AIP Conference Proceedings

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Cite as: AIP Conference Proceedings **2776**, 090003 (2023); https://doi.org/10.1063/5.0135993
Published Online: 12 April 2023

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AIP Publishing

# Thermal Analysis for Concrete Incorporated with Different Nano, Micro and Recycled Materials

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**Abstract.** This research aims to investigate the impact of employing various types of materials as partial cement replacements on the characteristics of high-strength concrete. As cement replacements, Nano $SiO_2$, Nano $CaCO_3$, micro $SiO_2$, micro $CaCO_3$, recycled silica gel (beads and powder), and limestone were employed, as well as binary combinations of (Nano $SiO_2$ + Nano $CaCO_3$), (micro $CaCO_3$ + micro $SiO_2$), and (recycled silica gel powder + limestone). In addition to the control mix, ten sets of concrete mixes were created with progressive cement replacement. Thermal analysis (TG-Thermogravimetric) and (DTG-Derivative Thermogravimetry) were employed to determine the CH content of each concrete group. The nano-silica mix had the lowest calcium hydroxide (CH) content, followed by the binary nano mix and crushed silica gel mix. In contrast, the other mixes had approximate values. Still, they were all less than the control mix, indicating that larger amounts of calcium silicate hydrate (CSH) gel formed after replacement, which has primarily contributed to improving the strength and durability of concrete.

## INTRODUCTION

Concrete is a multi-phased material having nanostructures and various elements. This structure comprises uneven crystal phases with sizes ranging from micrometers to nanometers [1]. Furthermore, the non-crystal phase and nanostructure of hydrated calcium silicate (C-S-H) result in the development of an adhesive material that holds concrete particles together [2]. It has been discovered that for each ton of cement produced, 0.9 tons of $CO_2$ is created. In addition, cement accounts for 10% of the weight in a cubic yard of concrete. As a result of the usage of green concrete, CO2 emissions in the atmosphere can be reduced, resulting in a more environmentally friendly construction process. [3]. The goal of using green concrete is to achieve three criteria: very low energy and resource use, no pollution, and long-term development [4]. To investigate and characterize the material composition, the varied thermal behavior of the components in cementitious materials can be exploited. Furthermore, these features enable the monitoring of temporal changes in the material's composition. For the assessment of cementitious materials, thermogravimetric analysis (TG) is a frequently utilized approach. This approach may be used to identify various hydrates and carbonates. Supplementary cementitious materials (SCMs) such as fly ash and blast furnace slags can also be investigated [5].

D. Vaičiukynienė et al. 2012 [6] study revealed that silica gel might be used as an additive in hardened cement paste beyond the thermal vitality at 800C after 28 days of curing, resulting in a significant increase in cement paste strength when the amount of addition was 10% by weight of cement. Furthermore, according to this study, the amount of Ca $(OH)_2$ in the body decreased with age as the amount of silica gel rose. D. R. Bentz et al., 2014 [7] presented multiscale research on the impact of fine limestone powder and typical limestone aggregate on the performance of concrete. Various types of limestone were utilized with different ratios of 5% limestone in conjunction with 20% fly ash and 10% cement by weight. All varieties minimize the time for concrete to set and enhance the connection between aggregate and cement paste. However, the compressive strength is reduced when fine powder limestone is used. Ivindra Pane et al. [8] used differential thermal analysis DTG-DTA to evaluate the hydration of Portland cement pastes, including three types of mineral additives: fly

*1st International Conference on Achieving the Sustainable Development Goals*
AIP Conf. Proc. 2776, 090003-1–090003-10; https://doi.org/10.1063/5.0135993
Published by AIP Publishing. 978-0-7354-4441-6/$30.00

ash, ground-granulated slag, and silica fume. The findings indicated that blended cement reacted more slowly than Portland cement and silica fume reacted faster than fly ash and slag. Faiz U. A. Shaikh et al. [9] conducted a thermal analysis for cement pastes to find evidence of pozzolanic reaction in high volume fly ash pastes. It was found that the addition of 2% nano-$SiO_2$ and 1% nano-$CaCO_3$ increased the volume fractions of high-density and low-density calcium silicate hydrate (C-S-H) gels. That conformed the capability of nanoparticles to decrease the porosity of high-volume fly ash pastes. Zemei Wu et al. [10] demonstrated that the calcium hydroxide (CH) content in ultra-high-strength concrete samples decreased significantly with the increase of nano-$SiO_2$ content but remained almost constant for those with nano-$CaCO_3$ using thermal analysis TG-DTG. Roman Gabrovšek**a** [11] examined the phase compositions by thermogravimetric and powder X-ray diffraction analysis for DTG decomposition profiles of portlandite and carbonate. The study enabled the evaluation of certain admixture-related parameters concerning portlandite formation and indicated specific carbonates' behavior during the hydration process.

