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TG–DTA STUDIES ON THE PYROLYSIS OF LIMESTONE–LATERITE MIXTURES

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ABSTRACT

TG and DTA studies conducted on 15 Indian laterite samples, limestone as well as three limestone–laterite mixes revealed the influence of minerals in laterite on the pyrolysis of limestone. Stanton Redcroft high temperature thermobalance HTSF and DTA model 674 were used.

The 15 laterites could be classified broadly into three groups based on DTA peaks up to 1000°C. The minerals identified by DTA were confirmed by X-ray diffraction study on one selected sample from each group. Their approximate quantification was possible from the chemical composition and TG studies done up to 950°C.

While gibbsite present in laterite showed no significant influence on the calcination of limestone, goethite retarded the rate of decomposition, particularly in the temperature range 700–840°C. From burnability experiments up to 1400°C, it was found that the sintering of limestone–laterite mixes is favourably influenced by goethite present in the laterite.

INTRODUCTION

Laterite occurs extensively in the tropical zones of the earth. Geologically, laterite is a form of regolith highly peculiar to India, believed to have resulted from the sub-aerial decomposition in situ of basalt and other aluminous rocks under the warm, humid, monsoonic climate of India. Being primarily a porous, pitted earthy rock, laterite is essentially composed of hydrated oxides of iron and aluminium, besides containing SiO_2, TiO_2, NiO and sometimes CaO. Typical minerals in laterite are of the kaolinite group, together with gibbsite, goethite and hematite. Many of these minerals are amenable to quantitative determination by DTA technique [1].

In the manufacture of Portland cement, laterite is extensively used in small quantities as a corrective material to balance the aluminium and iron contents of the raw mix feed. The grade of the laterite usually depends on the chemical composition of the principal cement raw materials, namely, limestone and clay. The reactivity of the cement raw mix is primarily a function of the minerals present in its constituents which on thermal decomposition yield the active oxides for the solid state reactions. In this

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context the influence of laterite mineralogy on raw mix sintering does not seem to have received sufficient attention. The present work was therefore undertaken to investigate the influence of minerals present in laterite on the pyrolysis of limestone with the help of TG and DTA studies.

EXPERIMENTAL

Selection of samples

Fifteen laterite samples from different parts of India were selected at random; these were, however, being used in cement plants. Likewise two different grades of limestone were chosen from one cement plant.

Chemical analysis

Oxide composition of the two limestone samples as well as of the 15 laterite samples was determined by following standard methods of chemical analysis.

Thermal analysis

To identify the minerals present in the 15 laterite samples, DTA studies were undertaken up to a temperature of 1000°C using a Stanton Redcroft DTA model 674. The experimental conditions are presented in Table 1.

Based on the minerals identified from the DTA curves, the 15 laterites could be broadly classified into three groups. Thermogravimetric analysis of one selected sample from each group, namely laterites S, JM and N, was conducted for approximate quantification of the major minerals present. This investigation up to 950°C was carried out in a Stanton Redcroft thermobalance HTSF; the details of the experimental conditions are included in Table 1.

Three limestone–laterite mixes were prepared with about 3% of laterite from each group (the proportion of the constituents is given in Table 4) to produce three typical cement raw mixes which on sintering will theoretically produce 75% of tricalcium silicate, 3 CaO SiO_2, in the product. The fineness of all mixes was maintained at 85% passing through a 90 μm sieve.

Thereafter TG and DTA experiments were conducted with a combination of the two grades of limestone, as well as with the aforementioned three mixes. The TG study for all the four samples was restricted up to the calcination stage, i.e., up to a temperature of 950°C, while the DTA run for the limestone combination was up to 1000°C. For the mixes the DTA runs were extended to the sintering stage, i.e., up to 1400°C.

