THERMOGRAVIMETRIC ANALYSIS OF CONCRETE

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Abstract—An effective estimation of concrete resistance to high temperatures requires a profound knowledge of phenomena that takes place during exposure to heat. These phenomena are connected directly with physico-chemical processes occurring in the components and are brought about by a temperature increase. The most important processes include chemical reactions, phase transformations and thermal deformations occurring in the microscopic scale in particular phases of concrete components. As hardened cement paste has multi-phase composition, a large number of physico-chemical processes occur at elevated temperatures. Investigation on the condition of cement paste when exposed to heat is performed by thermogravimetric analysis technique. The aim of the present study is to explain mass loss due to physico-chemical transformations occurring in the phase composition of Portland cement paste (concrete) in both standard concrete (M 30) and high strength concrete (M 90) grade at core as well as on surface.

Keywords— thermogravimetric analysis, standard concrete, high strength concrete, surface and core

I. INTRODUCTION

Portland cement consists of four main compounds tri-calcium silicate, di-calcium silicate, tri-calcium aluminium and tetra calcium aluminoferrite. The important products of hydrated cement are the calcium silicate hydrate (C-S-H) and portlandite, also called as calcium hydroxide (C-H). Many researchers [3, 4, 10-24] had reported the following physico-chemical transformations that occur in cement paste (mortar) at different temperature ranges as shown in Table 1.

| Temperature range (°C) | Transformation |
|------------------------|----------------|
| 27 - 110               | the evaporable water escapes |
| 110 – 180              | loss of water from interlayers of cement paste and aggregate |
| 180 – 400              | decomposition of C-S-H gel and evaporation of chemically bound water |
| 400 - 600              | dehydroxylation of portlandite |
| 600 - 900              | decarbonation of calcium carbonate |

To study the thermal effects in cement paste (concrete), thermogravimetric and differential thermal analysis (TG-DTA) studies are carried out.

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature with a constant heating rate. This method of thermal analysis is employed in order to determine the contents of portlandite, calcite and evaporable water in heated cement pastes.

Instrument used for TGA as shown in Fig.1 consists of (1) a sensitive microbalance (2) a furnace (3) a purge-gas system for providing an inert or sometimes reactive atmosphere (4) DTA detector and (5) a computer system for instrument control, data acquisition and data processing.
DTA detector helps in monitoring the temperature difference between the sample and reference. The sample is heated along with a reference under identical thermal conditions in the same furnace. The temperature difference between the sample and reference substance is monitored during the period of heating. As the samples undergo any changes in state, the latent heat of transition will be absorbed/evolved and the temperature of the sample will differ from that of the reference material. This difference in temperature is recorded. Any change associated with temperature can be studied by DTA. In general TG-DTA curves are used to get information about physico-chemical and temperature changes of mortar samples.

II. EXPERIMENTAL WORK

2.1 Materials used
The concrete used in this experimental work is made by mixing ordinary Portland cement with hard blue granite chips, sand, water, mineral admixture and chemical admixture. The properties of the individual materials are as follows.

2.1.1 Cement
Ordinary Portland cement of 53 grade conforming to IS: 12269-1987 [9] was adopted in this work. The properties of cement are given in Table 2

| S. No. | Particulars                     | Test Results | Requirements as per IS:4031-1988 [6] |
|--------|--------------------------------|-------------|--------------------------------------|
| 1.     | Insoluble material (% by mass)  | 0.68        | 28.96 Maximum                        |
| 2.     | Magnesia (% by mass)            | 1.16        | 6.00 Maximum                         |
| 3.     | Sulphuric anhydride (% by mass) | 1.73        | 3.00 Maximum                         |
| 4.     | Loss on ignition (% by mass)    | 1.15        | 5.00 Maximum                         |
| 5.     | Total chlorides (% by mass)     | 0.006       | 0.10 Maximum                         |

Physical requirements

1. Fineness as weight retained on IS 90 micron sieve | 5.5% | 10% Maximum
| 2. | Standard consistency (%) | 30 |
| --- | --- | --- |
| 3. | Setting time |  |
| a) Initial (minutes) | 155 | 30 Minimum |
| b) Final (minutes) | 225 | 600 Maximum |
| 4. | Soundness |  |
| a) Le-chatelier method (mm) | 1.0 | 10.0 Maximum |
| b) Autoclave method (%) | 0.026 | 0.8 Maximum |
| 5. | Compressive strength (MPa) (IS 12269:1987) |  |
| at 3 days | 39.61 | 27 Minimum |
| at 7 days | 50.05 | 37 Minimum |
| at 28 days | 63.60 | 53 Minimum |

2.1.2 Fine aggregate
Locally available river bed sand was used. Fineness modulus and specific gravity of the sand are 2.85 and 2.66 respectively. The sand used conforms to grading Zone II of IS: 383-1970 [7].

2.1.3 Coarse aggregate
In the present study, the coarse aggregate was used after soaking in water for 24 hours and then completely air dried. The fraction of coarse aggregate passing through 20 mm sieve and retained on 10 mm sieve is taken as 2/3 of total aggregate. The remaining 1/3 fraction is aggregate passing from 10 mm sieve and retained on 4.75 mm sieve. For M 30 grade of concrete, both sizes of aggregates were used but for M 90 grade of concrete, aggregate passing through 10 mm sieve was used in mix. The higher the targeted compressive strength, the smaller the maximum size of the coarse aggregate should be. The fineness modulus and specific gravity of coarse aggregate are 6.30 and 2.78 respectively.

2.1.4 Water
Water is the most important ingredient of concrete and a part of mixing water is utilized in hydration of cement to form the binding matrix and the remaining water acts as a lubricant to make the concrete readily in pouring state. Locally available potable water was used in the present work.

