

Thermal Studies on Manganese Ores of Sandur Area, Karnataka, India

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Abstract:- The manganese ore samples from Sandur were subjected to thermal studies. The thermal study of minerals involves the Differential thermal analysis (DTA) a method of mineral analysis that is particularly useful in the identification of the minerals which undergo transformation when heated to temperatures generally below 1200⁰c. If heat energy is absorbed the rate will decrease during the transformation and the reaction is endothermic. The temperatures at which endothermic and exothermic transformations take place are characteristic of certain substances. The DTA technique has been devised to determine these temperatures. Since it is unlikely that any two minerals have chemical bonds of identical strength, they will decompose, oxidize or change phase at different temperatures. The temperature at which the peak occurs often indicates which mineral is present. Since many minerals undergo several endothermic or exothermic changes in the temperature range studied, the aggregate peaks at the proper temperatures suffice in many instances to identify the mineral. In this study it has been the objective to define the thermal curves of the simpler manganese minerals and to study how the method can be applied to natural mixtures. Thermo gravimetric analysis (TGA) technique deals with the study of the loss in weight of a substance as it is being heated. The behavior of the minerals to the rising temperatures is studied. The studies are carried out with respect to their transformations and weight loss due to the rising temperature. The studies show the presence of Manganese minerals such as psilomelane, pyrolusite, manganite, cryptomelane and ramsdellite. The instrument used is SDT Q 600 TA instruments, Waters USA.

Keywords:- DTA, TGA, Manganese, Sandur, Endothermic and Exothermic.

I. INTRODUCTION

The Karnataka Manganese ore deposits are believed to have been derived mainly by the process of supergene enrichment of manganiferous phyllites belonging to Dharwar system. Sandur schist belt is one of the important greenstone belts of the Karnataka craton and is named after the town Sandur where it is typically exposed. The rich manganese ore deposits associated with schist belt have evoked the interest from very early times of economic geologists, mining engineers and metallurgist. The manganese ore samples from Sandur were subjected to thermal studies. The thermal study of minerals involves the Differential thermal analysis (DTA) and the Thermo gravimetric analysis (TGA). The behaviour of the minerals to the rising temperatures is studied. The studies are carried out with respect to their transformations and weight loss due to the rising temperature. If during the process of heating change occurs in the substance and heat energy is liberated, the rate will increase during the reaction because there is now a second source of heat, such a reaction is termed exothermic. In this study it has been the objective to define the thermal curves of the simpler manganese minerals and to study how the method can be applied to natural mixtures.

II. DIFFERENTIAL THERMAL ANALYSIS (DTA)

A method of mineral analysis that is particularly useful in the identification of the minerals which undergo transformation when heated to temperatures generally below 1200⁰ c is called differential thermal analysis (DTA) the method is suitable for both qualitative and semi-quantitative studies of minerals which absorb or liberate energy on heating resulting from such transformations as dehydration, oxidation, inversion, and decomposition and phase changes. Clay minerals, carbonates, hydrous oxides, and zeolites are particularly well suited for this method of analysis. In this study it has been the objective to define the thermal curves of the simpler manganese minerals and to study how the method can be applied to natural mixtures.

The temperature of the substance increases at a constant rate when heat is applied under a controlled condition as long as no transformations occur in which heat energy is involved. If during the process of heating change occurs in the substance and heat energy is liberated, the rate will increase during the reaction because there is now a second source of heat, such a reaction is termed exothermic. If heat energy is absorbed the rate will decrease during the transformation and the reaction is endothermic. This operation can be carried out dynamically (differential thermal analysis) in which the system is heated at constant rate. It is called differential because the temperature difference between an inert material and the sample is measured as both are being heated at constant rate.