TABLE 1

Details of TG–DTA equipment and experimental conditions

TG:	Stanton Redcroft thermobalance, HTSF	
	Sample wt.	205 mg
	Heating rate	10°C min^{-1}
	Atmosphere	static air
	Sample holder	Pt crucible
	Thermocouple	Pt/Pt Rh 13%
	Location	near the crucible
	Temp. range	ambient to 950°C
DTA:	Stanton Redcroft, Model 674	
	Sample wt.	128 mg
	Heating rate	16°C min^{-1}
	Atmosphere	static air
	Ref. material	Al_2O_3
	Sample holder	Pt crucible
	Thermocouple	Pt/Pt Rh 13%
	Location	TC tip in the crucible dimp.
	ΔT sensitivity	100 μV in 10 mV recorder
	Temp. range	ambient to 1400°C

'Burnability' determination

Pellets of 10–12 mm diameter were prepared from each of the mixes, dried, and calcined on a platinum boat at 950°C for 1 h in an electrically heated muffle furnace. These were then introduced into another furnace maintained at a temperature of 1400°C and sintered for 30 min. The burnt pellets were cooled in air, and unreacted lime, considered as a criterion for completeness of reaction, was determined by standard procedure in pellets of each mix.

X-Ray analysis

Supplementary characterization of minerals by X-ray diffraction for the three selected laterite samples, using Fe target was carried out.

RESULTS AND DISCUSSION

Chemical analysis results of the three selected laterite samples as well as of the two grades of limestone are given in Table 2. The results are expressed as percentages of oxide composition of the major constituent elements. As can be seen from Table 2, laterite S contains less SiO_2 and Fe_2O_3 but more Al_2O_3

TABLE 2

Chemical composition of laterites and limestone samples

	%					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI
Laterite						
N	17.4	13.2	53.6	Nil	Nil	12.2
JM	20.1	19.3	48.9	Nil	Nil	11.2
S	14.5	26.3	28.5	9.0	0.3	18.3
Limestone						
Gr.1	10.9	1.6	0.8	47.4	1.7	37.1
Gr.2	16.1	2.2	1.0	43.8	1.9	34.2

than the two other laterites, namely JM and N. Laterite S also contains lime, which is absent in the other two. The oxide compositions are indicative of the relative abundance of the different minerals bearing the respective elements. Thus, laterite S contains aluminium rich minerals more than that present in laterites JM and N, while these two contain more iron rich minerals. Besides, laterite S also contains calcium bearing mineral, probably calcite, also indicated by the relatively higher loss on ignition value.

Differential thermal curves of the three laterite samples, S, JM and N—one selected from each group—are given in Fig. 1. The DTA curve of laterite S shows three distinct endothermic peaks at 320, 551 and 844°C, respectively, while another peak around 931°C could not be clearly identified as endothermic or exothermic. Likewise in the case of laterite JM three endothermic peaks could be observed at 129, 360 and 570°, respectively, while a distinct exothermic peak could be recorded at 969°C; the peak at 360°C seems to be a complex peak. For laterite N, however, two endothermic peaks and one exothermic peak are observed at 369, 572 and 972°C, respectively.

A judicious conclusion could be arrived at as to the type of minerals present in the laterites by comparing their chemical composition and the peak temperatures observed in their DTA curves with those quoted for identified minerals in literature [2]. Thus, in the case of laterite S, the peak at 320°C can be attributed to gibbsite, at 551°C to kaolinite, at 844°C to calcite, and for laterite N, the peak at 369°C is due to goethite, those at 572°C and 972°C are due to kaolinite. Similarly, in the case of laterite JM, the peak at 129°C could be due to clayey impurities, and the complex peak at 360°C due to a mixture of gibbsite and goethite (goethite predominating), while the peaks at 570°C and 969°C are obviously due to kaolinite.