The goal of this study was to see the effect of variation of recycled, micro, and nanomaterials on the composition of hydrated cement paste. This was done using thermogravimetric/derivative thermogravimetric analysis (TG/DTG).

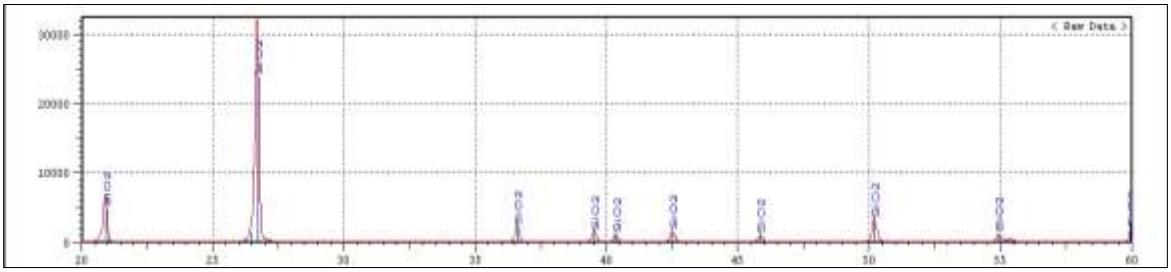
## EXPERIMENTAL WORK

### Materials

In this investigation, ordinary Portland Cement Type I meets Iraqi standards (I.Q.S.) No. 5/1984 [12] was employed. Table.1 and table.2 indicate the chemical composition and physical properties of cement. Natural sand readily available in the area is utilized as fine aggregate in concrete mixtures. As for coarse aggregate, crushed gravel with a 14 mm (Max. Size) and a value of 2.8g/cm$^3$ for specific gravity was utilized. Both fine and coarse aggregate were chosen within the limits of Iraqi Specification No. 45/1984 [13]. Table.3 and table.4 showed the grading of fine and coarse aggregate respectively. As for the cement alternatives, the following list of materials was used in this study:

1. Nano $SiO_2$
2. Nano $CaCO_3$
3. Micro $SiO_2$
4. $_M$icro $CaCO_3$
5. Recycled silica gel
6. Limestone from construction debris

**FIGURE 1.** Shows the XRD spectra for each replacement.



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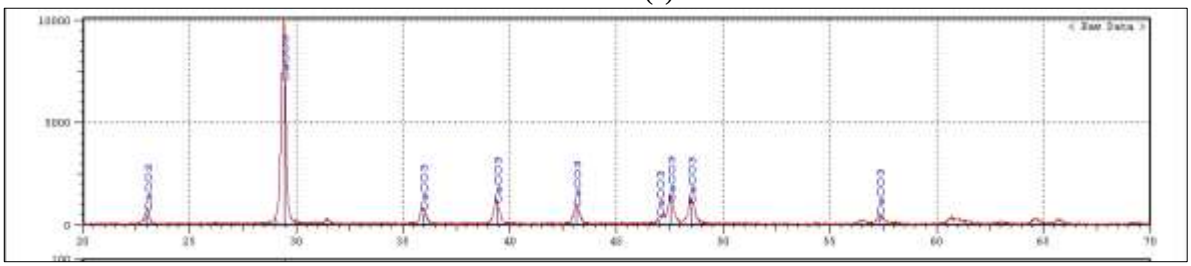

