% of sugar cane molasses



TG and DTA curves of the sample without molasses 0% show only two steps: at 300°C endothermic peak temperature, is observed a mass loss corresponding to the goethite decomposition into hematite; and around 480°C, a significant mass loss linked to the departure of water constitution and kaolinite decomposition and its transformation into metakaolin. The same levelling appears for stabilized samples at 8%, 12%, and 16% of molasses to the same peak of temperature. In addition, from the adding level to the temperature between 150-200°C, from the structure change and of saccharose colouring which is decompose into glucose, fructose, and carboxylic acid. And another step at the temperature of 680°C due to the degradation of decomposition products like the glucose into volatiles substance. At the temperature of 700°C, an endothermic peak linked to no particular mass loss (picture 20): at this level, there is a recrystallisation of decomposition products from saccharose into aromatic skeleton.

The appearance of thermal peaks attributed to the pyrolysis of saccharose the main component within cane molasses, ascertains the idea the molasses is existent in the soil matrix.

Between 150-200°C, Woo and al. (2015), have written the sucrose dehydroxylate around 200°C [20]. Mathlouthi Mohamed (2013) revealed the structure modification and saccharose colouring between 140 and 160°C [19]. Obviously, the thermal peak around 150-200°C, exclusively observed on stabilized soil concretes is also attributed to the saccharose dihydroxylation, main molasses constituent. As the peak is unobserved from the soil without molasses, Courard (2010) attributes in the case of clays at the temperature of 160°C the loss of adsorbed water [20]. Although, we have not observed a mass loss for the sample without molasses.

Around 300°C, according to Woo and al. (2015) above the temperature of 200°C is followed the sucrose degradation with the releasing of volatile gases, there is the formation of products such as 5-hydroxymethylfurfural [20]. Mathlouthi (2013) attributes to that temperature the releasing of water, of carbon monoxide and dioxide following the thermal decomposition of saccharose [19]. The indicator of the peak of mass loss at 300°C for all stabilized soil concretes is attributed to sugar thermal decomposition (saccharose, glucose, fructose) brought by soil molasses. Nevertheless, the soil without molasses also indicates a mass loss peak at 300°C, which we attribute to the goethite dihydroxylation. Millogo (2008) notes the goethite dihydroxylation at 310°C [9]. The presence of this thermal peak (around 300°C) of mass loss on stabilized concretes and on the non-stabilized concrete can definitely be related to the presence of goethite in the soil and to the presence of sugars brought by the molasses in the soil. The sugar degradation process caused a discharge of volatile products that hastened goethite decomposition at the temperature of 300°C. Whereas, drawing from Millogo (2008), the absence of accelerator products led to goethite decomposition at the temperature higher than 310°C.

Between 480-500°C occurs the most important mass loss for all concretes (stabilized and non-stabilized). This mass loss is chiefly associated to water leak from constitution, to the kaolinite dihydroxylation and its transformation into metakaolin. Courard (2010) has attributed in the case of clay the loss of the constitution water to the temperature of 550°C [18]. Millogo (2008), specifies the temperature of the kaolinite dihydroxylation at the temperature of 537°C [9]. Bouzidi (2012), Gamiz and al. (2005) opine that the leak of the constitution of water as well as kaolinite structure degradation into metakaolin between 460 and 600°C [21]. Laribi and al. (2007) have revealed an endothermic peak for the green clay from Romainville at 550°C, attributed to the dihydroxylation of kaolinite leaves [22]. In our specific case of study, the kaolinite dihydroxylation and its transformation into metakaolinite occur at lower temperature around 480 and 500°C for all stabilized concretes. This observation can be justified by the sucrose thermal degradation has produced volatiles components like the carbon monoxide and dioxide. Mathlouthi (2013) notes at the temperature of 450°C the releasing of dihydrogen (due to the thermal degradation of saccharose), which is a highly ignitable product [19]. The releasing of these volatile substances considerably speeds up the thermal intensity, and consequently the kaolinite decomposition at the very low temperature around 480-500°C. However, the sample without sugar cane molasses also indicates a mass loss peak attributed at the kaolinite dihydroxylation and its transformation into metakaolin around 450-500°C. As a matter of fact, the dihydroxylation temperature of a balanced kaolinite is around 600°C. Whereas an unbalanced one is much lower [Grimshaw (2013); Letellier (1986)] [23, 24]. Our kaolinite sample considered in this study, having the lowest dihydroxylation temperature, might have the most unbalanced structure in comparison with the samples tested by other authors (Millogo, Bouzidi, Laribi, and Courard). This is because the kaolinite is ordered or more and less unbalanced than the



other kaolinite, this is at the origin of the difference between dihydroxylation temperature and of weak dihydroxylation temperature.

At 680°C, a further mass loss has been observed from the stabilized sample at 16% of sugar cane molasses. The stabilized samples at 8%, 12%, and the sample without sugar cane molasses do not present any mass loss. This finding definitely ascertains that the peak is induced by the presence of sugar cane molasses. Indeed, the quantity of sugar cane molasses of 8% and 12% is too low to notice any reaction. In this connection, Mathlouthi (2013) denotes at the temperature of 550-600°C an important emission of volatile substances ( $> 150$ ) during the decomposition process within saccharose and of the related decomposition substances [19].

At 700°C, the Differential Thermal Analysis of the stabilized sample at 16% of sugar cane molasses indicates an endothermic peak which is linked to no mass loss, this means that there is a fusion of material. We attribute this fusion to microcrystalline products of thermal degradation of saccharose into aromatic component. Woo and al. (2015) observed an emission of products such as 5-hydroxymethylfurfural during sucrose pyrolysis [20]. Janekarn Intuorn and al. (2020) reported for the silicate composite of carbon drugged to warmed up sugar cane molasses to a temperature of 800°C, the presence of an infrared band at  $1582\text{ cm}^{-1}$  a characteristic of the vibration C=C of aromatic skeleton.

As for Bouzidi (2012), Gamiz and al. (2005) note a structural reorganization of metakaolin towards 950-980°C, associated to an exothermic peak [21]. Moreover, Laribi and al. (2007) unveiled another exothermic peak around 900°C, which they associate to a destruction and a recrystallization within the silicate network for smectite of type beidellite [22]. Nevertheless, drawing from our final findings, the recrystallization is not associated to kaolinite, as the sample of the natural soil, that is, the soil without sugar cane molasses shows no noticeable reaction at the temperature (700°).

### 3. Conclusion

Infrared analyses, X-rays and thermal tests, as well as the crystallinity of stabilized concretes with molasses have led us to these final findings:

- The molasses causes no alteration to the kaolinite' structure. For, the interaction between clayey fine soil and molasses proves essentially physical;
- The molasses is found within the matrix of clayey fine soil;
- The thermal decomposition of the stabilized soil with molasses occurs following five thermal peaks: 150-200 °C, 300°C, 480-500°C, 680 °C and 700 °C;
- The Kaolinite of our soil shows a bad crystallinity;
- The molasses contributes to improve the structural disorder in the crystalline network of the kaolinite up to the content of 12%.

As a conclusion, the crystalline unbalance considerably decreases with the added molasses on the plan (001) or the basal surface of the kaolinite.

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