The observations from the aforementioned DTA curves could be con-

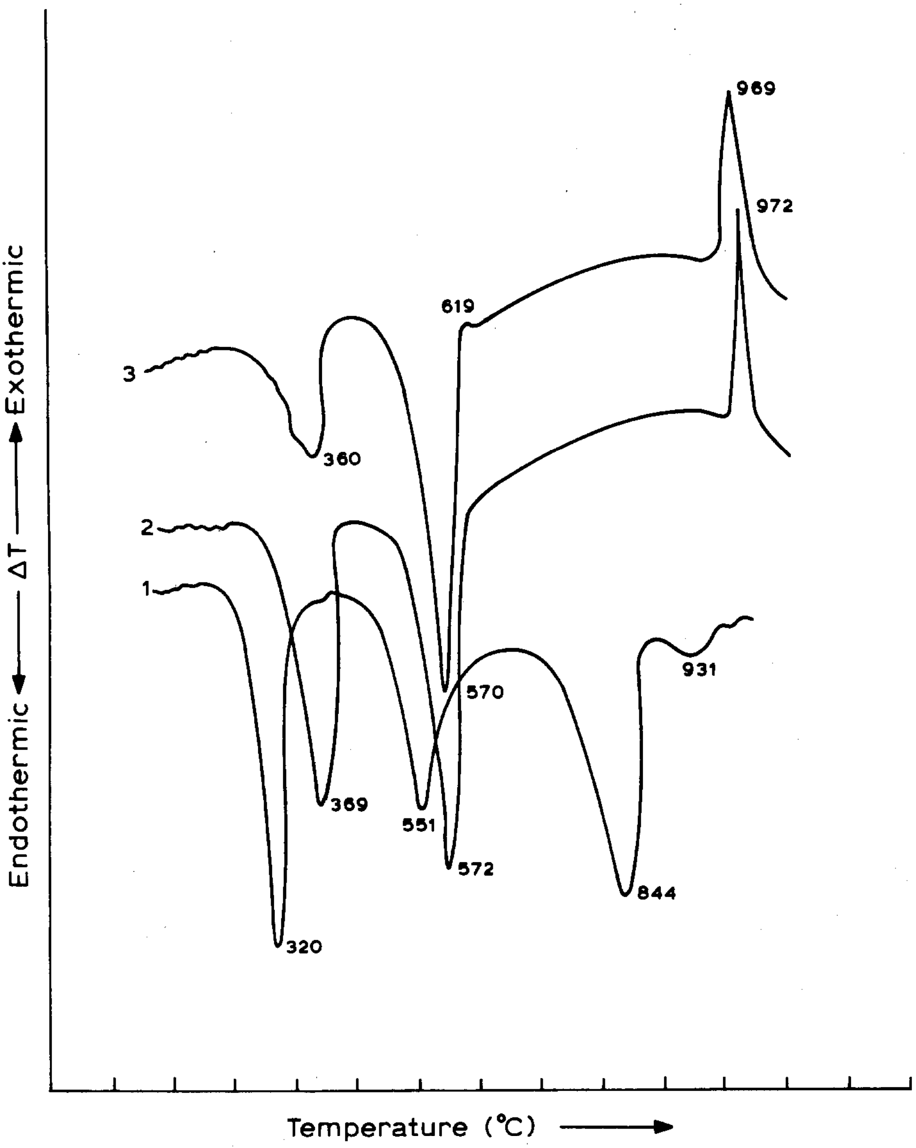

Fig. 1. DTA curves of laterites. 1, S; 2, N; 3, JM.

firmed from the supplementary characterization by the X-ray diffraction studies on the selected laterite samples. Figure 2 reproduces the diffractogram of laterites S and JM from which it is seen that in addition to kaolinite and goethite/gibbsite, hematite was also present in all the samples. The latter could not be detected by DTA.

An approximate quantification of the major minerals present in these laterites was done by TG studies. Figure 3 shows the TG curves of the three laterites, whereas their approximate mineral composition is given in Table 3.