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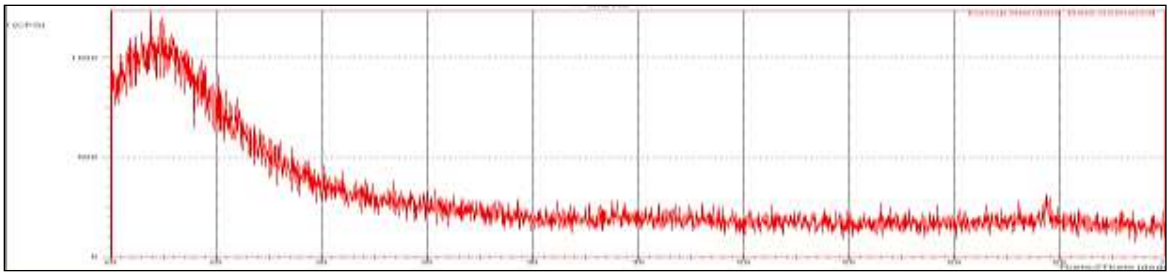

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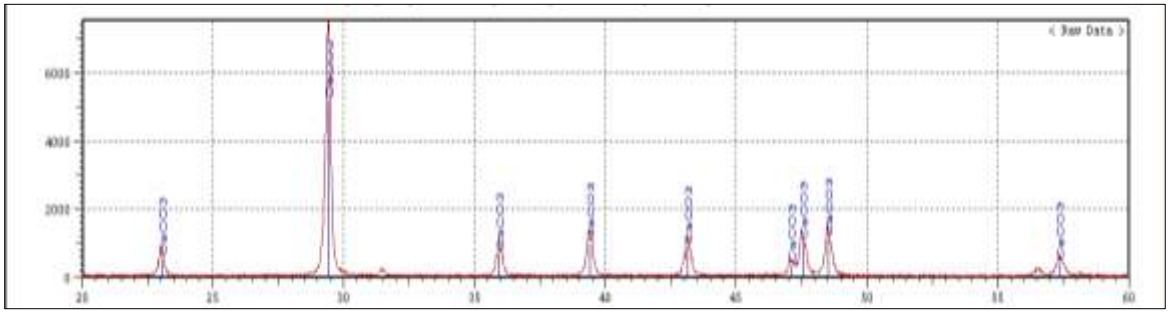


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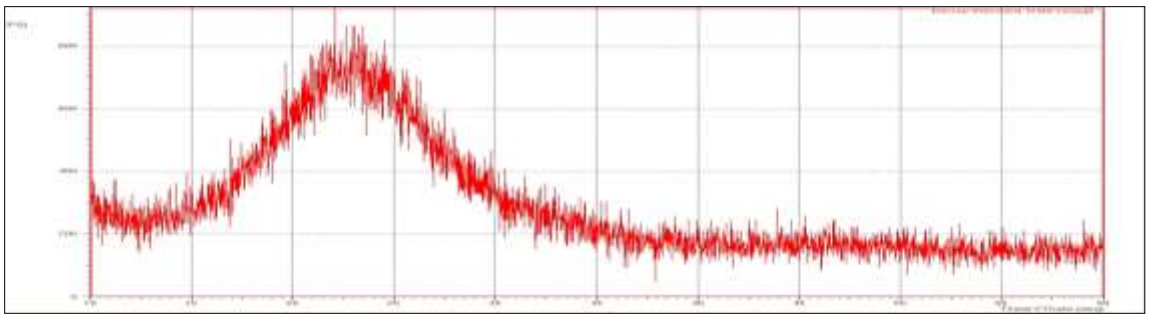

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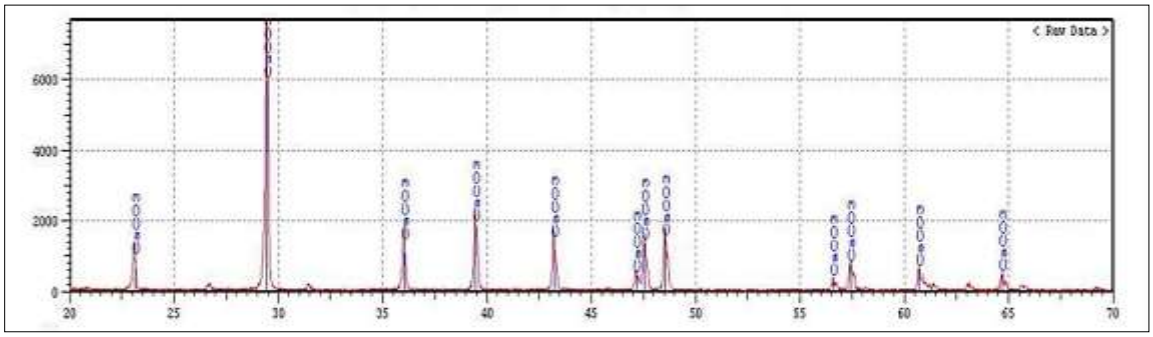


