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RESEARCH ARTICLE

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THERMOGRAVIMETRIC ANALYSIS OF LIMESTONE IN GUNTUR DISTRICT

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ABSTRACT
TGA is one of the important techniques in thermal analysis. In Thermal analysis specific physical properties of materials are measured as a function of temperature production of new high technology materials and the resulting requirements for a more precise characterization of these substances have increases the demand for thermal gravimetric analysis. Collected limestones samples from different places in Guntur district i.e., Piduguralla, Machavaram, Dachepalli, Gurazala, Rentichintala, Karampudi mandals. In this paper we discussed about the properties of the limestone and its composition according to the temperature by using thermogravimetric analysis.

Keywords: Thermogravimetric Analysis, Decomposition, Limestone.

INTRODUCTION

Limestone is a general term denoting both carbonate rocks and fossils. It is composed mostly of calcium carbonate or is a combination of calcium and magnesium carbonates with varying amount of impurities. There exists in Palnaduarea i.e, Piduguralla, Mahcavaram, Dachepalli, Gurazala, Rentichintala, Karampudimandals of Guntur dist. Andhra Pradesh an abundant low cost and readily accessible supply of limestone. The aim of the present investigations is to evolve suitable conditions to avoid the clinker formation during the manufacturing of lime from limestone. Due to the clinker formation production of lime decreases so lime manufacturers are economically at loss. Lime (quicklime) is a manufactured form of limestone. Hydrated (slaked) lime is created from it upon addition of water. The term of Lime is understood to represent both quick lime and Hydrated lime. The lime may be high calcium or Dolomite type, dependently on the type of raw limestone. Contrary to $CaCO_3$ which is among the most chemically stable compounds calcium oxide and calcium hydroxide are not stable under atmospheric air. They are hygroscopic and react with moisture (H_2O) or carbon dioxide. This is the main reason why quick lime is usually a mixture of three compounds (CaO, $Ca(OH)_2$, $CaCO_3$).

Also, quicklime and hydrated lime may change their phase during storage and handling. Being derived from natural limestone they may also contain mineral usually non-calcium impurities mostly silica and alumina and also magnesium compounds from the dolomite impurities of limestone.

The use of limestone, quicklime, or hydrated lime in chemical synthesis (as a raw material or catalyst) calls for high –grade specifications for these materials. TGA is one of the important techniques in thermal analysis. In Thermal analysis specific physical properties of materials are measured as a function of temperature production of new high technology materials and the resulting requirements for a more precise characterization of these substances have increases the demand for thermal gravimetric analysis.

The present application of TGA include–

- Limestone Analysis
- Composition Analysis
- Product Reliability
- How the Clinker Formation is Avoided

TGA has been used to determine the physical and chemical properties of the substances. In thermo gravimetric analysis the mass of sample in a controlled atmosphere is recorded continuously as a function of temperature or time. A plot of mass or mass percent as a function of time is called a thermo gram or a thermal decomposition curve. This analysis relies on a high degree of precision in three measurements. They are

- Weight
- Temperature
- Temperature Change

MATERIALS AND METHODS

Study Area

Palnadu area in Guntur district in Andhra Pradesh state.It is famous for white cement and limestone industries, cotton, rice and mirchifarming fields. Natural limestone is found in abundance in the earth's crust of Palnaduareai.e, Piduguralla, Machavaram, Dachepalli, Gurazala, Rentichintala, Karampudimandals of Guntur district. Around Palnadu area 4 bigcement factories namely, 1. K.C.P Cement, Macherla. 2. J.P Cement, Dachepalli. 3.Bhavya Cement, Tangeda. 4. Parashakthi Cements, Rentichintala. There are 2 middlescale cement industries namely 1. KLPK Cements, Macherala. 2. Sri Chakra Cements,Karampudi in the area. There are 200 Lime Kilns around Piduguralla town in thePalnadu area. Nearly 90 rice mills (par boiled and raw rice) and around 300 Lime &Lime Stone Pulvarizers in this area. Many Cotton mills are there in the Palnadu area.

