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Special Issue

A Themed Issue in Honour of Professor Onukwuli Okechukwu Dominic (FAS).

This special issue is dedicated to Professor Onukwuli Okechukwu Dominic (FAS), marking his retirement and celebrating a remarkable career. His legacy of exemplary scholarship, mentorship, and commitment to advancing knowledge is commemorated in this collection of works.

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Investigating thermal effect of castor seed shell use as cement raw mix admixture

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Abstract
This study investigated the thermal effect of castor seed shell inclusion as a cement raw mix admixture. Four samples of cement raw mix were designed using different formulations. Samples 1, 3, 4 have castor seed shell additive while sample 2 is the control of the research and was designed without castor seed shell additive. Temperature measurement recorded during the calcination of the raw mix showed that for samples 1, 3 and 4, the inclusion of castor seed introduced fluxes into the mix and acted as an additional fuel which rapidly increased the calcination temperature and resulting in a more rapid dissociation of raw mix thereby lessening the time needed for the formation of the clinker by 30 minutes and above. Thermogravimetric analysis of the samples showed that the inclusion of castor seed shell in the cement raw mix impacted positively on the thermal stability of the cement sample. Sample 1 had the highest thermal stability and two stages of decomposition. However, the inclusion of castor seed in sample 1, 3 and 4 resulted in an increased loss in mass above the thermal stability temperature. Sample 2 had a four-stage decomposition process when heated at a constant rate to a temperature of 1000^0C but exhibited a higher level of thermal stability temperature higher than sample 3 and 4.

Keywords: cement admixture; thermal stability; castor seed shell; calcination, temperature

1. Introduction

Cement is one of the most important materials used by the construction and civil engineering industries as binders in the construction of buildings and other concrete works. It is a finely ground powder consist mainly of lime and silica with smaller amounts of alumina and iron. Cement exhibits excellent durability and strength and is highly useful in the construction of houses, civil work and industrial estates. It provides noise insulation and helps to withstand extreme changes in climatic conditions and weather attacks (Roman et al., 2021). Limestone, clay, laterite, gypsum are the major primary raw materials used in cement production. Limestone, a naturally occurring material composed mainly of limes with small quantities of silicon oxide and aluminium oxide, constitutes over 70% of the aggregate mixture of the raw mix in cement production (Duhui 2018). Clay and sometimes in addition with laterite constitutes between 10 to 25% of the raw mix and contributes to the chemical composition of cement by providing essential elements such as aluminium, silicon, iron and magnesium and other alkaline earth metal (Lidia 2020).

About 5% or less of gypsum was added during the grinding of the clinker it is used as raw material, mineralizer, retarder, or activator in cement plants. The sulfur oxide parts of the gypsum compound can be particularly useful in balancing the sulfur-alkali ration in the calcining of the clinker thereby improving the calcining operation and the service life of the refractory material (Frigione 2022).The primary role of gypsum in cement production is to regulate the setting time of the cement. The addition of gypsum to the cement clinker helps to slow down the reaction between cement and water allowing more time for workability and reducing the risk of premature setting. Gypsum also controls the hydration reaction of cement preventing the rapid hydration of tricalcium aluminate compound in cement which is responsible for early strength development (Frigione 2022).

Environmental concerns and the need for sustainability in cement production have gained momentum in recent time. The cement industry is one of the major contributors to greenhouse gas emission. Studies showed that about 8% of CO_2 emission comes from the cement industry due to the high energy clinker manufacturing process and the chemical release of CO_2 from the limestone during the calcination (Hryoje et al., 2020). Industry players have adopted a number of approaches towards sustainability and these include the use of alternative fuels and raw materials such as biomass, waste materials and recycled byproducts (such as fly ash and slag), clinker substitution which involves the uses of pozzolans and limestone other low carbon additives, carbon capture, utilization and storage, energy efficiency and process optimization and the use of alternative cement and concrete types (Lochana et al., 2021).

The use of alternative raw materials holds greater promise to the achievement of the sustainability objectives of the 21^{st} century cement industry. Biomass materials which are materials from animal and plant remains are increasingly being used in the cement industry as alternative fuel for the firing of fire Kiln. Studies on the potential of biomass materials as an alternative fuel source showed that biomass material are carbon neutral and can be used on a considerable proportion to replace fossil fuel thereby helping to reduce the greenhouse gas emission from cement production (Tade 2019). The use of biomass fuel mixture was studied on an industrial production line of 6000 tons cement plant in order to reduce dependency on bituminous coal and the results showed a significant reduction on the levels of CO_2, SO_2 and NO_X emission but an increase in the emission of CO which however still fall within below the environmental limits (Saleh 2019). The positive impact of biomass energy use in Indonesian cement plants showed a reduction in energy consumption by 499.000mwh and decrease in CO_2 emission by 361.309.000 tons per year and these highlighted the need for a gradual shift from coal based energy production to biomass energy due to the abundance biomass materials such as rice husk, plantation crops, wood, palm kernel shaft etc (Murodef 2023).

Again, biomass materials are increasingly being used as a substitute to cement and cement raw materials as results of their cementitious properties of some biomass ash. Biomass fly ash used as substitute for chemical admixture for viscosity enhancement for self-consolidating cement tailing grout (CTG) at low mass fractions (50% and 60%) was found to significantly improvement on the work-ability and mechanical strength of the cement (Jiaxu et al., 2022).Biomass power plant ash used to replacing parts of sulfoaluminate cement to produce SAC blended cement showed that at 10-15% replacement, a significant improvement on the mechanical strength of the cement is achieved however by increase in the replacement level above 15%,there is an increase in the fluidity and setting time of the cement paste (Honzhang et al., 2022). Biomass ash as a supplementary cementitious material have been found to offer advantages to traditional mineral additive by improving its characteristics and decreasing its environmental impact (Olatoyan et al., 2023).The compressive strength cubes produced with cement replaced by rice husk ash at percentage between 10 to 50% showed that there improvement in the strength of the mix from 14 to 28days of curing at 10 to 20% replacement (Dabai, et al., 2019). Rice husk ash also showed cementitious properties when used as a partial replacement for cement in a concrete mix and the result showed an improvement in the compressive strength curing for 7 to 28 days (Bandaba 2022).