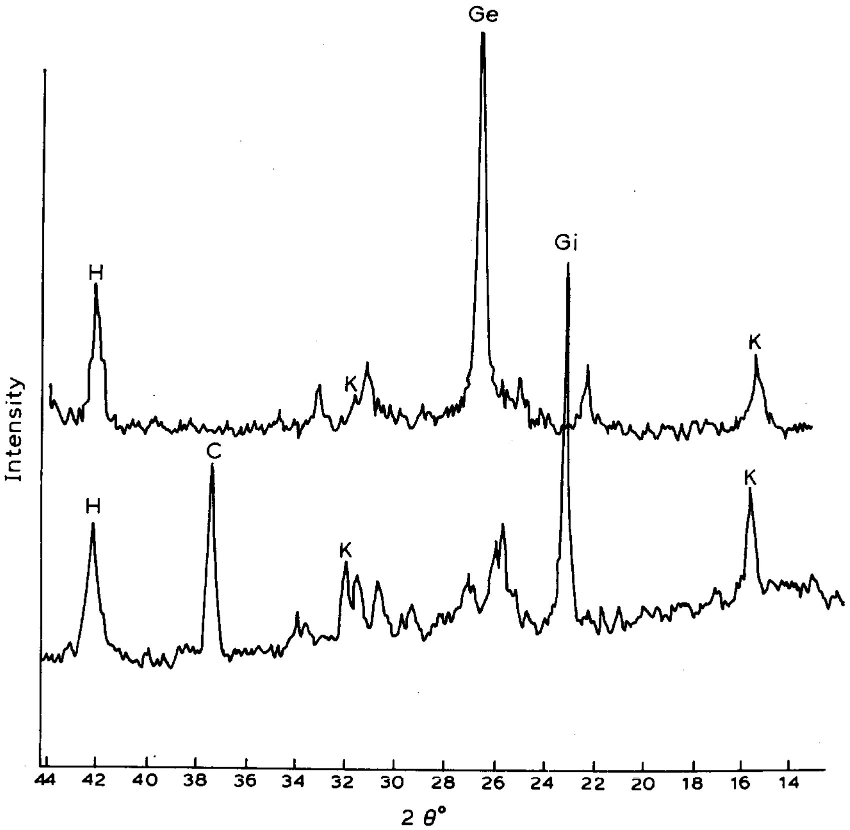

Fig. 2. X-Ray diffractograms of laterites S and JM. K, Kaolinite; Gi, gibbsite; Ge, goethite; C, calcite; H, hematite.

The percentages of silica, alumina and lime calculated from the quantity of kaolinite, gibbsite and calcite as determined by the TG studies agreed very well with the chemical analysis results. However, in the case of iron oxide, the chemical analysis showed a higher value than that calculated from the amount of goethite present. Thus, the balance amount of iron oxide could be attributed to hematite, whose presence in the laterite samples is identified from the X-ray diffraction studies, as shown in Fig. 2.

Laterite S thus differs greatly in mineralogical composition from the other two, in the sense that it contains no goethite. Likewise, laterites JM and N contain no gibbsite and calcite. However, kaolinite and hematite are found to be present in all the three laterite varieties.

Table 4 gives the compositions of the three limestone–laterite mixes, namely RM–S, RM–JM and RM–N, as well as the percentage of major oxides calculated from the chemical analysis of the individual components. As can be seen from the Table, the variation in the oxide composition of the three mixes is not significant since, as stated above, these have been

