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Thermal Analysis of Cement Paste Partially Replaced With Neem Seed Husk Ash

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Abstract— Chemical changes that occurred during cement hydration at microstructure level can be identified using thermal analysis method. Calcium hydroxide (CH) is one of the major hydration products that determine both the hydration characteristics and the degree of hydration of a given cement paste. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) methods were carried out on cement pastes partially replaced with 0%, 5%, 10%, 15%, 20% and 25% Neem seed husk ash. The chemical changes at various stages were identified, while the Calcium hydroxide (CH) contents were calculated for each sample. The results show that the CH contents increases with increase in Neem seed husk ash replacements, and it is deduced that Neem seed husk ash is not acting as a pozzalana but rather as filler.

Index Terms— Neem seed husk ash, cement, calcium hydroxide, differential thermal analysis (DTA), thermogravimetric analysis (TGA), pozzalana, filler

1 Introduction

Calcium hydroxide (CH) is one of the major hydrated products that comprise over 20% of the hydration products in a fully cured cement paste [1]. Calcium hydroxides (CH), along with calcium silicate hydrate (C-S-H) are the end products of the reaction of alite and belite with water [2]. Calcium hydroxide is present predominantly in the form of well-defined crystals and of a precisely determined composition, so that estimation of the CH content determines both the hydration characteristics and the degree of hydration of a given cement paste. The formation and the change of the amounts of CH formed in hydrating Portland cement not only determines the percentage of reaction hydration, but also influences the ultimate mechanical properties of the paste [3].

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Among the various thermal analysis techniques, the Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) methods are most popularly used to study cement hydration [4]. TGA is a technique which examines the mass change of a sample as a function of temperature and/or time. TG analysis allows the estimation of the content of CH from the weight losses.

While, in DTA, the difference of temperature between a sample and a reference material is measured, so that heat absorption, during endothermic reactions, or heat emission, during exothermic reactions, is recorded [5].

A Neem seed husk ash is obtained by burning a waste husk obtained during the extraction of oil from neem seed. The objective of this paper is to determine the CH content of cement paste partially replaced with Neem seed husk ash using TGA/DTA thermal analysis techniques.

2 Materials And Methods

2.1 Materials

Dangote Ordinary Portland cement was used in this study. The cement has chemical properties as shown in Table 1. The

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Neem seed husk used was obtained from Neem fertiliser processing plant, it was dried and burned in an open air, after which it was calcinated in an oven at temperature of 600°c to produce an ash. The chemical composition of the Neem seed husk ash was determined using X-Ray Fluorescence (XRF) and shown in Table1.

Table 1: Chemical Composition of Dangote OPC and Neem seed husk ash

% Oxide	Cement	Neem seed husk ash
Al2O3	2.8	3.0
SiO2	28.57	25.4
CaO	79.12	32.9
Fe2O3	4.28	8.67
K2O	0.24	14.3
MnO	0.01	0.18
SO3	1.6	4.42
LOI	4.05	9.03

2.2 Methods

The analysis was carried out on powdered samples which were prepared by partially replacing cement with various percentages of Neem seed husk ash. The percentages by weight are 0%, 5%, 10%, 15%, 20% and 25%. The 0% is the control specimen. For other percentages, cement and Neem seed husk ash were thoroughly mixed in dry powdered form in correct proportion. The samples were then mixed with water using water-cement ratio of 0.5 and made into paste cubes. The paste cubes were then cured in water for 28 days and then grinded into powder in preparation of the test.

TGA/DTA was done on a DTA-TG apparatus, Shimadzu DTG –60 simultaneous, Japan, with samples heated over the temperature range of 40 ° C – 900° C at a constant rate of 10°C/min under nitrogen atmosphere. Since TG analysis was carried out to determine the relative amount of CH in the Cement paste, From TG curves, mass loss of CH was calculated using a formula in Eq.(1) [6].

$$CH = \left[\frac{4.11dW480}{W120}\right](100)$$

----Eqn. (1)

Where

CH =calcium hydroxide (mass %)

dW480 = mass loss at 480°c

W120 = mass loss at 120°c

3 Result and Discussion

The results of TGA/DTA on cement pastes replaced with various percentages of Neem seed husk ash are given in Figs 1 to 6.