(f)

**FIGURE 1.** XRD spectra of (a) Micro silica powder (b) Micro $CaCO_3$ (c) Nano silica powder (d) Nano $CaCO_3$ (e) Silica gel powder (f) Limestone powder

**TABLE 1.** Chemical Composition of Cement

| Oxide | % |
|---|---|
| CaO | 66.1 |
| $SiO_2$ | 21.2 |
| $Al_2O_3$ | 4.98 |
| $Fe_2O_3$ | 3.1 |
| MgO | 2 |
| $K_2O$ | 0.75 |
| $Na_2O$ | 0.35 |
| (L.O.I) | 2.25 |
| (L.S.F) | 2.39 |
| (I.R) | 0.93 |
| (F.L) | 0.76 |

**TABLE 2.** Physical Properties of Cement test

| Physical Properties | Test Results |
|---|---|
| Fineness , Blaine , $cm^2/gm$ | 3300 |
| Setting Time : | |
| Initial hrs. ; min | 2;05 |
| Final hrs. ; min | 4;00 |
| Compressive Strength MPa | |
| 3-days | 20,0 |
| 7-days | 25,0 |

**TABLE 3.** Grading of Fine Aggregate.

| Sieve opening (mm) | Accumulative passing, % |
|---|---|
| 10 | 100 |
| 4.75 | 94 |
| 2.36 | 85.6 |
| 1.18 | 76.9 |
| 0.60 | 46.3 |
| 0.3 | 10.8 |
| 0.15 | 1.1 |
| 0.075 | 0.5 |

**TABLE 4.** Grading of Coarse Aggregate

| Sieve opening (mm) | Accumulative passing, % |
|---|---|
| 14 | 97 |
| 10 | 62 |
| 5 | 10 |
| 0.075 | 0.037 |

## Mixes proportion

In this work, eleven different concrete mixtures are used. All mixes had the same fixed parameters: 32 percent water/cementitious, 721 and 1030 $kg/m^3$ coarse and fine aggregate content, respectively, and 6.43 $kg/m^3$ superplasticizer content. Table.5 shows a mix of information and symbols.

**TABLE 5**. Mixes information and symbols.

| Mix symbol | Cement, kg/m$^3$ | Replacement content (kg/m$^3$) (%) | Replacement type |
|---|---|---|---|
| Control | 515 | --- | --- |
| 3MS | 499.55 | 15.45 (3%) | Silica fume |
| 3MC | 499.55 | 15.45 (3%) | Micro CaCO3 |
| 3MS+MC | 499.55 | 7.725 + 7.725 (1.5%) +(1.5%) | Silica fume+ Micro CaCO3 |
| 3L | 499.55 | 15.45 (3%) | Limestone |
| 3SG | 499.55 | 15.45 (3%) | Silica gel |
| 3SGC | 499.55 | 15.45 (3%) | Crushed silica gel |
| 3L+SGC | 499.55 | 7.725 + 7.725 (1.5%) +(1.5%) | Limestone+ crushed silica gel |
| 3NS | 499.55 | 15.45 (3%) | Nano silica |
| 3NC | 499.55 | 15.45 (3%) | Nano CaCO3 |
| 3NS+NC | 499.55 | 7.725 + 7.725 (1.5%) +(1.5%) | Nano silica+ Nano CaCO3 |

# TESTING

## Thermogravimetric Analysis TG-DTG

Thermogravimetric analysis (TG/DTA) was used to examine eleven samples. The powder samples were placed in a ceramic crucible and heated at a rate of 10 °C/min using nitrogen as a medium in a thermo-analyzer TG 209 (NETZSCH) under static conditions from ambient temperature to 1000 °C. As a reference material, alumina powder was employed. Both TG and DTG were carried out at the same time. All samples were dried in an oven at 105°C and chilled to room temperature before TG/DTA analysis