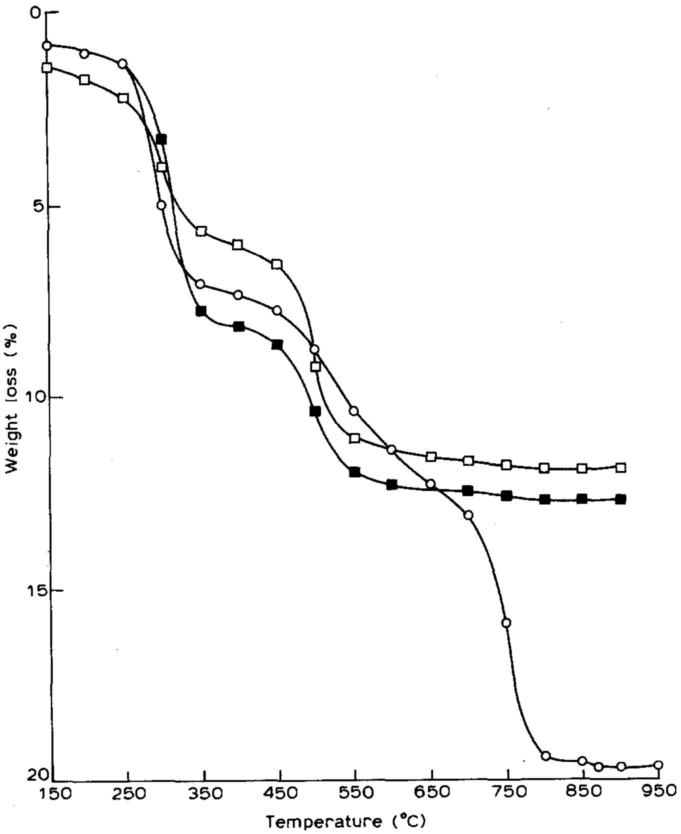

Fig. 3. TG curves of laterites. ○, S; □, JM; ■, N.

proportioned in such a manner so that all of them will theoretically yield 75% of tricalcium silicate in their sintered products.

The thermogravimetric behaviour of limestone combination LM as well as

TABLE 3

Mineral composition of laterites from TG analysis

Laterite	% Minerals (approx.)					
	Gibbsite	Goethite	Kaolinite	Calcite	Hematite (by diff.)	Free silica (by diff.)
S	19.5		35.8	15.7	28.0	
JM		45.5	42.4		8.0	
N		58.1	34.9		1.4	1.1

Gibbsite: $Al(OH)_3$; goethite: $FeO(OH)$; kaolinite: Al_2O_3, 2 SiO_2, 2 H_2O; calcite: $CaCO_3$; hematite: Fe_2O_3.

TABLE 4

Composition of limestone–laterite mixes

Components (%)	LM	RM–S	RM–JM	RM–N
Limestone Gr. 1	36.1	34.7	36.0	34.8
Limestone Gr. 2	63.9	62.0	61.0	62.0
Laterite S		3.3		
Laterite JM			3.0	
Laterite N				3.2
Chemical analysis (%)				
SiO_2	14.2	14.2	14.3	14.3
Al_2O_3	2.0	2.8	2.5	2.4
Fe_2O_3	1.0	1.9	2.4	2.6
CaO	45.1	43.9	43.8	43.6
LOI	35.3	34.7	34.6	34.5

limestone–laterite mixes is shown in Fig. 4. For the same percent weight loss, the mixes RM–JM and RM–N require a higher temperature than for RM–S, which in turn needs a higher temperature than LM. This behaviour may be due to the difference in mineralogical composition of the laterites. Thus, the retardation of the decomposition rate of calcite present in the limestone combination is more marked with goethite containing laterites in the mixes RM–JM and RM–N than with the gibbsite containing laterite in RM–S. The iron oxide obtained from goethite decomposition can be reasonably expected to be more reactive than hematite already present. Thus, in a given instant of time, more dicalcium ferrite is expected to be formed in the temperature interval 550–800°C by the reaction of Fe_2O_3 and $CaCO_3$ [3] during the calcination of the mixes RM–JM and RM–N. The amount of calcite present in the three mixes can, however, be assumed to be the same, since the percentages of CaO as given in Table 4 for the three cases are more or less the same.