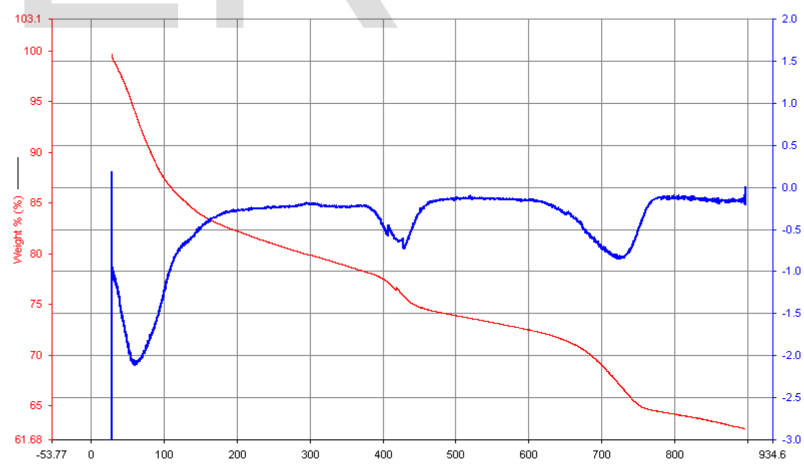

Fig 1: TGA/DTA of Cement paste containing 0% Neem seed husk ash replacement

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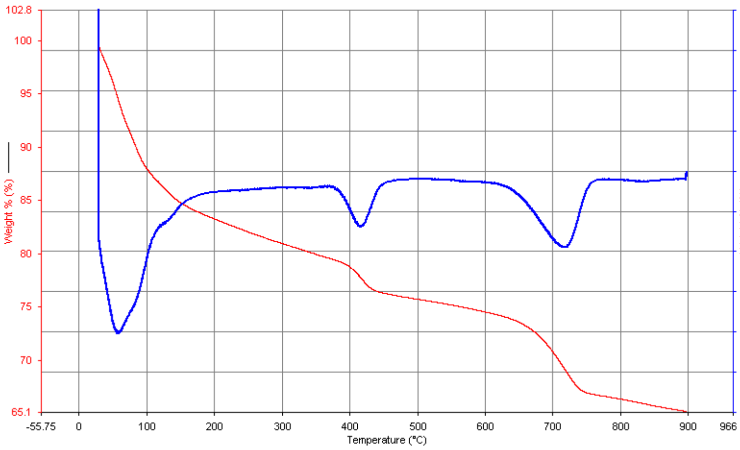