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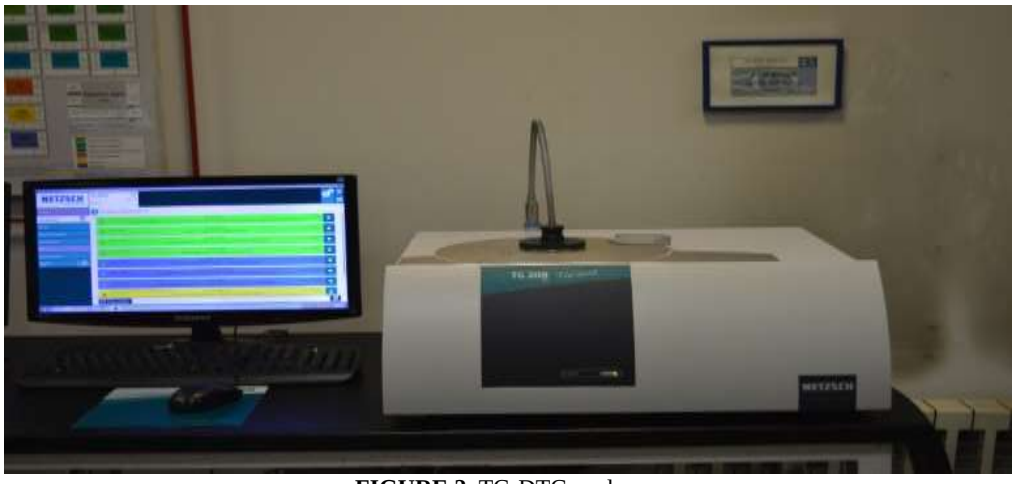

**FIGURE 2.** TG-DTG analyzer.

## TG-DTG Analysis

Thermogravimetry (TG) is a technique for determining the change in mass of a substance over time at a specific temperature or over a temperature range using a specified heating rate [14]. The results of the TG/DTA for eleven typical samples as weight loss with temperature range and peak temperature are illustrated in Figures 3,4 and 5.

The four distinct endothermic effects may be seen in all TG-DTG charts. The first effect is related to the evaporation of surface adsorbed water in the temperature range of 25 to 100 °C, attributed to the samples' water adsorption from the air after the cooling-to-room-temperature process when drying at 104 °C. The dehydration of C–S–H and ettringite are responsible for the second endothermic effect, which occurs at temperatures of (100 – 350) °C. This effect is accredited to C–S–H dehydration ettringite and calcium aluminate hydrate. The temperature at which these compounds lose water relies on the CaO: $SiO_2$ ratio in the hydrated cement mixture. Finally, the third effect occurs at a peak temperature of (430 – 460) °C, implying $Ca(OH)_2$ decomposition formed throughout hydration. The $Ca(OH)_2$ was calculated using the weight loss calculated from the TG curve in between the initial and final temperatures of the relevant TG peak, taking into consideration the following decomposing reaction:

$$Ca(OH)_2\,(s) \rightarrow CaO\,(s) + H_2O\,(g)$$

The calcium carbonate's decarbonation of the hydrated molecule is indicated by an endothermic at approximately 790 °C. By considering the following decarbonation process, the CaCO3 was calculated from the weight loss. [15].