Castor seed shell is a biomass material found in abundance in Nigeria and has been extensively studied to determine its suitability for different engineering applications. A study demonstrated the potency of castor seed shell in the development of composites (Ogah et al., 2024). Castor seed shell has also been applied in the development of less dense and low-cost fiber reinforced aluminum matrix and the micro and chemical analysis of the shell showed a cementitious material (Dara et al., 2021). Studies on the mechanical effect of castor seed shell on polyester composite showed an improved strength of the polyester composite (Nwigbo et al., 2019). Castor seed shells are found in abundant quantity in many local and remote villages and these constitute environmental nuisance due the indiscriminate disposal and lack of proper handling. Previous studies showed that the chemical composition of the castor seed ash are made of significant percentage of calcium, silicon, iron, potassium and smaller traces of manganese, chromium, copper, vanadium and cobalt (Nwigbo et al., 2019), making it a good material for cement

admixture due to the presence of calcium, silicon and iron which are essential chemical composition of cement raw materials.
Therefore, there is a need to find a better utilization of the abundant supply of castor seed shell in order to solve the problem of environmental pollution and harness other benefits that can be derived from the chemical composition of the castor seed shell when applied as cement raw mix. Inclusion of castor seed shell in cement production is another approach towards the conservation of the environment, better waste management and the introduction of innovation in cement production. By studying the thermal effect of castor seed shell during cement production and on the final product, we can gain insight into their advantages and disadvantages and find better ways to optimize the process.

2.0 Materials and methods

2.1 Materials

Limestone, clay, gypsum and laterite and castor seed shell are the major cement raw materials used in this study. Samples of high grade limestone and laterite were obtained from Nkalagu mines in Ebonyi State, while clay was obtained from Ukpo clay mines in Anambra State. Gypsum was obtained from Otukpo in Benue State. The castor seed shell was obtained from a village close to Awka in Anambra State. Charcoal and automotive gas oil (AGO) sourced from Awka and environs are the main sources of heat energy used for the firing of the kiln and are simultaneously used together to achieve a faster calcination process.

An optical pyrometer, a stop watch for time measurement and a digital weighing scale was obtained from the materials laboratory of the department of Mechanical Engineering Nnamdi Azikiwe University, Awka. Optical pyrometer that measures temperatures in the range of 700°C to 4,000°C was used to monitor the temperature changes during the calcination process. A thermogravimetric analyser (TGA 2950) equipped with a TA instrument universal analysis 2000 software was procured from a private laboratory was used for the measurement of temperature and mass changes during the procedure.

A furnace used for the calcination process was obtained from the Nnamdi Azikiwe University mechanical engineering workshop. It has a heating chamber made of steel on the outside and lined on the inside with a refractory material. The design of the furnace is such that it accommodates different sources of heat e.g. charcoal, coal and AGO. There is also a crucible made with a caste refractory cement that contains the cement raw mix during the calcination process.

2.1.1 Methods

2.1.1.1 X-ray fluorescence analysis

Four samples of cement raw mix were designed using the results of the chemical characterization of the cement raw materials earlier performed using XRF analysis. The design for the different samples was done in order to achieve a lime saturation factor of 0.92-0.98, silicon modulus ratios of 2.0-3.0 and aluminum modulus ration of 1.2-1.5. The raw mix maintains the ASTM C1567 recommendation value of minimum of 50-65% calcium oxide (CaO), 20-25% of silicon oxide (SiO,), 1-2% of iron oxide (FeO) and 3-8% of aluminum oxide (Al_2O_3) which ensures that the mix are burnable and consisting of the necessary oxide for the formation of the correct phase composition of the clinker and the final cement product (Barath et al., 2022). Sample 1 was designed using 1.2kg of limestone, 0.294kg of clay and 0.075kg of castor seed shell. Sample 2 contains only 1.2kg of limestone and 0.294kg of clay. Sample 3 was designed with 1.172kg of limestone, 0.303kg of clay, 0.0255kg of laterite and 0.075kg of castor seed shell. Sample 4 was designed with 1.113kg of limestone, 0.387kg of clay and 0.075kg of castor oil seed shell.

Samples 1, 3 and 4 had a constant ratio of castor seed shell of 0.075kg ensured that the shell provided an optimal addition for minor adjustment to the raw mix chemistry, potentially reducing the reliance on other materials while contributing to silica, calcium and optimizing the burn-ability of the samples. We carefully measured out the quantity of each cement raw materials using a digital measuring instrument and they were thoroughly mixed together in order to obtain a uniform raw mix. All other samples except sample 2 had castor seed shell as an additive. Sample 2 is the control of the experiment and the basis of comparison because the effect of castor seed shell inclusion in other samples will be absent from the sample 2 which is designed with only limestone and clay. The raw mix samples were placed in a crucible in the middle of the furnace and fired using a combination of charcoal and automotive gas oil as fuel source. During the calcination, temperature measurement was taken every 30 minutes to monitor and track the temperature changes. On reaching to a temperature above 1450^oC the firing was stopped and the clinker for each sample was allowed to cool down and 5% gypsum was added to the clinker while grinding to a powder.

2.1.1.1.1Thermogravimetric analysis

Thermo gravimetric analysis of the resulting cement sample was carried out using TA instruments thermal gravimetric analyzer (TGA 2950). The samples were put in ceramic pan and placed in the sample position and another empty ceramic pan was placed in its position as a reference pan. The selected ceramic pan was placed on the sample platform and tarred. Experimental parameters; sample name, operator name and instrument information (heating rate, start and end temperature etc.) were entered through the TA Instruments universal analysis 2000 software. The pan with sample was placed on the sample platform. Prior to this, nitrogen purge gas was set at 60 ml/min and 40 ml/min for the furnace and balance chambers.

3.0 Results and Discussion

3.1 Calcination temperature

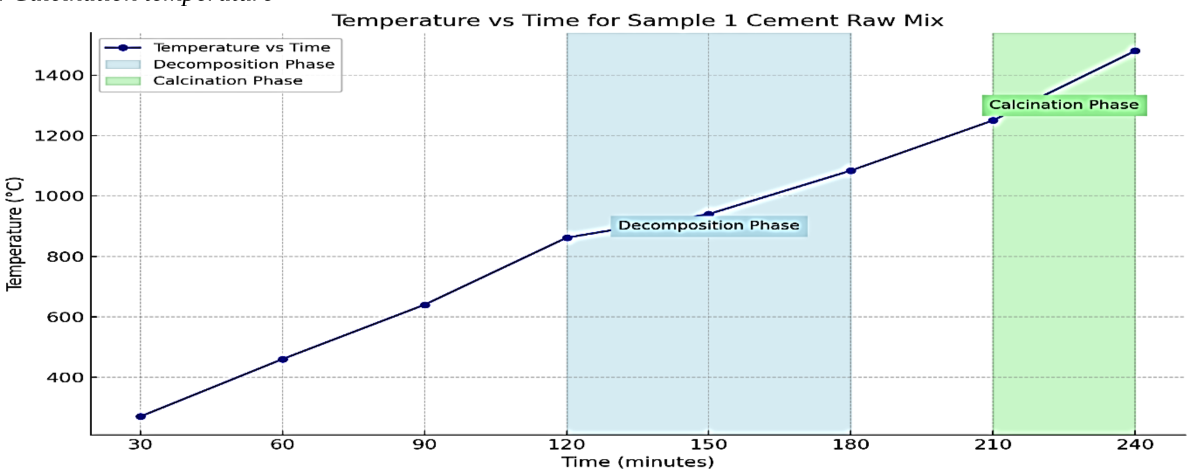

Figure 1: Temperature-time measurement for calcination of sample 1 cement raw mix