Figure 5 shows the DTA curves of limestone–laterite mixes and also the limestone combination. The major endothermic peaks at 908°C (RM–JM and RM–N), 904°C (RM–S) and 884°C (LM) are due to decomposition of the calcite present. This observation is consistent with the thermogravimetric behaviour of these samples. Further, it can be seen that immediately after this endothermic peak, the DTA baseline is drifting endothermically in the case of LM and RM–S, while this drift is not observed in the case of RM–JM and RM–N. This may be due to the presence of a large amount of free lime just after the decomposition of calcite in the samples LM and RM–S. However, in the case of the other two mixes, the lime produced would have already started reacting with Fe_2O_3 even before the decomposition of calcite is complete, thus reducing the amount of free lime present

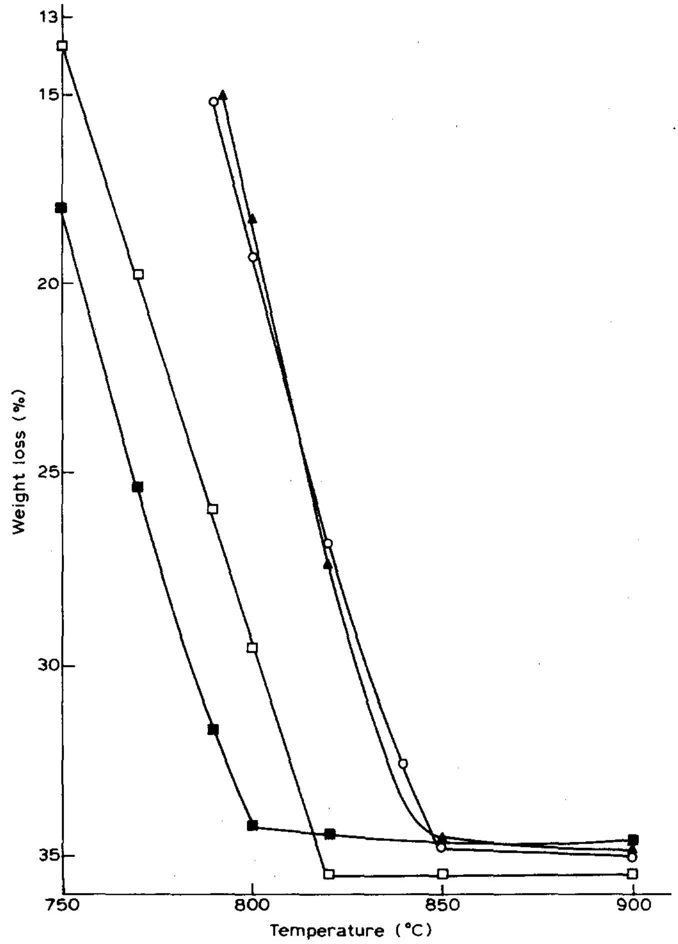

Fig. 4. TG curves of limestone combination and limestone–laterite mixtures. ■, LM; □, RM-S; ○, RM-JM, ▲, RM-N.

after the calcite decomposition. Around 1250°C another endothermic peak is observed for all the three mixes. This is understood to be due to the melt phase formation in the system, and the DTA behaviour thereafter up to 1400°C is found to be similar.

TABLE 5

Burnability results of limestone–laterite mixes

Temperature, 1400°C; residence time, 30 min.