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

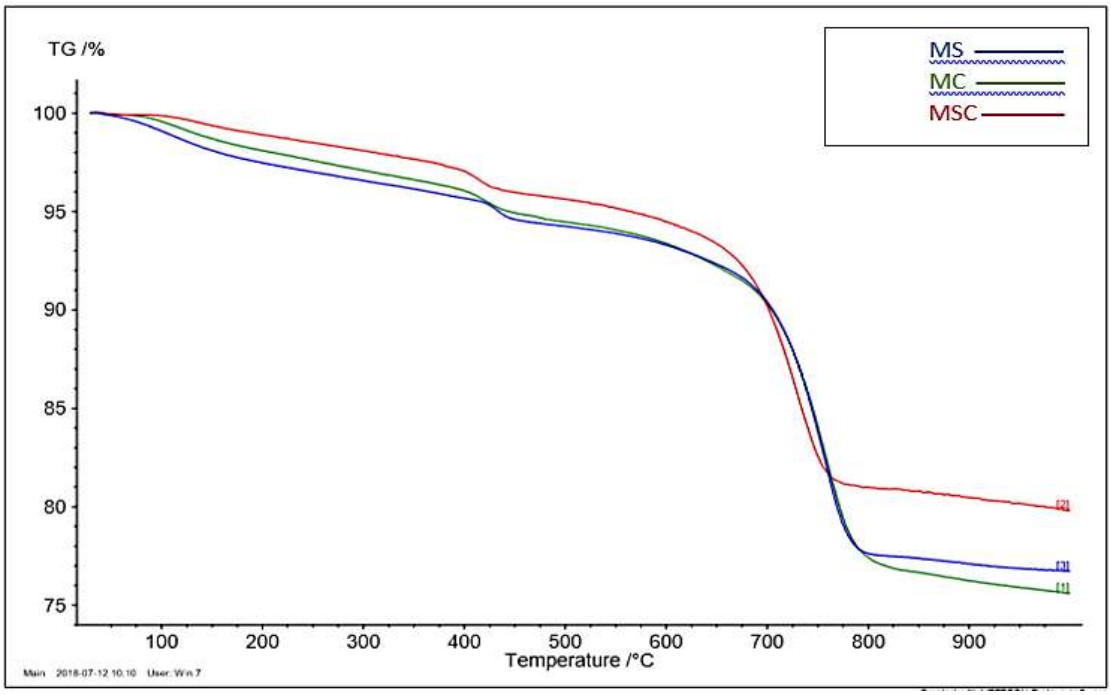


**FIGURE 3.** TG curves for concrete mixes with micro replacements

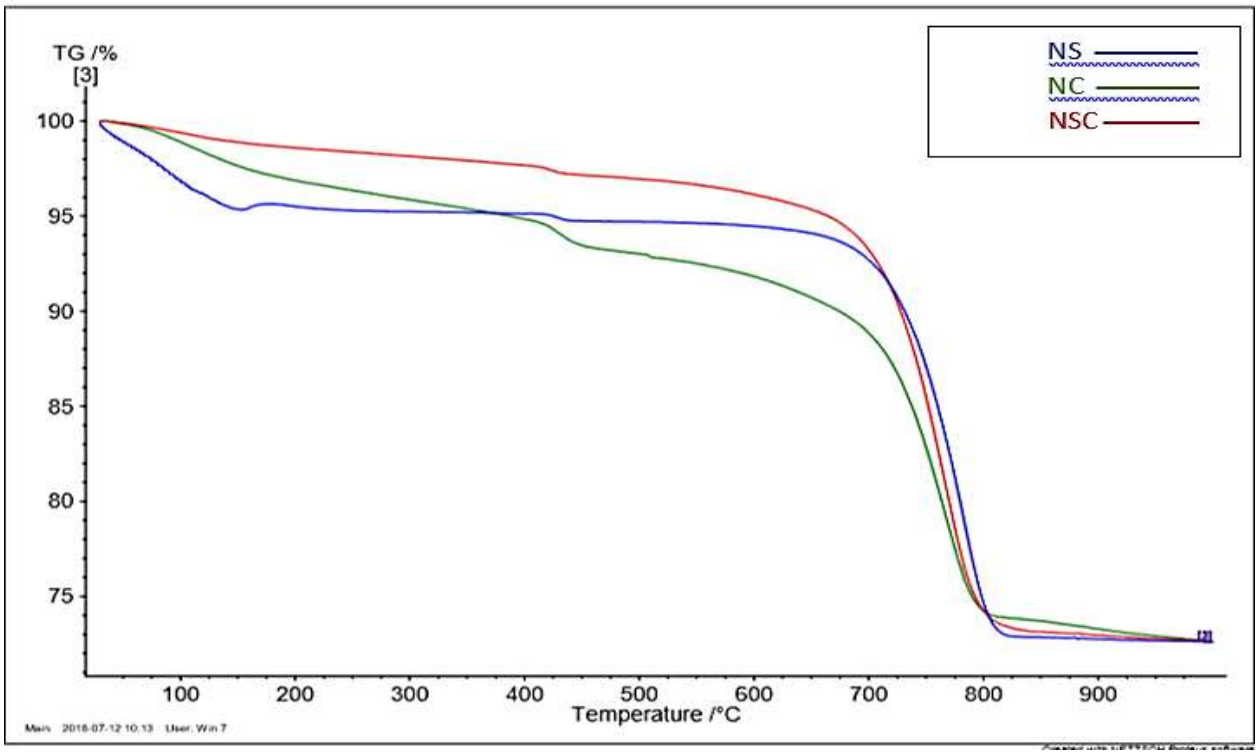


**FIGURE 4.** TG curves for concrete mixes with nano replacements.

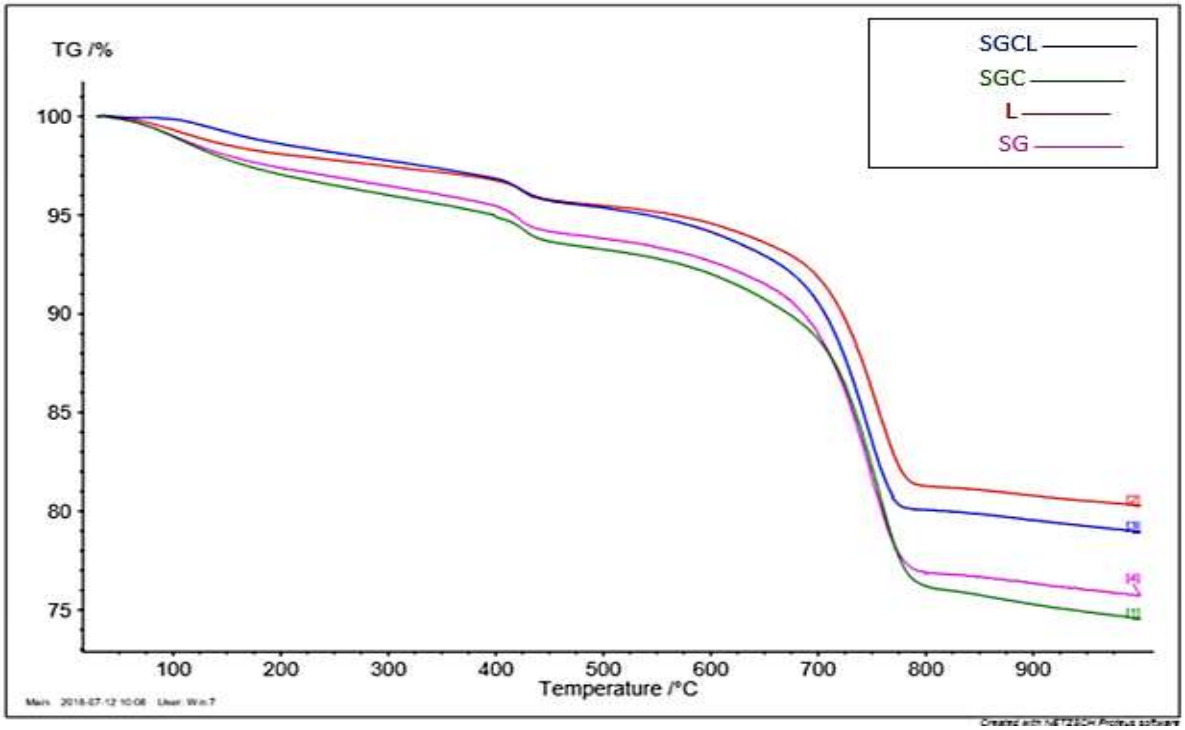


**FIGURE 5.**TG curves for concrete mix with recycled replacement.

## CH Content

The assessment of CH content in concrete samples is a useful tool for tracking the degree of hydration over time. The strong endothermal curve showed the breakdown of CH produced during hydration at about 465C. Considering the following reaction, the CH was determined from the weight loss observed from the TG curve between the beginning and final temperature of the relevant peak.

$$Ca(OH)_2\ (s) \rightarrow CaO\ (s) + H_2O\ (g)$$

The analysis also allows the estimation of the CH content from the weight losses in paste samples. The CH content can be calculated according to Taylor's formula [9].

$CH\% = WL_{CH}\% \ (MW_{CH} / MW_{H2O})$

Where:

$WL_{CH}$ = weight loss during the dehydration of CH as a percentage of the ignited weight;

$MW_{CH}$ = molecular weight of CH; and

$MW_{H2O}$ = molecular weight of $H_2O$. [9]