There was an initial steady temperature rise between 30-90 min from 270^{0}C to 640^{0}C.This phase represent the removal of free water of dehydration of clay mineral and other components of the raw mix. This process is an endothermic reaction requiring a moderate energy. Between 90-180 min, there was a sharp rise in temperature from 640-1084^{0}C and the decomposition of the limestone into calcium oxide and carbon dioxide occurred. The castor seed shell was believed to have contributed to the rapid increase in temperature due to its combustion which released heat that aided in the decarbonization process. The temperature plateaus around 1250-1480^{0}C resulted in the calcination of the raw mix forming clinker minerals such as tricalcium silicate (C_3S) and the dicalcium silicate (C_2S) which were critical to the cement strength. The combustion of the organic castor seed shell left a residual ash which potentially influenced the clinker composition.

3.1.2 Effects of castor seed shell on the calcination process

The castor seed shell as an organic matter underwent combustion between temperature 200-400^{0}C, providing additional heat which accelerated the decomposition of the limestone thereby reducing the overall energy requirement for the calcination reaction. This made the process more energy-efficient. The castor seed shell ash residue consisted of calcium, silicon, iron, sodium and potassium influenced the chemical composition of the clinker (Nwigbo 2019). The potassium, sodium and silica acted as fluxing agent which lowered the melting point of the raw mix and enhanced the clinker formation (Pawhik 2019). Addition of castor seed shells on the raw mix contributed to the sustainability of the production process by utilizing agricultural waste thereby reducing the reliance on fossil fuel. However, excessive use of castor seed shell may impact negatively on the quality of the final product reducing strength of the product.

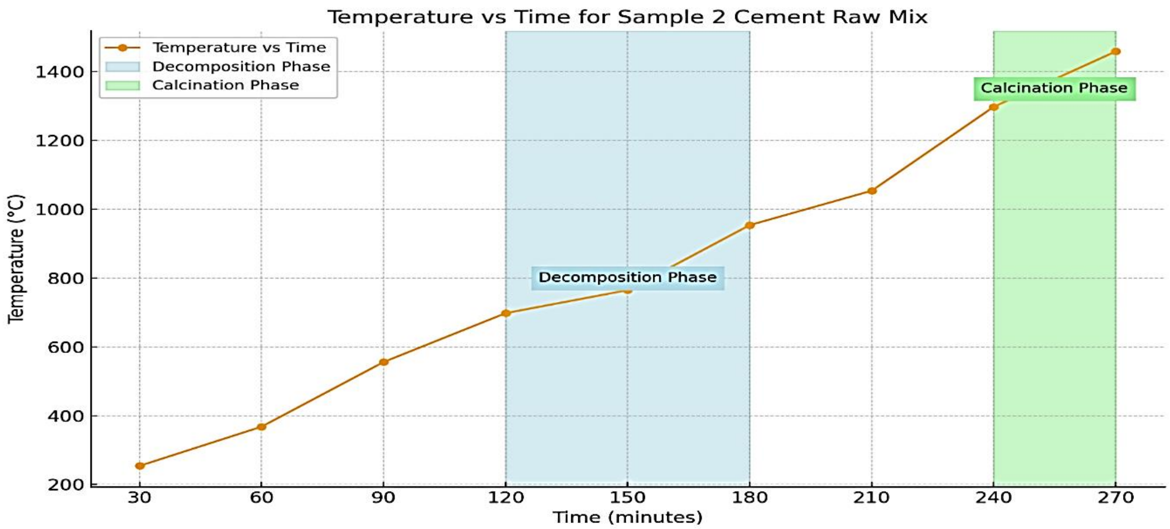

Figure 2: Temperature-time measurement for calcination of sample 2 cement raw mix

There was a steady increase in temperature from 270-600^{0}C at 30-90 min leading to the evaporation of free water and the dehydration of clay minerals. This was an endothermic process with moderate energy input. The decomposition phase occurred between 120-180 min at the temperature range of 862-1084^{0}C where the decarbonization of the limestone ($CaCO_3$) into calcium oxide (CaO) and carbon dioxide (CO_2) occurred. The decomposition trend was consistent but the absence of castor seed shell implied that no additional heat contribution from the organic matter combustion and this resulted to more external energy requirement for the calcination process. The calcination phase occurred between temperatures 1250-1480^{0}C corresponded to the time between 240-270 min. Here, the high temperature facilitated the formation of key clinker phases such as tricalcium silicate (C_3S) and dicalcium silicate (C_2S) which are essential to the strength and durability of the final cement product.

3.1.3 Effects of absence of castor seed shell on the calcination process

The absence of castor seed shell in sample 2 raw mix implied that there was no energy contribution from the combustion of the shell unlike in other samples. This led to more energy requirement from an external source especially during the decomposition phase. Also, the temperature surge was observed to be more gradual during the decomposition phase and the calcination process required more time (about 30 min and more) to complete the reaction. Without the flux from the ash (potassium or sodium compounds) that could lower the melting point of the raw mix, a higher temperature requirement will be needed for the formation of the clinker. However, the final cement product may have lower porosity, fewer impurities which may lead to a more consistent and stronger cement product as organic matters may introduce unwarranted variability into the product.