The temperatures at which transformations endothermic and exothermic, take place are characteristic of certain substances. The DTA technique has been devised to determine these temperatures. It involves the use of dual terminal thermocouple. One terminal is placed in the sample to be tested; the second is placed in a substance that is thermal inert over the range of the temperatures to be employed. Here we have used calcined Alumina. Both substances are placed in a furnace and heated at a constant rate. No current will be generated as long as both sample and inert material are at a same temperature. When either an exothermic or an endothermic reaction occurs in the sample, the two terminals of the thermocouple will be at different temperatures and a current will flow. This current is amplified and then led into an automatic recorder.

Pavlovitch (1935) stated that the response of minerals to rising temperature depends on the conditions of heating. When the rate of heating is constant, the thermogram is straight line. If an endothermic reaction occurs in a sample a peak appears in a certain direction on the thermogram. If the reaction is exothermic, the peak will be in opposite direction. The position of the peak on the graph indicates the temperature of transformation, and its height is a measure of the magnitude of the transformation.

Since it is unlikely that any two minerals have chemical bonds of identical strength, they will decompose, oxidize or change phase at different temperatures. The temperature at which the peak occurs often indicates which mineral is present. Since many minerals undergo several endothermic or exothermic changes in the temperature range studied, the aggregate peaks at the proper temperatures suffice in many instances to identify the mineral. The relative amplitude and shape of a peak is a function of the type of change, as well as the rate at which it occurs. The amplitude of the peak is related to the concentration of a particular mineral, and hence semi-quantitative estimates are possible by simple inspection. Since each mineral will ordinarily yield a characteristic set of peaks independent of the foreign constituents, frequently the members of a mixture in a fine-grained aggregate may be defined. Obviously the more complex the mixture and the larger the number of components with overlapping peaks the more difficult becomes the interpretation.

Pure substances have characteristic peaks. Mixed substances have thermograms which are composites of the thermograms of the substances that make up the mixture. In the present investigation samples subjected for thermal studies comprise of the mixture of different minerals of manganese.

Instrument- The instrument used is SDT Q 600 TA instruments, Waters USA.



Fig. 1: SDT Q 600 TA instruments, Waters USA.

Ten samples were subjected to DTA and TGA analysis; the results are discussed below, for respective samples. The DTA curves are shown in the fig 2.

Sample No. Mg 2- The DTA curve of the sample shows, a gradual endothermic depression at 359°C, this matches with the curve given in the literature for manganite. Endothermic depression observed at 583.56°C corresponds to manganite. Endothermic depression observed at 856.41°C corresponds to the curves given in the literature for cryptomelane.

- 1) Sample No. Mg 3- The DTA curve of the sample shows, an exothermic bulging (peak) around 380-391.16°C depicts the presence of Pyrolusite.
- 2) Sample No. Mg 4- The DTA curve of the sample shows, an endothermic depression seen between 590-600° C depicts presence of pyrolusite.
- 3) Sample No. Mg 13- The DTA curve of the sample shows, an endothermic depression seen at 288.67° C corresponds to the dehydration of goethite. Endothermic depression observed between 597.53 to 600° C can be attributed to the presence of pyrolusite. Endothermic depression at 861.41° C can be attributed to the cryptomelane.
- 4) Sample No. Mg 14- The DTA curve of the sample shows, endothermic depression observed between 575.51 to 600°C depicts the presence of manganite; the same temperature range corresponds to conversion of manganite to pyrolusite. Endothermic depression observed at 858.91°C can be attributed to the presence of cryptomelane.
- 5) Sample No. Mg 15- The DTA curve of the sample shows, endothermic depression at 586.18°C depicts the presence of manganite.
- 6) Sample No. Mg 16- The DTA curve of the sample shows, exothermic peak at 415.68°C corresponds to ramsdellite to pyrolusite conversion (Kulp and Perfetti 1950)
- 7) Sample No. Mg 17- The DTA curve of the sample shows, endothermic depression at 485.57°C depicts the presence of ramsdellite.
- 8) Sample No. Mg 20- The DTA curve of the sample shows, an endothermic depression observed at 579.44°C can be attributed to the presence of manganite. Endothermic depression observed at 864.50°C can be attributed to the presence of cryptomelane.
- 9) Sample No. Mg 21- The DTA curve of the sample shows, endothermic depression observed at 509.34°C can be attributed to the presence of manganite. Endothermic depression observed at 891.05°C depicts the presence of cryptomelane.