SAMPLECOLLECTION

Various Samples were collected from different mines, located at different places from Palnadu area in Guntur district, Andhra Pradesh. The coarse size of the sample collected at the mines was in the range of two to four inches all these samples in one mine arranged in a cone shape and the cone is divided into four parts. The opposite side samples of the cone were taken for the analysis.[6-10]

Preparation of Samples for Chemical Analysis

Limestone in each gross sample shall be first crushed in a jaw crusher, roll crusher or manually using a hammer or pounder and a suitable steel plate, till the material in gross sample is of 10 mm size. Duplicate moisture samples of 1 kg each may be collected at this stage, if not already done. The rest of the material shall be mixed well and reduced, to 20 kg which shall then be further processed in stages as detailed in Fig1, to prepare the laboratory samples for chemical analysis. For reduction at various stages one of the methods detailed in 8.2.1 to 8.2.3 shall be followed. The mass of the each laboratory sample shall be at least 200g.The lumps obtained while collecting the increments (see 3.1.1.1) shall be crushed separately and one spoonful for each lump (approximately 4kg for run of mine ore) shall be taken along with the materials of other sizes in the gross sample for reduction.

SAMPLING

Lime Stone sample (LMS-1) collected from the mines of Nadikudi village of Dachepalli mandal, sample (LMS-2) collected from the mines of Chennaipalem village of Machavaram mandal, sample (LMS-3) collected from the mines of Gadevaripalle village of Karampudi mandal, sample (LMS-4) collected from the mines of Patha Ganeshunipadu village of Piduguralla, sample (LMS-5) collected from the mines of Goli village of Rentichintala mandal, sample (LMS-6) collected from the mines of Gottimukkala village of Gurazala mandal.

TEST RESULTS

SAMPLE PARTICULARS: LMS- 1, LMS- 2, LMS- 3, LMS- 4,LMS- 5, LMS- 6

QUANTITY:2 gms

S.No.	Test Parameters	Units Of Measurements	Results Obtained					
			LMS1	LMS- 2	LMS- 3	LMS- 4	LMS- 5	LMS- 6
1.	Calcium as CaO	%bymass	52.47	43.71	49.35	66.58	55.78	39.07
2.	Magnesium as MgO	% bymass	0.57	0.72	0.66	0.79	0.85	0.77
3.	Silicon as SiO_2	%bymass	11.60	11.20	10.90	11.40	11.10	10.85
4.	Iron as Fe_2O_3	% bymass	0.62	0.54	0.59	0.56	0.59	0.56
5.	Aluminium as Al_2O_3	% bymass	0.30	0.25	1.08	1.06	0.91	1.14

INSTRUMENTATION

Mettler's TGA/DSC1 Thermo gravimetric Analyzer is a high performance TGA instrument which is one of the very best instruments of its kind for a very simple reason. The balance cell is the most important part of any TGA system; **Mettler Toledo's (TGA|SDTA).**instruments are made with the best micro and ultra-micro balances in the world. Using three different removable sensors, the TGA/DSC1 can measure weight change and heat flow simultaneously. The modular design of this instrument allows it to fit perfectly into manual applications as well as for applications requiring fully automated operation in research and development, quality assurance, production and more [11-19].

The following are the specifications of the instrument:

Furnace: Temperature range: RT to 1100°C, Temperature accuracy: ±0.3K, Heating time 10min (RT to 1100°C) Cooling time 22min (1100°C to 100°C), Heating rate 150K/min, Cooling rate -20K/min (=150°C), Sample Volume =900Ml.

Balance (MX1/MX5): Measurement range: =1g/5g, Resolution 1.0µg.

Calorimetric: Sensor type: SDTA(simultaneous differential thermal analyser) Surface material: Platinum, Number of thermocouples: 1, Signal time constant at 900°C: 15s, Sensivity: 0.5mW, Furnace temperature resolution: 0.005K, Enthalpy reproducibility: better than 5%.