	RM-S	RM-JM	RM-N
CaO_{free}(%)	1.85	1.68	1.51

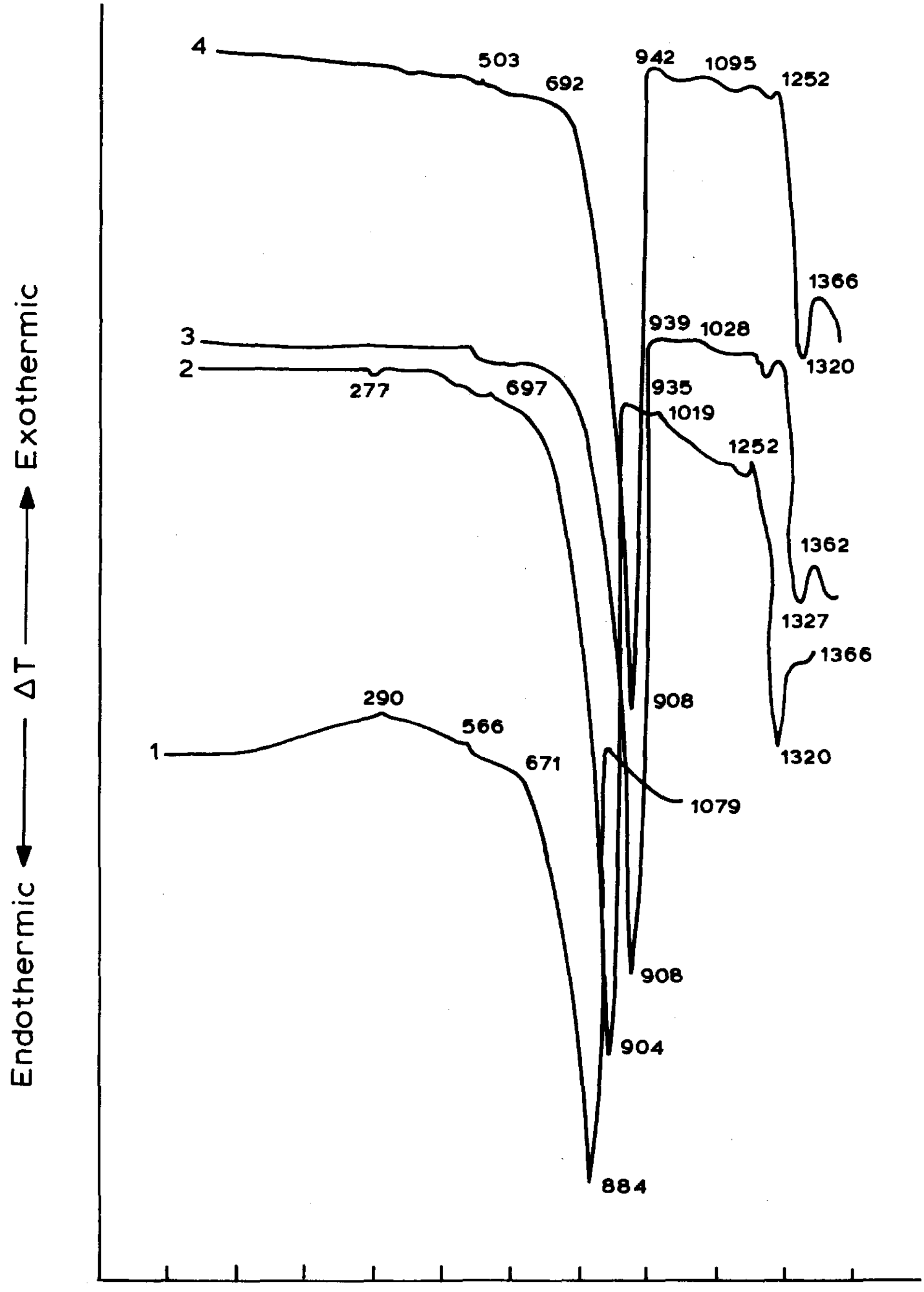

Fig. 5. DTA curves of limestone–laterite mixtures and limestone combination. 1, LM, 2, RM–S; 3, RM–JM; 4, RM–N.

The unreacted lime in the products of sintering of the three mixes is given in Table 5. No significant variation in the unreacted lime could be observed, although the mix RM–S showed a slightly higher free lime value. Thus, considering the speed of the solid state reactions leading to the formation of the desired mineral phases in the final product, the mixes RM–JM and RM–N seem to be more favourable than RM–S.

CONCLUSION

TG and DTA investigations on calcination as well as sintering of three limestone–laterite mixes up to 950°C and 1400°C, respectively, have indicated that laterite containing geothite as the major iron mineral influences the solid state reactions both during calcination and sintering. In the temperature range 700–840°C goethite seems to have retarded the rate of decomposition of calcite in limestone. The sintering reactions, however, seem to have proceeded faster, with Fe_2O_3 decomposed from goethite rather than with Fe_2O_3 present as hematite. Further investigations with a large number of mixes and preferably with laterites of known geology are to be carried out for generalization of the present observations.

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