The results are tabulated in table no 1.

Table I: DTA observation Table

Sr. No	Sample No.	Endothermic peak ° C	Minerals Identified	Remarks
1	Mg 2	359 583.56 856.41	Manganite Manganite Cryptomelane	-
2	Mg 3		Pyrolusite	-
3	Mg 4	590-600	Pyrolusite	-
4	Mg 13	288.67		Dehydration of Goethite
5	Mg 14	575-600	Manganite	Conversion of Manganite to Pyrolusite
6	Mg 15	586.18	Manganite	-
7	Mg 16	415.68		Conversion of Ramsdellite to Pyrolusite
8	Mg 17	485.57	Ramsdellite	-
9	Mg 20	579.44	Manganite	-
10	Mg 21	509.34 891.05	Manganite Cryptomelane	-

III. THERMO GRAVIMETRIC ANALYSIS (TGA)

This technique consists of studying the loss in weight of a substance as it is being heated. The applications of the TGA methods are various and have been widely used in mineralogy and silicate technology. In many cases the TGA curve may be related to the DTA curve of the corresponding mineral. The loss of weight of known amount of powdered sample is noted by heating up to a temperature of 1000°C, each time for period of 10 minutes at a regular intervals of temperature as follows 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000°C. 0.5 gm of powder has been used and the percent weight loss has been calculated and plotted in the graph.

In the present investigation ten samples of the Deogiri manganese ores are subjected for the TGA analysis. The TGA curves of the samples are shown in fig.3 the results for the respective samples are discussed below and tabulated in table 2,

Sample No. Mg 2- The TGA curve shows, a gradual weight loss up to 511.25° C is observed. The rate of loss of weight is increased rapidly temperature range 511.25 to 609.59° C (9.413 %), which corresponds to the temperature where pyrolusite is transformed to bixbyte (-Mn₂O₃).

Sample No. Mg 3- The TGA curve shows, the loss of weight between temperatures 491.35 to 607.37° C (8.646%) corresponds to the presence of cryptomelane. The minimum rate of loss of weight (2.336%) between temperatures 607.67 to 783.61° C is attributed to the presence of psilomelane.

Sample No. Mg 4- The TGA curve shows, a gradual weight loss up to 551.33° C is observed. The rate of loss of weight is increased rapidly temperature range 551.33 to 606.68° C (12.42 %), which corresponds to the temperature where pyrolusite is transformed to bixbyte (-Mn₂O₃). A gradual weight loss (3.945%) is observed between 767.71 to 857.54° C which can be attributed to change of Mn₂O₃ to Mn₃O₄.

Sample No. Mg 13- The TGA curve shows, the rate of loss of weight is increased rapidly between temperature range 527.06 to 614.84° C (8.609 %), which corresponds to the temperature where pyrolusite is transformed to bixbyte (-Mn₂O₃).

Sample No. Mg 14- The TGA curve shows, the rate of loss of weight is increased rapidly between temperatures 513.20 to 602.22° C (7.282 %), which corresponds to the presence of pyrolusite. The loss of weight (9.647%) between 400 to 900° C corresponds to dehydration of psilomelane as stated by Fleischer (1960).

Sample No. Mg 15- The TGA curve shows, the loss of weight between temperature range 491.35 to 613.47° C corresponds to the presence of cryptomelane. Further the minimum rate of loss of weight (2.030%) between temperatures 650 to 800° C is attributed to the presence of psilomelane.

Sample No. Mg 16- The TGA curve shows, the loss of weight between temperatures 487.61 to 608.08° C corresponds to the presence of cryptomelane.

Sample No. Mg 17- The TGA curve shows, the maximum loss of weight between temperatures 450.17 to 529.37° C attributes to the presence of cryptomelane. The loss of weight (9.029%) between 450 to 940° C corresponds to dehydration of psilomelane as stated by Fleischer (1960).