RESULTS AND DISCUSSION

The thermogram of (LMS-1) limestone sample collected from the mines of Nadikudi village of Dachepalli mandal is shown in Fig 1. The % of mass loss of the sample at various temperatures are measured from the TGA graph and data presented in table 1. The data indicates that the decomposition starts at 680 OC and completes at 826 °C. The maximum % of mass loss in the sample is 17.18.

TABLE :1 The mass loss of the sample (%) against temperature of LMS-1.

S.No.	Temperature (°C)	Mass Loss (%)
1.	28.82	0.00
2.	135.09	1.10
3.	241.36	14.05
4.	347.64	14.12
5.	453.91	14.31
6.	560.18	14.49
7.	668.45	14.49
8.	772.73	14.89
9.	879.00	15.03
10.	986.27	17.18

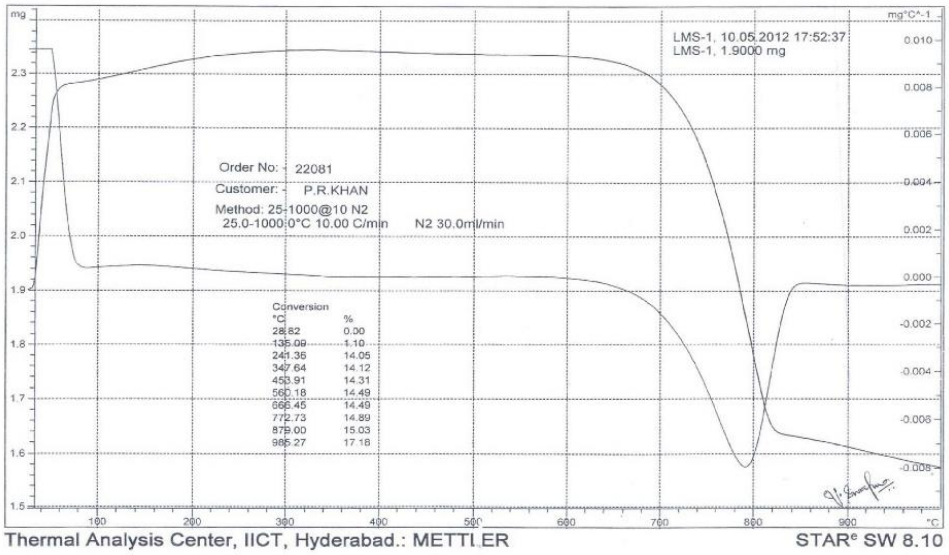

FIG.1: THERMOGRAM OF LMS-1

The thermogram of (LMS-2) limestone sample collected from the mines of Chennai Palem village of Machavaram mandal is shown in Fig 2. The % of mass loss of the sample at various temperatures are measured from the TGA graph and data presented in table 2. The data indicates that the decomposition starts at 680 °C and completes at 850°C. The maximum % of mass loss in the sample is 40.09.

TABLE: 2 The mass loss of the sample (%)against temperature of LMS-2.

S.No.	Temperature (^{O}C)	Mass Loss (%)
1.	28.96	0.00
2.	135.49	7.77
3.	242.01	8.86
4.	348.54	9.03
5.	455.07	9.26
6.	561.60	9.57
7.	668.12	9.63
8.	774.65	9.81
9.	881.18	39.75
10.	987.70	40.09