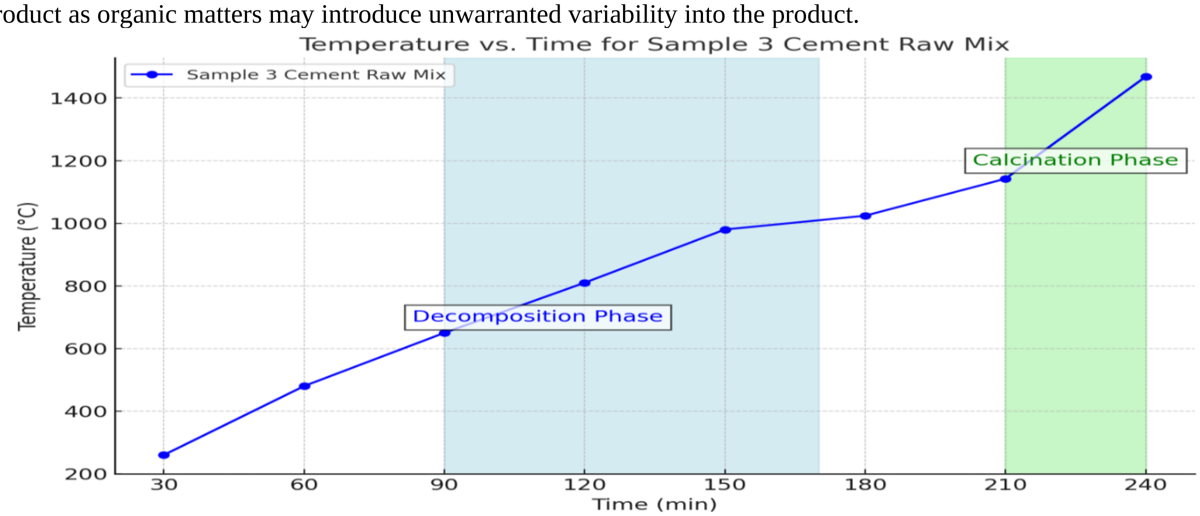

Figure 3: Temperature-time measurement for calcination of sample 3 cement raw mix

There was an initial heating phase between 30-90 min which rapidly increased the temperature from 260-650^{0}C resulting in the evaporation of moisture and some early reactions in the raw mix. The decomposition phase was an intensive energy process of the calcination reaction and occurred between 90-180 min which dissociated the limestone into calcium oxide and releases carbon dioxide after which there was also a steady rise in temperature from 980-1142^{0}C at 150- 210 min. This temperature change signaled a preparation for the intense reaction of the calcination phase which occurred between 210-240 min. The temperature rose steadily from 1142^{0}C to 1468^{0}C leading to calcination of raw mix and formation of essential phase composition of clinker for example tricalcium silicate and dicalcium silicate.

3.1.4 Thermal effect of castor seed shell and laterite on the calcination process

The major thermal effect of castor seed shell as observed from the temperature measurement is that the presence of castor seed shell contributed additional heat energy during the calcination process thereby reducing fuel requirement from external source. This energy contribution from the castor seed shell is believed to have accelerated the decomposition of the limestone thereby improving the efficiency of the clinker formation however the addition of castor seed shell introduced minor impurities and this has an effect on the final composition of the cement product

Laterite and castor seed shell introduce iron oxide and other fluxing agents into the mix helping to lowers the melting point of the raw mix thereby facilitating the clinker formation at lower temperature.

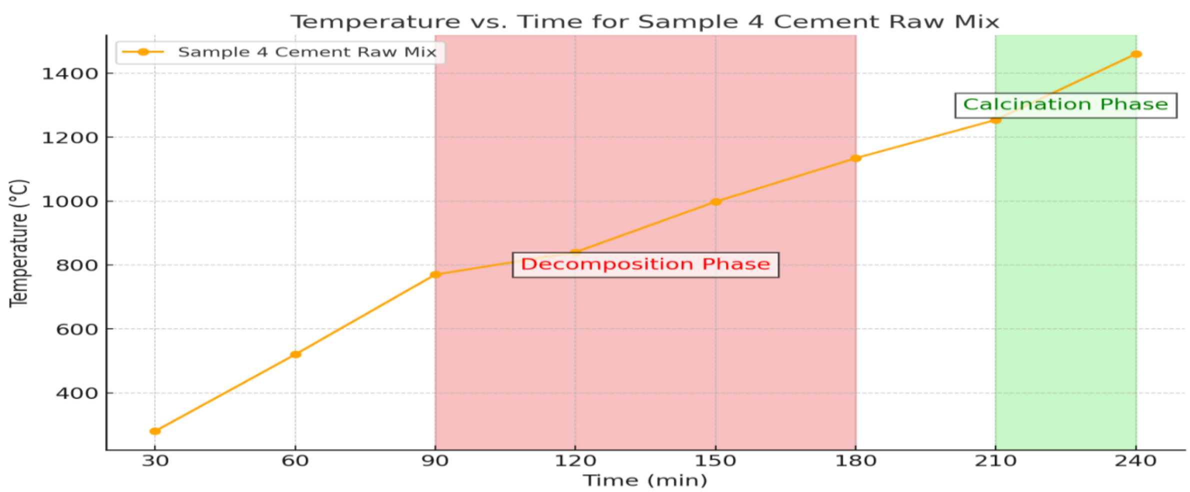

Figure 4: Temperature-time measurement for calcination of sample 4 cement raw mix

From the graph of figure 4, there was a rapid temperature rise from 280-770^{0}C indicating an initial heat absorption by the raw mix in preparation for the decomposition reaction and the evaporation of moisture present in the raw mix. Between 90-180 min corresponding to 770^{0}C to 1134^{0}C the decomposition of the raw mix occurred and limestone was decomposed into calcium oxide (CaO) and carbon dioxide (CO_2).The next phase was the calcination phase which occurred at 210-240 min and temperature between 1254^{0}C and 1460^{0}C. This phase represented the chemical reaction which the forms of tricalcium silicate and dicalcium silicate which are the major essential phase composition of a clinker.

3.1.5 Thermal effect of castor seed shell on the calcination process

The inclusion of castor seed shell introduces organic material. This additive acts as an additional fuel source and introduces flux agents into the raw mix, potentially reducing the overall energy requirement during calcination and increases the burn-ability of the raw mix due to its combustion properties. There is an efficient temperature distribution and quicker reaction times however the organic residues from castor seed shell combustion might integrate trace elements into the clinker could influence the cement's final properties, such as setting time, strength, and durability.