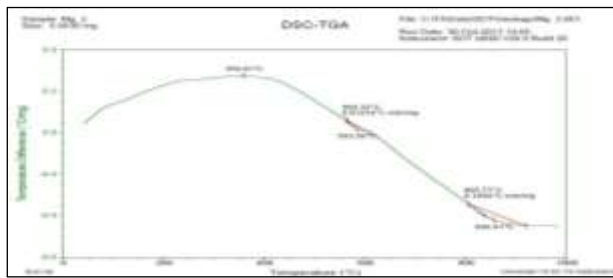
Sample No. Mg 20- The TGA curve shows, the rate of loss of weight is increased rapidly between temperature range 502.85 to 590.94° C (8.857 %), which corresponds to the temperature where pyrolusite is transformed to bixbyte (-Mn₂O₃).

Sample No. Mg 21- The TGA curve shows, the maximum loss of weight between temperatures 471.00 to 557.88° C attributes to the presence of cryptomelane. Further the minimum rate of loss of weight (2.557%) between temperatures 650 to 800° C is attributed to the presence of psilomelane in the given sample.

Table II: TGA observation Table

Sr. No	Sample No	Loss of weight %	Temperature Range ° C	Corresponding Mineral	Remarks
1	Mg 2	9.413	511.25-609.59		Temp range corresponds to conversion of Pyrolusite to Bixbyte.
2	Mg 3	8.646 2.336	491.35-607.37 607.67-783.61	Cryptomelane Psilomelane	-
3	Mg 4	12.42	551.33-606.68		Temp range corresponds to conversion of Pyrolusite to Bixbyte.
4	Mg 13	8.609	527.06-614.84		Temp range corresponds to conversion of Pyrolusite to Bixbyte.
5	Mg 14	7.282 9.647	513.20-602.22 400-900	Pyrolusite	- Dehydration of Psilomelane
6	Mg 15	7.617 2.030	491.35-613.47 650-800	Cryptomelane Psilomelane	-
7	Mg 16	6.795	487.61-608.08	Cryptomelane	-
8	Mg 17	6.312	450.17-529.37 450-950		Dehydration of Psilomelane Dehydration of Psilomelane
9	Mg 20	8.857	502.85-590.94		Temp range corresponds to conversion of Pyrolusite to Bixbyte.
10	Mg 21	7.407 2.557	471.00-557.88 650-800	Cryptomelane Psilomelane	-