Figure (6) depicts the CH content of concrete mixes with various substitutes utilized in this study. With increasing nano-SiO2 concentration, CH content showed a declining trend. All of these suggested a pozzolanic interaction between CH and nano-$SiO_2$. Even though both micro silica and silica gel (beads and powder) have pozzolanic reactivity, nonsilica had a substantially lower CH concentration due to its much larger specific area than micro silica and silica gel. Furthermore, nano-$SiO_2$ possesses multiple unsaturated Si-O- and Si- bonds on the surface, which would lead to diverse hydration reactions, resulting in a reduction in CH and the formation of extra CSH [10]. The drop in CH content for concrete mixes, including nano $CaCO_3$, micro $CaCO_3$, and limestone, was smaller than that seen for the silica series, indicating that the hydration mechanisms of the $CaCO_3$ and silica series are different. While nano-$CaCO_3$ mostly combines with C3A to make carboaluminates in the $CaCO_3$ series, various investigations have shown that limestone lacks pozzolanic characteristics to produce C-S-H gel [16,10]. This explains the modest variation in CH in mixtures prepared with various $CaCO_3$ forms. However, adding nano-$CaCO_3$ to concrete can alter the C-S-H structure, such as the Ca/Si ratio, changing the mechanical capabilities of the material. These findings corroborated previous studies [9] [10][17]. According to these findings, the addition of nano-$SiO_2$ reduced the CH content of HVFA pastes, whereas the inclusion of 1% nano-$CaCO_3$ reduced the CH content of pastes, yet, not as much as nano $SiO_2$ did. When compared to a single mix, binary mixes had a moderate effect.

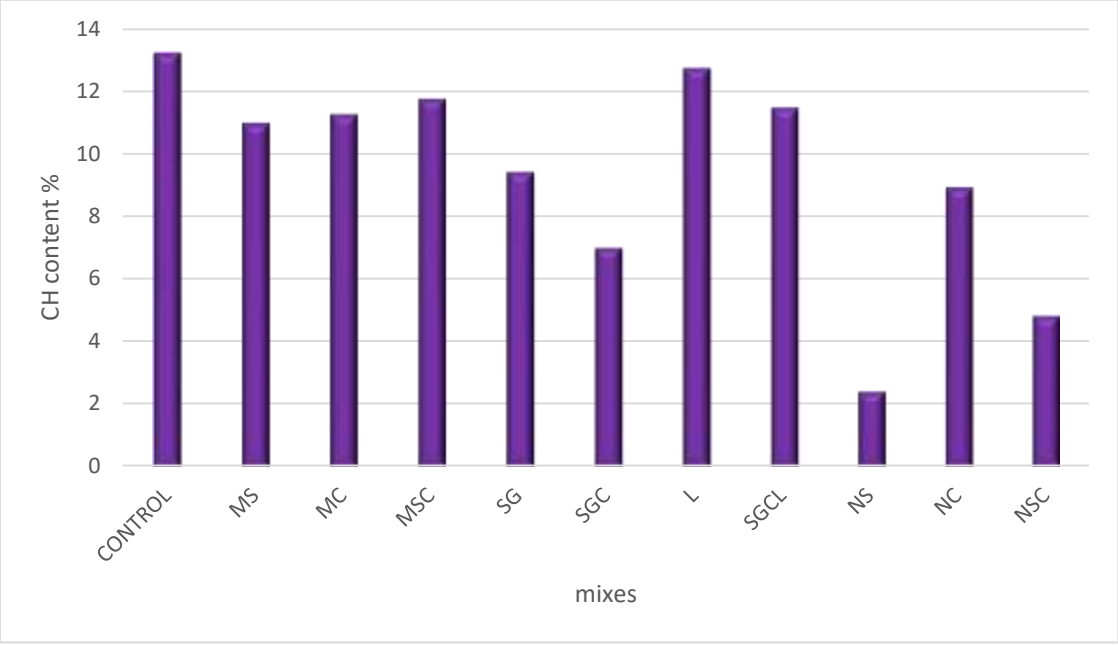


**FIGURE 6.** CH content for different concrete mixes incorporated with various materials

## CONCLUSION

Based on the previous results, the following can be concluded

1- All replacements (nano, micro and recycled) showed a remarkable trend toward consuming the calcium hydroxide, this could be due to the reactivity of replacements with cement paste and the consumption of CH by the pozzolanic reaction, which lead to formation more C-S-H gel and developed the mechanical and microstructural properties of concrete.
2- Maximum reduction in CH content found in NS, NSC, and SGC mixes, respectively, this attributed to the pozzolanic properties of these replacements compared with other substitutes.
3- On the basis of real measurement, the determined peaks in DTG –TG graph allow one to evaluate the variety of activity different materials incorporated in the mortars under study.

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