3.2 Thermal decomposition and thermal stability

3.2.1 Thermal decomposition of cement sample 1

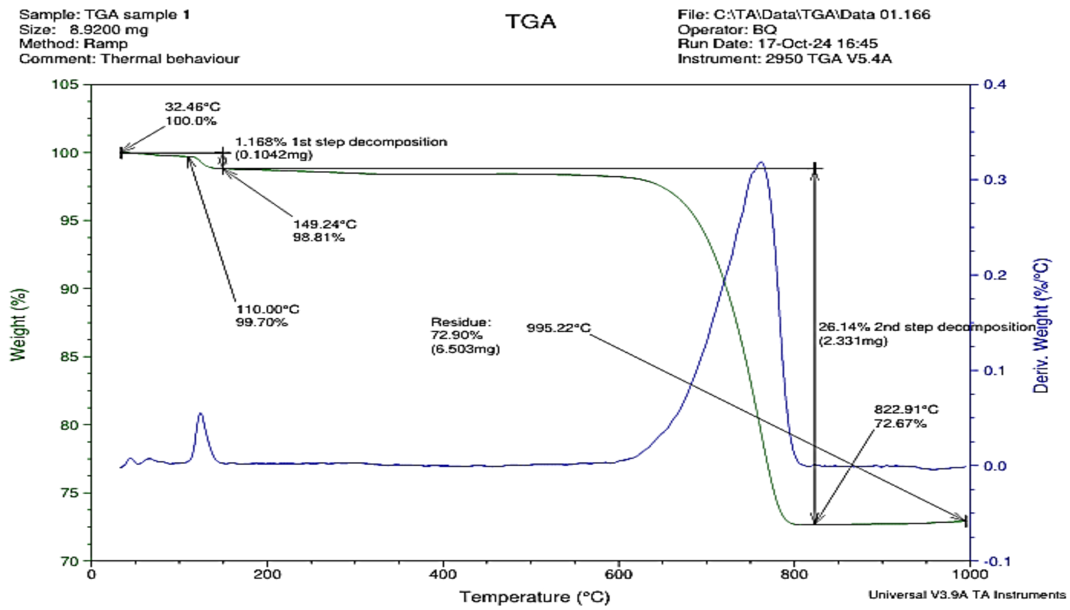

Figure 5a: Thermal decomposition of cement sample 1

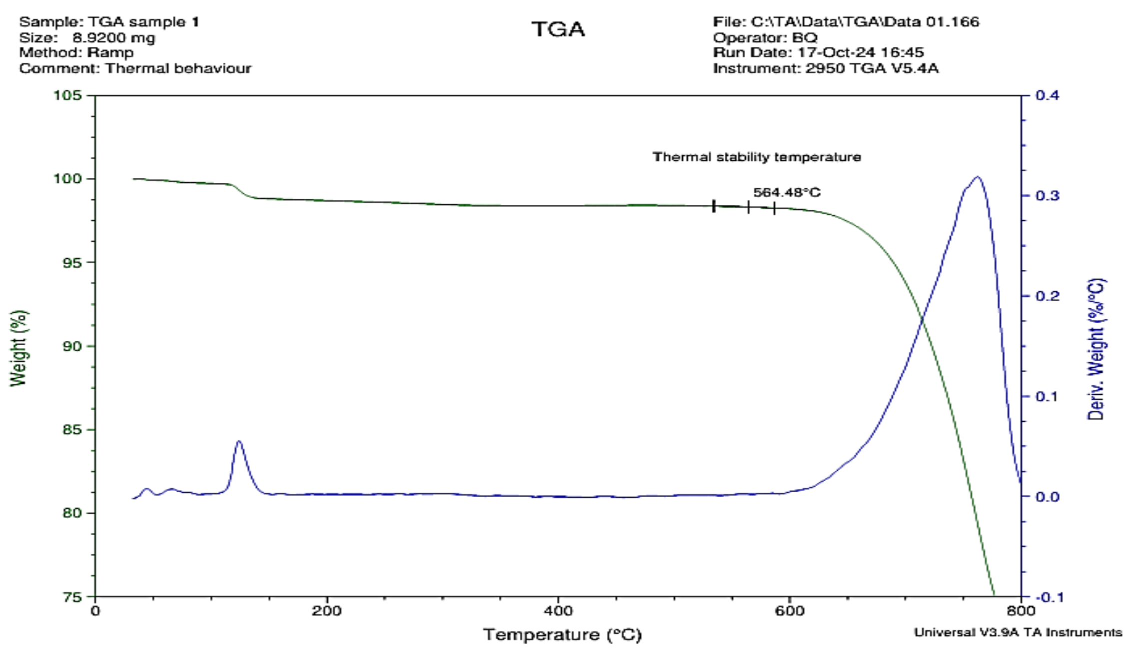

Figure 5b: Thermal stability of cement sample 1

Figure 5a shows the effect of heat on the mass of the cement sample 1 when heated at a constant rate to a temperature of 1000^0C. There was an initial weight loss of 0.3% from 32.46^0C to110^0C and this was attributed to the evaporation of free and bound water from the cement sample present due to gypsum, hydration products or atmospheric absorption. The first stage of decomposition occurred between 110^0C and 149. 20^0C resulting in a 1.168% (0.1042mg) weight loss of the sample and this was attributed to the small molecular organic compounds present in the cement sample. The second stage of the decomposition occurred at a slower rate between temperature

149.24^{0}C and 600^{0}C and then a sharp increased decomposition was observed between 600^{0}C and 1000^{0}C resulting in 26.14% weight loss of the sample due to the decomposition of some free limestone in the cement and some residue from the castor seed shell ash. The cement sample was observed to be thermally stable at 564.48^{0}C as shown in figure 5b and at this temperature the cement sample remained thermally stable without a significant weight loss. This level of thermal stability was attributed to contribution of castor seed shell to the mineral composition of the cement whose ash analysis showed a higher level of calcium, silicon, aluminum and ferrous composition (Nwigbo 2019).

3.2.2 Effect of castor seed shell on thermal decomposition of cement sample 1

The presence of the castor seed shell increased the thermal stability temperature of the cement sample 1. This suggested that the admixture enhanced the durability of the cement at a higher temperature. The castor seed shell ash contributed to the chemical composition of the cement by providing essential elements such calcium, silicon, aluminum and ferrous iron and minor additions of fluxes such as potassium and sodium modified the thermal behavior of the sample giving it a higher thermal stability. These minerals integrated into the cement potentially affected the mineralogical composition of the cement by influencing the mechanical strength and setting properties of the cement. 98.90% of the sample weight remained intact at the thermal stability temperature of 564.48^{0}C. This was associated to the presence of castor seed shell ash which contributed to the chemical composition of cement by addition of more pozzalonic materials into the chemical mix of the cement.