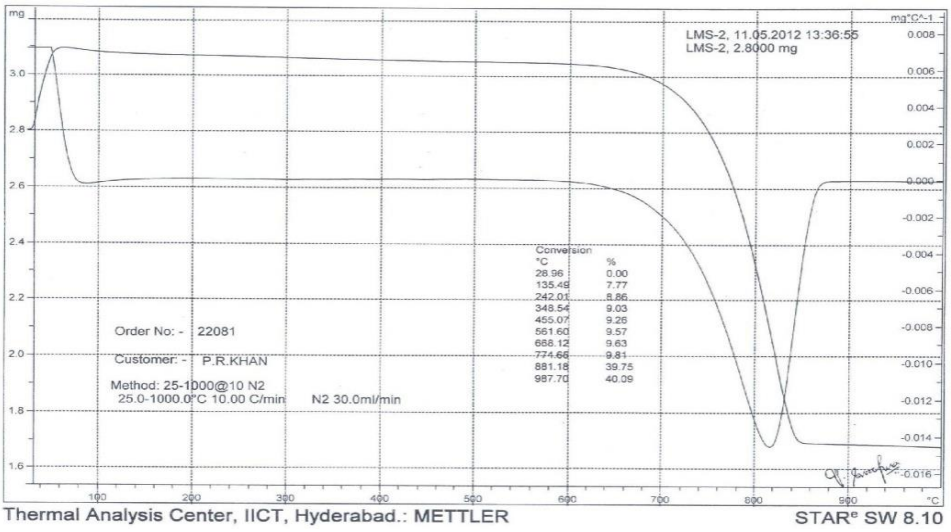

FIG.2:THERMOGRAM OF LMS-2

The thermogram of (LMS-3.) limestone sample collected from the mines of Gade Vari Palle village of Karamapudi mandal is shown in Fig 3. The % of mass loss of the sample at various temperatures are measured from the TGA graph and data presented in table 3. The data indicates that the decomposition starts at 640 ^{O}C and completes at 825 ^{o}C. The maximum % of mass loss in the sample is 13.98.

TABLE: 3The mass loss of the sample(%) against temperature of LMS-3.

S.No.	Temperature (^{O}C)	Mass Loss (%)
1.	28.48	0.00
2.	134.69	3.36
3.	240.90	3.43
4.	347.11	3.47
5.	453.32	3.55
6.	559.53	3.83
7.	665.74	3.91
8.	771.95	4.88
9.	878.16	13.07
10.	984.37	13.98

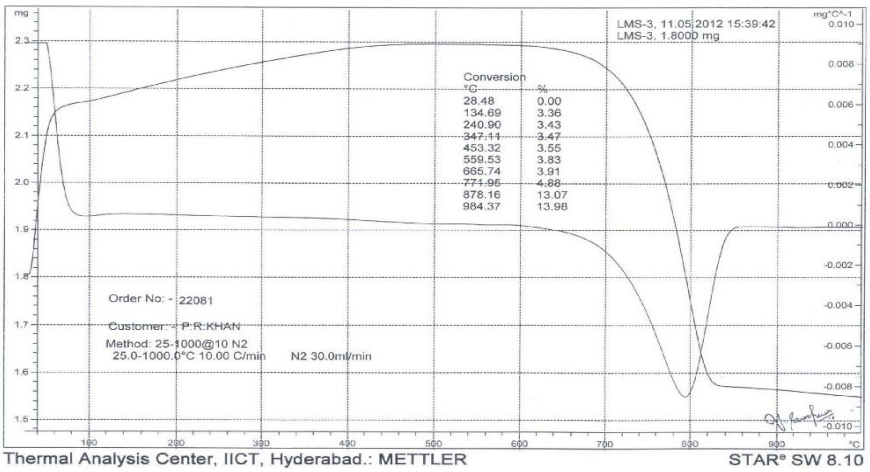

FIG.3:THERMOGRAM OF LMS-3

The thermogram of (LMS-4.) limestone sample collected from the mines of Patha Ganeshuni Padu village of Piduguralla mandal is shown in Fig 4. The % of mass loss of the sample at various temperatures are measured from the TGA graph and data presented in table 4. The data indicates that the decomposition starts at 680 OC and completes at 855 ^{o}C. The maximum % mass loss in the sample is 24.33.