2.1.5 Superplasticizer
Chemical admixture based on second-generation poly carboxylic technology conforming to IS: 9103 -1999 [5] with specifications light orange colour, specific gravity of 1.09, no chloride content and solid content of 34% was used in this work.

2.1.6 Micro silica
The specific gravity of micro silica used in the work is 2.2. Specific surface area of micro silica was 19,000 m²/kg (from manufacturer’s data). The high surface area of micro silica would increase the water demand. The use of micro silica can reduce bleeding and improve cohesion of the mix. The cohesiveness of concrete containing micro silica is good for pumping and for underwater concrete.

2.2 Casting, curing and testing
The sequence of feeding ingredients in the pan mixer depends on the properties of mix and those of mixer. In this work, a small amount of water is fed first, followed by coarse aggregate in saturated surface dry condition and fine aggregate. These materials are mixed uniformly and then cementitious material is fed into the mixer. After attaining uniform mixture of all dry ingredients, water is added.

Usually mixing is done in two different stages for HSC. Dry mixing is done before the addition of water and wet mixing is done after addition of water. After dry mixing of the ingredients
for one minute, 60% of water is added to the ingredients and mixed uniformly. The remaining 40% of water is mixed with superplasticizer and is introduced into the mixer and ingredients are mixed for 3 minutes until the mix is uniform. The total mixing time is 4 minutes. After mixing, the concrete is poured on the pre-wetted platform then filled into moulds. The cube moulds of size 100 mm are used to prepare specimens. All moulds are retained for a period of 24 hours in a moist air. Then the specimens are demoulded, marked and cured in a curing tank with fresh water. They are cured for a period of 28 days.

The mix proportions were arrived after carrying out trial mixes and finally mix proportion were adopted for M 30 and M 90 grades of concrete according to IS:10262-2009 [8] and ACI 211.4R-2008 [1] respectively. The quantities of ingredient materials used in these mixes and workability results are shown in Table 3.

| S.No. | Ingredient                  | Standard concrete M 30 | High strength concrete M 90 |
|-------|-----------------------------|------------------------|----------------------------|
| 1     | Cement (OPC 53 grade)       | 370 kg/m³              | 594 kg/m³                  |
| 2     | Micro silica (10% of total cementitious material) | Nil                     | 66 kg/m³                  |
| 3     | Fine aggregate              | 740 kg/m³              | 650 kg/m³                  |
| 4     | Coarse aggregate            | 1214 kg/m³             | 1105 kg/m³                 |
| 5     | Water                       | 165 l/m³               | 145 l/m³                   |
| 6     | Superplasticizer            | Nil                     | 0.8% by weight of cementitious material |
| 7     | Workability                 | 45 mm slump             | 0.85 compaction factor     |

TG-DTA studies are carried out on the mortar part of the cubes drawn from areas representing the exposed surface as well as the core according to ASTM E 1131-2008 [2], using simultaneous HITACHII 7300 thermo-analyzer to study the thermal stability of the both standard concrete (M 30) and high strength concrete (M 90). The present study considered the thermal effects on concrete and reported the physicochemical changes.

III. RESULTS AND DISCUSSIONS

TG-DTA results obtained for both M 30 and M 90 grades of concrete at surface as well as core of samples are shown in Fig. 2 to Fig. 5. It is observed that, there is increase in mass loss of both M 30 and M 90 grades of concrete. Up to 400°C, the loss may be attributed to expel of capillary water and interlayer water in concrete constituents. Desorption of chemically bound water from portlandite (C-H) takes place in the range of 400 to 500°C which significantly affects the mass. There is slight decrease in mass of samples in the temperature range of 600 to 700°C and might be caused by the decomposition of calcium carbonate (calcite). The chemical reactions for the decomposition processes can be described as follows.

Decomposition of C-H: \[ \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \uparrow \]
Decomposition of CaCO₃: \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \uparrow \]

Therefore, reduction in mass is observed due to the expel of water and carbon dioxide.

An endothermic peak is observed in all DTA curves below 100°C i.e decrease in temperature due to slow expel of capillary water from the sample. Beyond 100°C, an exothermic peak is observed as there is an increase in temperature up to 400°C. In the range of 400 to 500°C, sudden change in temperature is observed due to decomposition of portlandite.

Referring to the Fig. 6 and 7, it is concluded that the mortar samples drawn from surface have more loss compared to core at high temperatures. This might be due to the slower rate of dehydration in core caused by a temperature gradient from surface.
IV. CONCLUSION

Thermogravimetric analysis of concrete close to the industrial furnaces or samples extracted from the structure exposed to fire is used to determine the temperature to which the concrete has exposed to. The extent of damage in concrete depth wise when exposed to elevated temperatures can be predicted by knowing the mass loss caused due to decomposition of portlandite and calcite. The mortar samples drawn from surface have more loss compared to core at high temperatures. If portlandite is observed to be completely disintegrated from concrete (no mass loss from TG-DTA studies), it is concluded that the structure was subjected to a maximum temperature of 500°C. Similarly, disintegration of calcite disappears after 800°C. Such data can also be useful for making necessary recommendations for rehabilitation of fire damaged concrete structures.

Figure 2 TG-DTA curve for mortar sample of M 30 grade concrete surface

Figure 3 TG-DTA curve for mortar sample of M 30 grade concrete core
Figure. 4 TG-DTA curve for mortar sample of M 90 grade concrete surface

Figure. 5 TG-DTA curve for mortar sample of M 90 grade concrete core

Figure. 6 Thermogram for mortar sample of M 30 grade concrete at surface and core
Figure. 7 Thermogram for mortar sample of M 90 grade concrete at surface and core

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