3.2.3 Thermal decomposition of cement sample 2

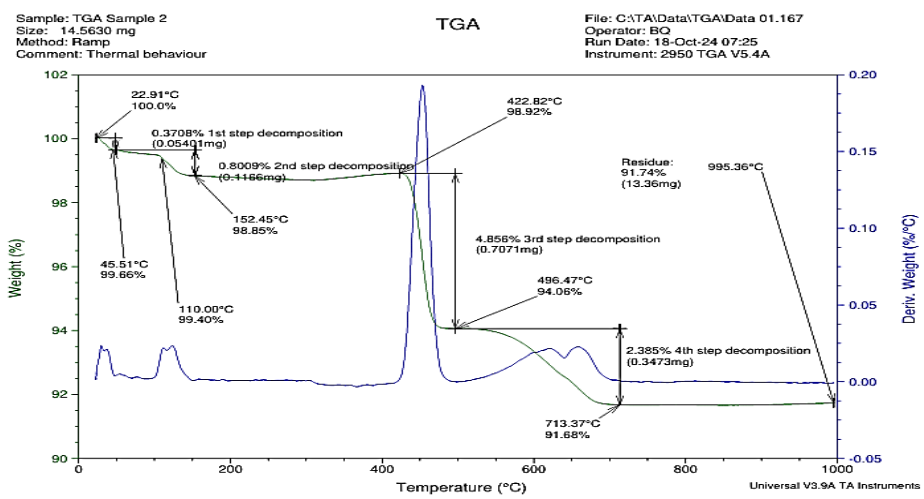

Figure 6a: Thermal decomposition of Cement Sample 2

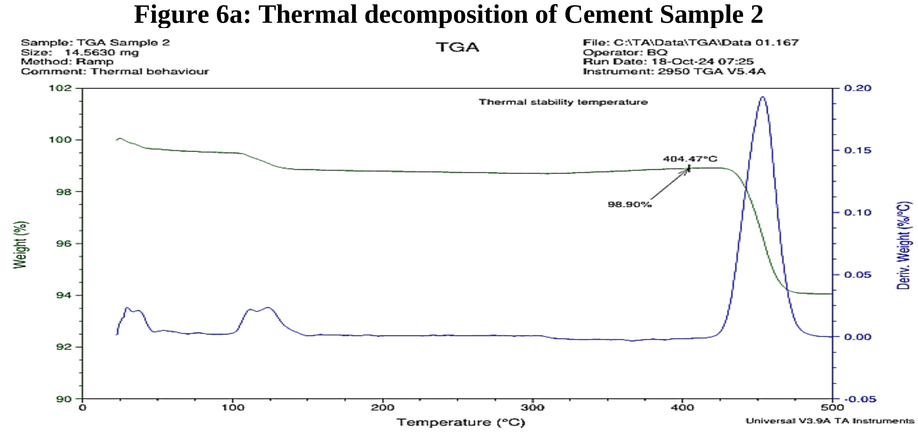

Figure 6b: Thermal Stability of Cement Sample 2

Figure 6a summarized the decomposition of the cement sample 2 when heated at a constant rate to a temperature of 1000^{0}C. At 22.91°C, the sample showed 100% weight and at the 45.51°C, a minor weight loss of 0.34% occurred as a result of evaporation of moisture on the surface of the cement particles. The first stage of decomposition occurred between 45.51^{0}C and 110^{0}C with 0.3708 % (05491mg) weight loss of the sample and this was attributed to the removal of free and loosely bound water in the cement matrix and any other remaining moisture in the sample. The second stage of decomposition occurred between 110.00^{0}C and 152.45^{0}C with 0.8009 % (0.1166mg) weight loss as a result of dehydration of gypsum to form hemi-hydrate and anhydrate phases which released water from the sample (Pradip and Tanuj 2019). The third stage decomposition occurred between 422.82^{0}C and 498.47^{0}C with a peak weight loss of 4.856 % (0.7071mg) attributed to the decomposition of dehydroxylation of kaolinite (Zanata 2020) and other related phases and liberation of water and other organic volatile compound. The stage 4 decomposition occurred between temperature 713.37^{0}C and 995.36^{0}C with 2.385 % (0.3473mg) weight loss of the sample and this was attributed to the decomposition of free limestone into calcium oxide and carbon dioxide.

3.2.4 Effect of the Absence of Castor Seed Shell Additive on Thermal Behavior Sample 2

91.68% of mass of sample 2 consisting of stable phase like calcium oxide and other oxides remained after complete thermal decomposition at temperature of 1000^{0}C, showed that sample 2 maintained its weight at higher temperature more than the other samples. The absence of castor seed shell ash additive in sample 2 implied that there was less organic matter in the cement which burnt off resulted in weight loss. The thermal stability of sample 2 cement occurred at 404.47^{0}C which was a lower temperature compared to thermal stability of sample 1.This was attributed to the fact that the chemical composition of sample 2 was not modified with castor seed shell ash.