Fig 2: TGA/DTA of Cement paste containing 5% Neem seed husk ash replacement

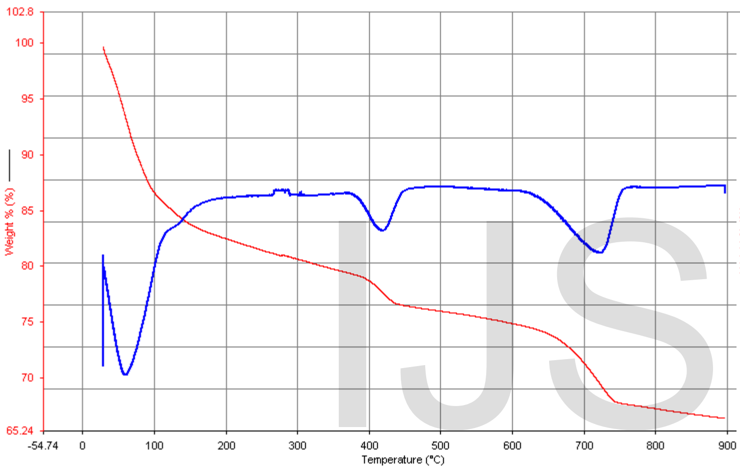

Fig 3: TGA/DTA of Cement paste containing 10% Neem seed husk ash replacement

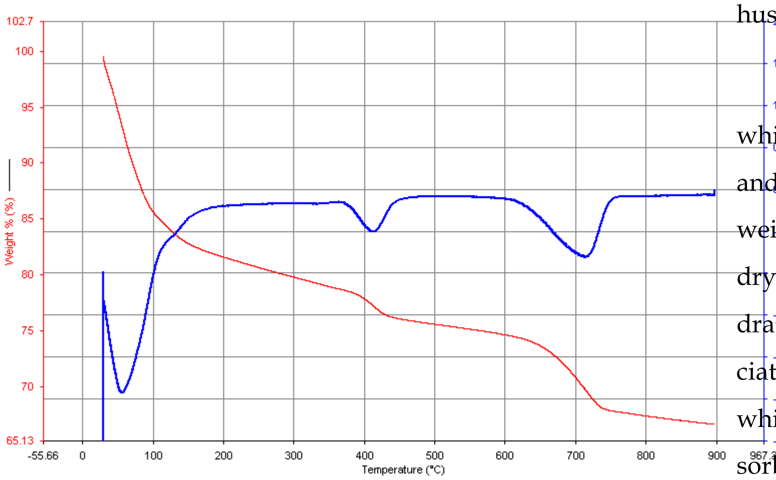

Fig 4: TGA/DTA of Cement paste containing 15% Neem seed husk ash replacement

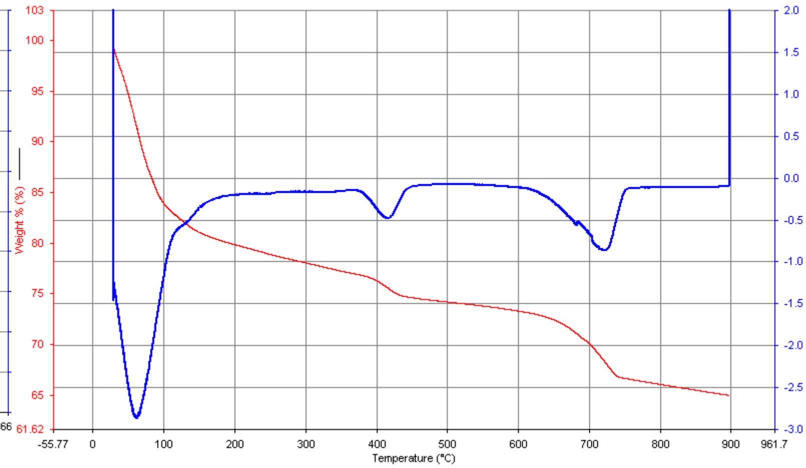

Fig 5: TGA/DTA of Cement paste containing 20% Neem seed husk ash replacement

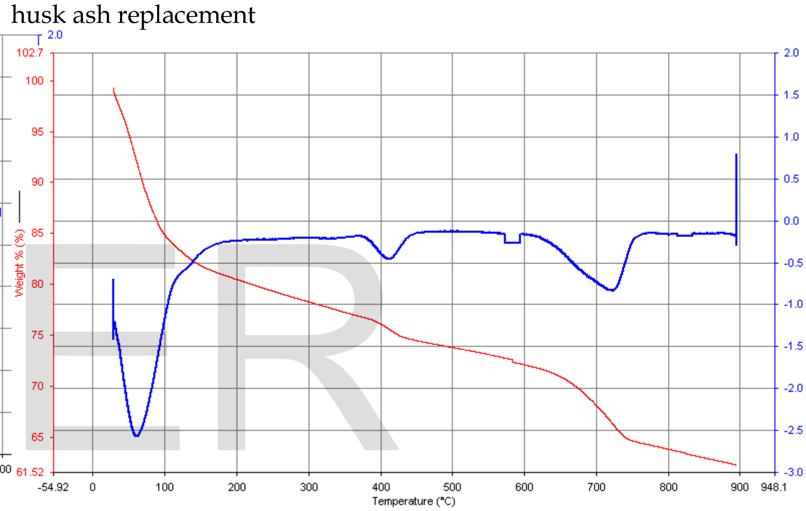

Fig 6: TGA/DTA of Cement paste containing 25% Neem seed husk ash replacement

Figure 1 shows result of TGA/DTA of control paste which is cement without Neem seed husk ash replacement, and cured for 28 days. The TGA curve shows three significant weight loss steps. The first at about 100°C has to do with the drying (capillary pore residual water) and / or with the dehydration of ettingrite. This first weight loss step is usually associated with several minor steps that are likely to take place which includes capillary pore water, interlayer water and adsorbed water. The corresponding peaks overlap each other because of the dynamic heating process [7]. This phase accounts for the major part of the weight loss as can be seen from the relatively sharp peak on the derivative curve.

The second weight loss step at about 400^oC – 450^oC is due to the dehydration of CH. Following chemical reaction usually takes place in this region:

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

The third weight loss step at about 700^oC can be attributed to the de-carbonation of $CaCO_3$. The carbonate is however not present in the original mixture and must therefore arise from a carbonation reaction. Equation (3) shows the carbonation reaction, while equation (4) shows the subsequent de-carbonation equation [8].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \text{ (carbonation)} \quad (3)$$

$$CaCO_3 \rightarrow CaO + CO_2 \text{ (de-carbonation)} \quad (4)$$

The DTA curve show that the three weight loss steps each correspond to endothermic processes. Endothermic process is a process or reaction in which the system absorbs energy from the surroundings in the form of heat. It can be identified on the DTA curve by the U-shaped depression in the curve which symbolizes rapid loss of weight followed by rapid gain in the weight.