TABLE 4: The mass loss of the sample (%) against temperature of LMS-4

S.No.	Temperature (^{O}C)	Mass Loss (%)
1.	28.63	0.00
2.	135.08	10.11
3.	241.53	10.34
4.	347.98	10.49
5.	454.43	10.66
6.	560.87	10.69
7.	667.32	10.88
8.	773.77	10.88
9.	880.22	23.96
10.	986.67	24.33

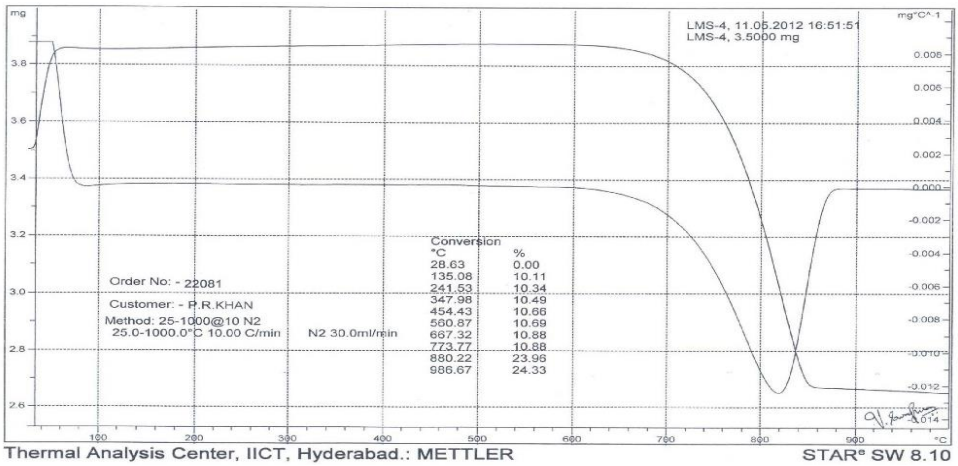

FIG.4: THERMOGRAM OF LMS-4

The thermogram of (LMS-5.) limestone sample collected from the mines of Goli village of Rentichintala mandal is shown in Fig 5. The % of mass loss of the sample at various temperatures is measured from the TGA graph and data presented in table 5.5 the data indicates that the decomposition starts at 700 OC and completes at 872 ^{o}C. The maximum % of mass loss in the sample is 16.14.

TABLE5: The mass loss of the sample(%) against temperature of LMS-5.

S.No.	Temperature (^{O}C)	Mass Loss (%)
1.	28.29	0.00
2.	132.78	7.29
3.	237.27	11.04
4.	341.75	11.09
5.	446.24	12.01
6.	550.73	12.29
7.	655.21	12.71
8.	759.70	12.89
9.	864.19	15.14
10.	968.68	16.14

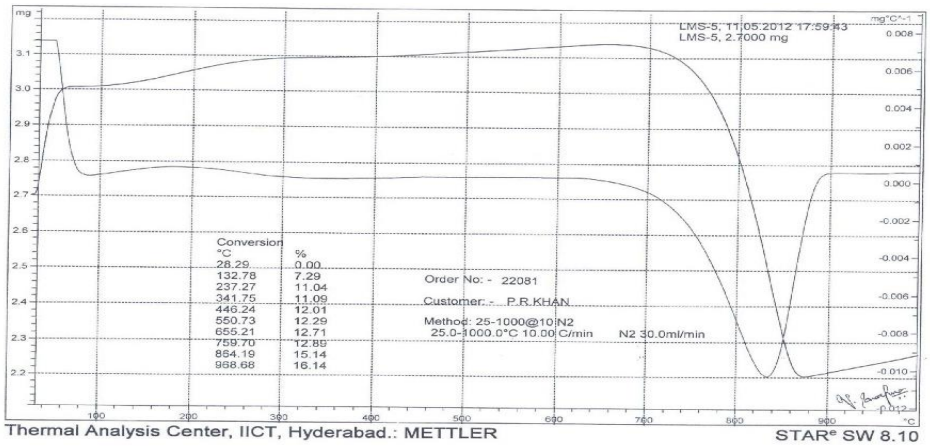

FIG.5:THERMOGRAM OF LMS-5

The thermogram of (LMS-6.) limestone sample collected from the mines of Gotti Mukkala village of Gurazala mandal is shown in Fig 6. The % of mass loss of the sample at various temperatures are measured from the TGA graph and data presented in table 5.6. The data indicates that the decomposition starts at 600 ^{O}C and completes at 755 ^{o}C. The maximum % of mass loss in the sample is 23.93.