3.2.5 Thermal decomposition of cement sample 3

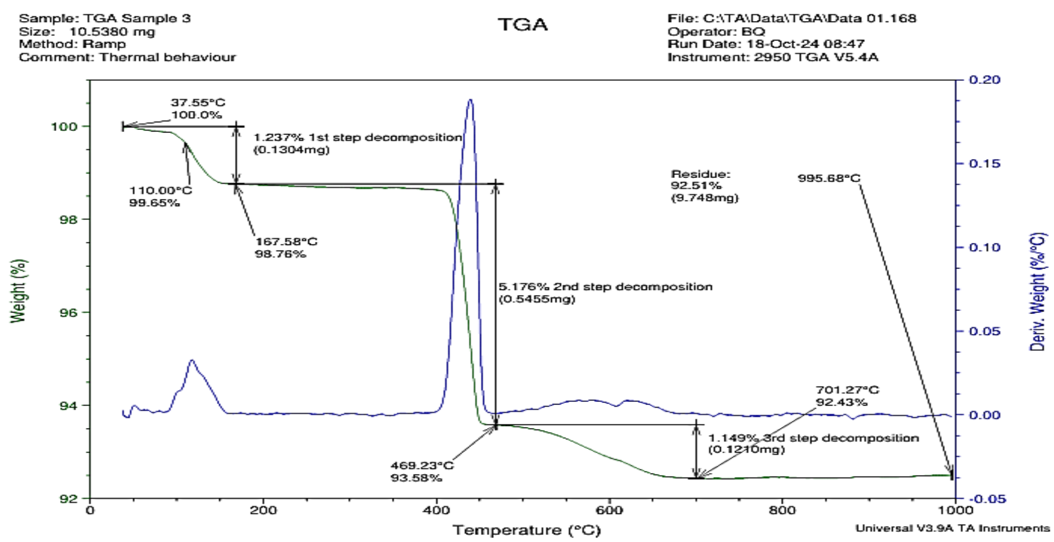

Figure 7a: Thermal decomposition of cement sample 3

There were three stages of decomposition in sample 3 as observed in the figure 7a. The first stage decomposition occurred between 37.55^{0}C and 110^{0}C with 1.237% (0.1304mg) weight loss. This was typical of cement and reflected the initial dehydration caused by evaporation of free water and absorbed moisture present in the cement sample. The second stage decomposition occurred between 110^{0}C and 469.23^{0}C at a region involving multiple thermal process such as the dehydration of gypsum and the dehydroxylation of clay minerals from limestone, clay and laterite resulted in 5.176% weight loss indicated a substantial water removal, and early thermal decomposition of clay phases (Pradip and Tanuj 2019 and Zanata 2020). The third decomposition stage occurred between 469.23^{0}C and 701.27^{0}C with 1.149% (0.1210mg) weight loss attributed to minor decomposition of phases introduced by laterite and organic carbon residues in the castor seed ash. The lower weight loss here reflected the contribution of stable additives from the castor seed shell ash, which helped retain structural stability under thermal load. At higher temperatures between 701.27^{0}C and 995.68^{0}C the free limestone present in the sample decomposed into calcium carbonate and calcium oxide leaving behind a residue of 92.53% of the total sample weight. The thermal stability temperature of cement sample 3 occurred at 398.69^{0}C with 98.54% of the sample weight remaining intact.

3.2.6 Effect of castor seed shell additive and laterite on thermal stability of the cement sample 3

The presence of castor seed shell was believed to have provided pozzolanic elements to the cement composition contributed organic content which decomposed at temperature between 300^0C-400^0C. The derivative weight loss peak at 398.69^0C was due to organic residue decomposition from the castor seed shell ash. Also the pozzolanic reaction between the castor seed shell ash derived silica and lime might be less significant in sample 3 as a result of the lower values of limestone used in the formation of sample 3. The laterite composition of the cement also introduced thermally unstable phases like kaolinite and other hydrated minerals which lowered decomposition temperature (Zanata D, 2020). Also the difference in phase composition due to the different proportion of limestone, clay and laterite used in the formation of the raw mix led to higher fraction of thermally unstable phases (hydrated silica's) and earlier weight loss due their decomposition at lower temperature.

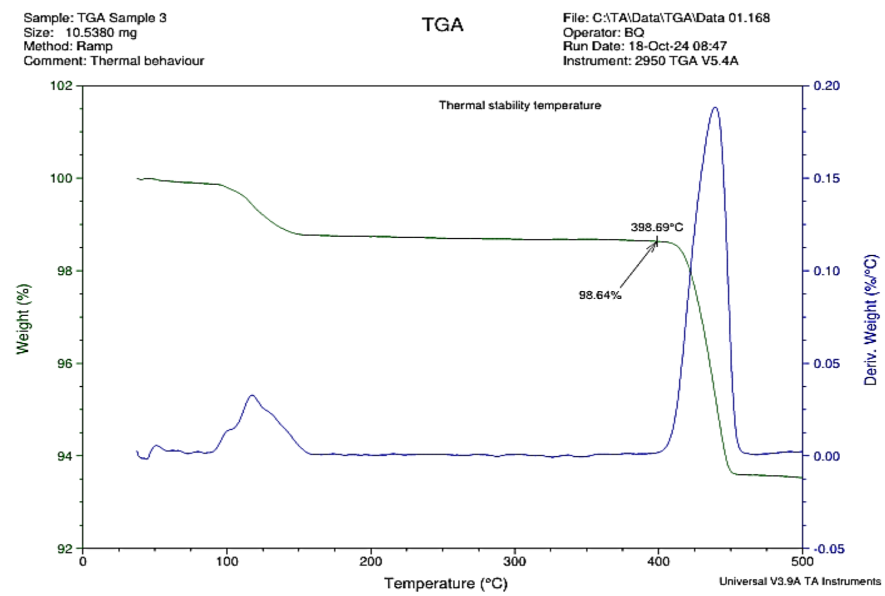

Figure 7b: Thermal stability of cement sample 3

3.2.7 Thermal decomposition of cement sample 4

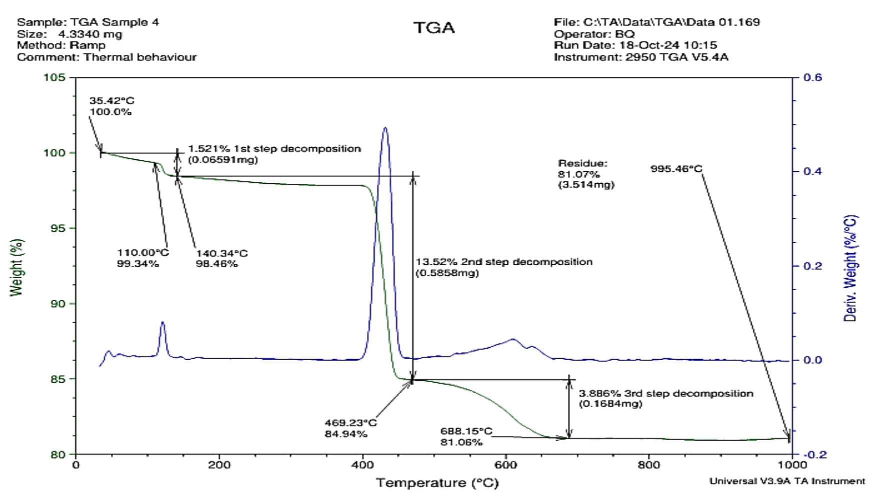

Figure 8a: Thermal decomposition of cement sample 4

Three stages of decomposition are observed in this sample leaving 81.08% of the sample weight at the end of the decomposition. The first stage decomposition occurred between 35.42^0C and 140.39^0C with 1.521 % (0.659mg) weight loss of sample attributed to evaporation of free and bound water in the cement sample. The second stage decomposition occurred between temperatures 469.23°C to 688.15°C and resulted in a 13.52 % (0.5858mg) weight loss. The significant weight loss was due to decomposition of organic content from the castor seed shell ash, hydrated phases and frees clay mineral in the sample which decomposed to dehydroxylation and formation meta koalin. The third stage decomposition occurred between 688.15°C and 995.46°C with a 3.886 % (0.1684mg) weight loss of sample which corresponded to decarbonation of free $CaCO_3$ present in the cement into CaO and CO_2. At 995.46°C, 81.07% of the sample remained suggested the presence of clay based materials and thermally stable inorganic phases which resisted decomposition. The presence of castor seed shall ash also had a stabilizing effect on the residue through organic-inorganic reactions. The thermal stability of the cement sample 4 occurred at 396.30^0C as shown in the figure 8b. At this temperature the sample remained stable with minimal weight loss indicated resistance to early decomposition attributed to clay and castor seed shell ash (Ravi and Suresh 2022).