From Figures 1 to 6, the derivative loss of weight losses from the DTA curves representing various Neem seed husk ash replacements at various temperature ranges are presented in Table 2.

Table 2: Derivative loss of weight from the DTA curves at various temperature ranges and different Neem seed husk ash replacements.

Neem seed husk ash Replacement	0 – 100^oC	400 -500^oC	700 – 800^oC
0%	2.13%	0.70%	0.80%
5%	2.00%	0.65%	0.86%
10%	2.26%	0.59%	0.77%
15%	2.33%	0.50%	0.74%
20%	2.81%	0.48%	0.80%
25%	2.57%	0.47%	0.78%

The derivative loss weight can be seen more clearly from Table 2. As earlier stated the temperature range of 0-100^oC has to do with the drying (capillary pore residual water) and / or with the dehydration of ettingrite. It can be seen from the table that the derivative weight loss reduces from 0% to 5%, after which it increases up to 20% Neem seed husk ash replacement, and then there is decrease at 25%. The second temperature step of 400^oC – 500^oC is as earlier stated due to the dehydration of CH. It can be seen from the Table that there is decrease in derivative weight with increase in Neem seed husk ash content. The third temperature range of 700 - 800^oC is attributed to the de-carbonation of $CaCO_3$ as earlier stated, and its effect can be seen from the table.

Also, From Figures 1 to 6, the TGA and DTA curves shows similar pattern, which provides every reason to believe that Neem seed husk ash participate in the hydration process of the system. The TGA curves are used to calculate the amount of Calcium hydroxide (CH) in the system based on the formula given in equation 1, the result is shown in Figure 7.

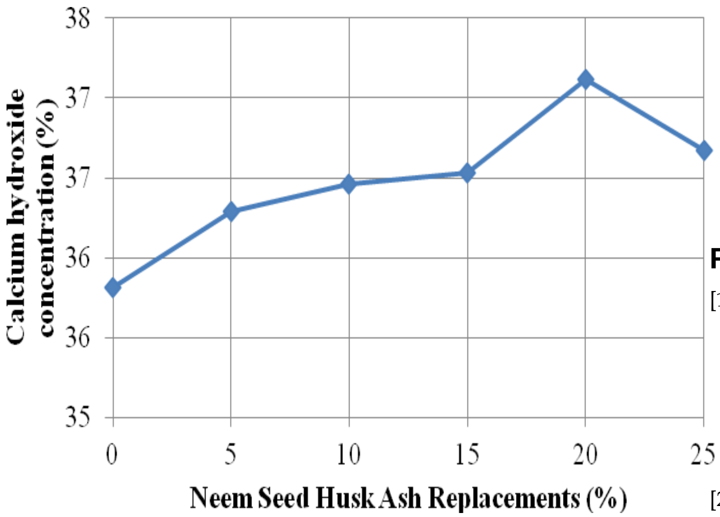

Fig 7: Calculated Calcium hydroxide concentrations derived from TGA curves

It can be seen that paste 0% replacement has the lowest concentration of calcium hydroxide at 28 days. The contents increases with increase in Neem seed husk ash replacements. But, it is well believed that in pozzolanic reaction, the CH behaves as an activator and reacts with the active part of a pozzalana (SiO_2, Al_2O_3) [9]. The reaction consumes the existing CH rather than releasing it. Based on this, it can be deduced that Neem seed husk ash is not acting as a pozzalana but rather as filler.

4 Conclusions

Based on the experimental results and discussions, the following conclusion can be drawn:

1. Thermogravimetric and Differential Thermal Analysis (TGA/DTA) curves for the control (0%) and cement replaced with Neem seed husk ash shows similar pattern, which provides every reason to believe that Neem seed husk ash participate in the hydration process of the system.
2. The TGA curves are used to calculate the amount of Calcium hydroxide (CH) in the system. It was observed that cement paste without Neem seed husk ash has the lowest concentration of calcium hydroxide at 28 days. The contents increases with increase in Neem seed husk ash replacements, and it is deduced that Neem seed husk ash is not acting as a pozzalana but rather as filler.

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