TABLE6: The mass loss of the sample (%) against temperature of LMS-6.

S.No.	Temperature (^{O}C)	Mass Loss (%)
1.	30.14	0.26
2.	136.02	0.37
3.	241.89	6.72
4.	347.76	7.95
5.	453.64	7.95
6.	559.51	8.50
7.	665.38	10.22
8.	771.25	23.01
9.	877.13	23.43
10.	983.00	23.93

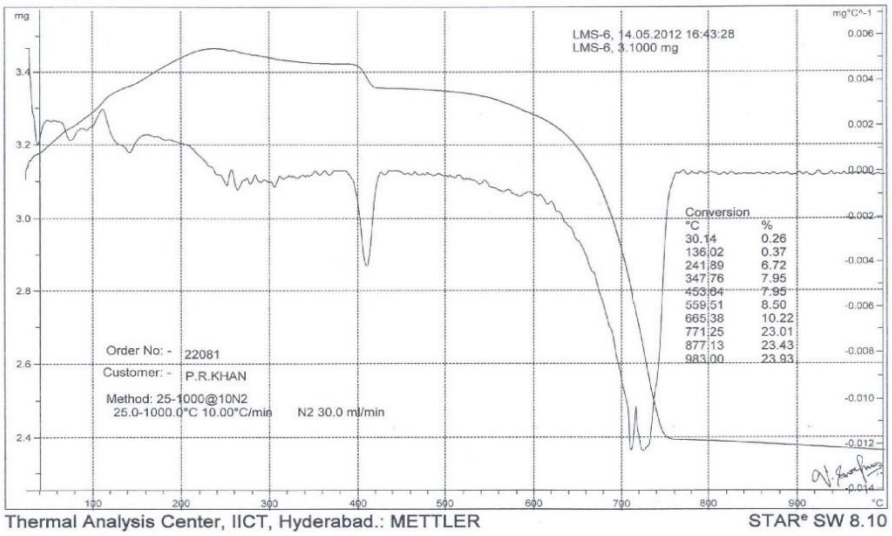

FIG.6:THERMOGRAM OF LMS-6

CONCLUSION

The above said Thermogravimetric analysis data of all the Lime stone samples analysed exhibiting the decomposition in the temperature range of 6000 – 895^{0}C. Conventionally this was achieved using the Bitiminous coal with a calorific value of 6.8 to 8.8 Kw/Kg. and with a Carbon content 45 to 86% supplied from Singareni coal mines. But the current practical scenario does not allow the process run in the above-mentioned way.

The manufacturers today are using the coal from Jhariya (Jharkund state) which is Anthracite coal with a calorific value above 9 Kw/Kg and has highest Carbon content of 86 to 98%, as the Govt. of Andhra Pradesh has stopped giving subsidy on Singareni coal. Due to this remarkable change in quality of coal utilized in the process, the temperature in the Lime stone kiln is found to be > 13000C, when used in the ratio 6:1 (Raw material:Coal). This process of using Anthracite coal in the Lime manufacturing by the manufacturers as they find lime stone getting decomposed quickly and with less amount of coal. They will be economically benefited. But the undesired part is the formation of

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Thisimpurityiscausinglosstothemanufacturersinyieldoflime.Hencethe following steps are to be taken to avoid Clinker formation.

- Supply of more air.
- Decrease in the quantity of coal.
- Decrease in the size of the coal particles.
- Increase in the height of the Lime kiln.
- Ratio of raw material to the coal must be changed from 6:1 to 8:1.

Hence by following the above proposed modifications and ratio between raw material and coal depending on the calorific value of the coal to generate only the required temperature in the kiln for the formation of lime (high yield), thus avoiding clinker formation.

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