3.2.8 Effect of castor seed shell additive clay and limestone on thermal stability of cement sample 4

The castor seed shell additive influenced the thermal behavior of the cement sample in two key ways: firstly the lower weight loss at initial stage of the heating occurred because organic additive ash tends to decompose over a broader range of temperature contributing to subtle shifts or increase in weight loss peaks. It also enhanced the thermal stability by creating an organic-inorganic matrix which delayed the complete decomposition of the same phases. Limestone content was responsible for weight loss at 900^0C due to decarbonization of free limestone present in the cement while the higher clay content contributed to 13.52% weight loss at the second decomposition that occurred between 400^0C-700^0C as a result of the dehydroxylation process (Zanata 2020). Clay also contributed to the thermal stability due to production of thermally resistance residues at 995.46^0C.

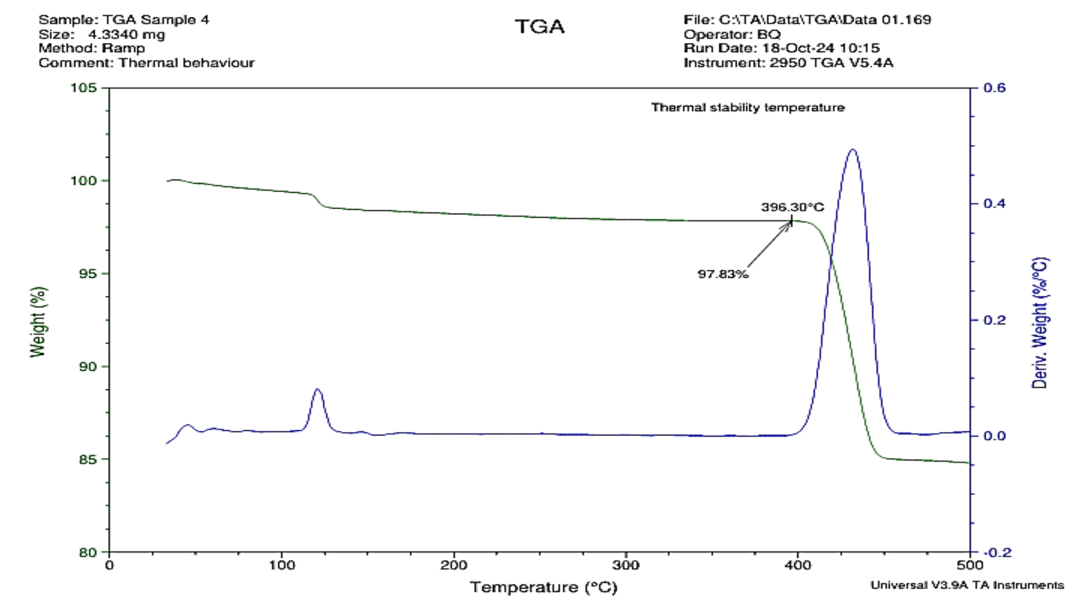

Figure 8b: Thermal stability of cement sample 4

Castor seed shell as an agricultural waste product can be useful as a cement raw material for the actualization of the sustainability goals in cement production. The inclusion of castor seed shell in cement raw mix can exhibit a significant thermal effect that influences the cement overall properties and production efficiency. The castor seed shell due to its organic content enhanced the burning process by contributing additional fuel which can reduce the external energy input and time required during cement production. This bio-additive not only aids in sustainable production practices by utilizing waste material but also potentially lowers the cost associated with the manufacturing process. Also, the addition of castor seed shell can lead to a favorable modification in the clinker formation potentially impacting cement strength, durability and chemical composition and the again the cement quality as found in the chemical analysis conformed to the standards requirement.

4.0. Conclusion

The thermal effect of castor seed shell as cement raw mix admixture was investigated. A two stage decomposition (fewer than other samples), a thermal stability of 564^0C and a total weight loss of 26.14% was recorded at end of the decomposition of cement sample 1.The castor seed shell ash additive was believed to have contributed to high thermal stability and moderate decomposition reflected thermal resilience. Sample 2 had a lower thermal stability 404^0C compared to sample 1 and a four stage decomposition and retained the highest weight post decomposition (91.74%). The absence of castor seed shell ash which in other samples contributed to the chemical composition was believed to have contributed to its lower thermal stability, higher reactivity and more gradual thermal breakdown over a wider range of temperature. Sample 3 has three stages of decomposition and thermal stability of 398.69^0C which is lower than that of sample 1 and 2 but comparable to sample 4. Sample 3 retained a 92.51% of its mass suggesting better structural integrity during thermal processes.

The castor seed shell ash together with the laterite was believed to have contributed to the increased thermal retention due its contribution to chemical composition of the cement. Sample 4 had three stages of decomposition with the highest weight loss of 13.52% at the second stage of the decomposition, a slightly lower thermal stability of 396.30^0C (lower than sample 3) and retained 92.51% of its weight at the end decomposition which indicated improved thermal performance. The reduced limestone content combined with higher clay content and the castor seed shell ash resulted in moderate thermal stability and improved mass retention. The addition of castor seed shell ash in samples 1, 3, and 4 significantly enhanced their thermal stability and decomposition resistance. The castor seed shell ash contributed to fewer decomposition stages and higher thermal stability especially in sample 1 and improved mass retention after decomposition. The absence of castor seed shell ash in sample 2 resulted in lower thermal stability and more complex decomposition profile, demonstrated castor seed shell ash critical role in improving the thermal performance of cement composites. The study acknowledged limitations such as small sample size, potential variability in raw material quality, or environmental impacts of castor seed shell sourcing. Overall, the inclusion of castor seed shell appeared promising in making cement more eco-friendly, sustainable and energy efficient without having a negative effect on the quality of the cement.

5.0 Recommendation

Recommendations for future research, such as testing the modified cement's mechanical properties or conducting a life cycle analysis to address whether the modified cement meets industry performance standards, such as compressive strength or durability. The research requires further studies to optimize the proportions and thoroughly understand the long-term effects on cement performance especially in diverse environmental conditions.

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