Fig. 2: DTA curves of Manganese ores of Sandur



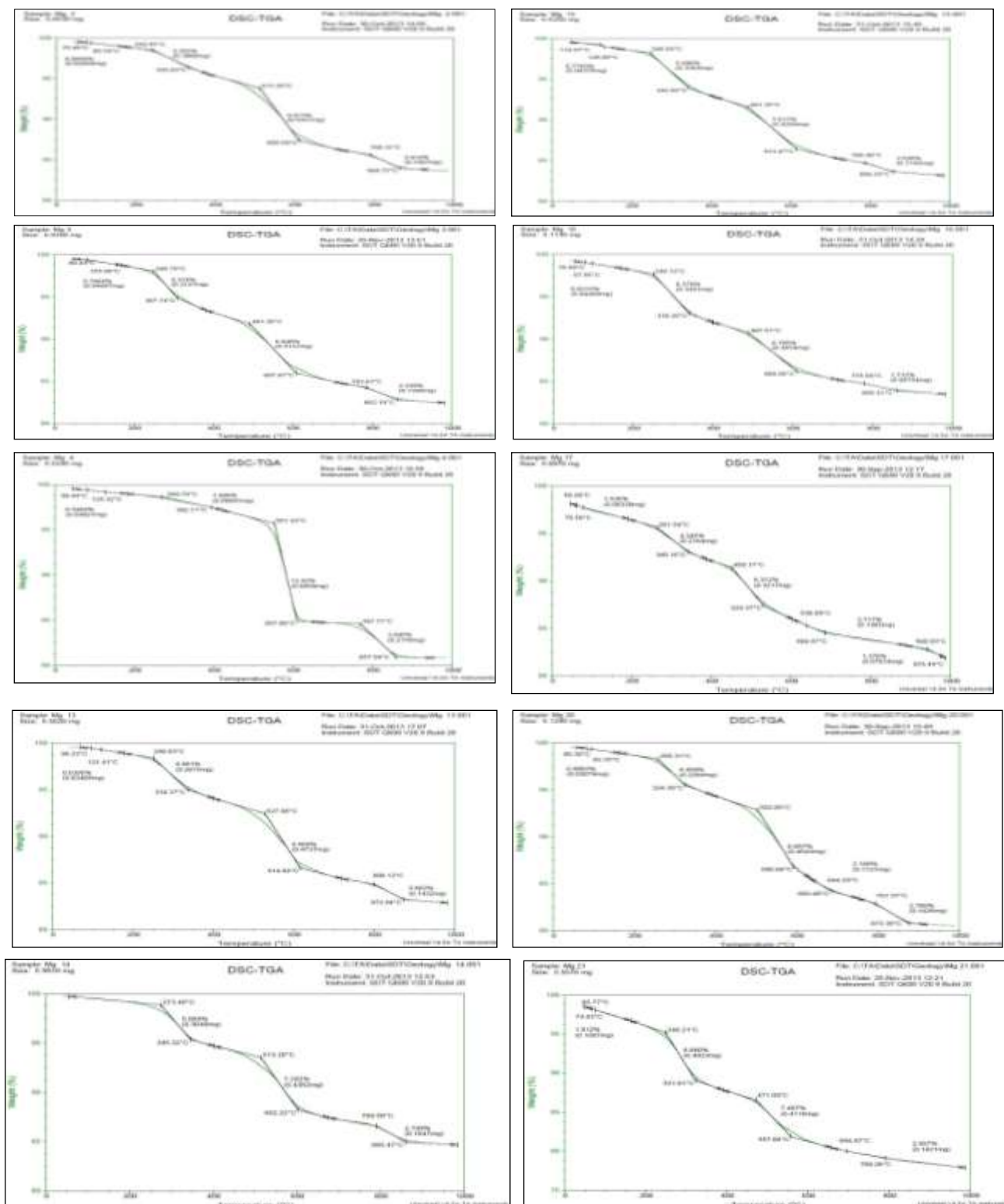


Fig. 3: TGA curves of Manganese ores of Sandur

IV. CONCLUSIONS

From the Differential thermal analysis and Thermo gravimetric analysis of Sandur Manganese ores following conclusions may be drawn: Endothermic peaks for Manganite are observed at 359°, 509° and between 580° to 590°. Endothermic peak between 590-600°c and a exothermic peak between 380-391°c shows the presence of Pyrolusite. Endothermic peaks at 856.41 and 891.05°c shows the presence of Cryptomelane. Ramsdellite shows exothermic peak at 485.57°c. The temperature range 575-600°c corresponds to the change

conversion of Manganite to pyrolusite. Exothermic peak at 415.68°C corresponds to the conversion of Ramsdellite to Pyrolusite. The TGA studies shows presence of cryptomelane, psilomelane and pyrolusite. The presence of Cryptomelane is observed by the weight loss of 8.646% in 49.35-607.37°C range. The loss of weight of 2.556% between 790-852°C marks the presence of psilomelane. Pyrolusite can be identified with the loss of weight 7.282% between 513.20-602.22°C. The curves obtained in the study match with those given in the literature for Manganese minerals. There is a minor shift in the values in some samples, which can be attributed to the accessory and gangue minerals present in the samples.

ACKNOWLEDGMENT

I would like to thank Mr. Ganesh Kundargi, USIC Karnatak University Dharwad for his efforts to analyze the Manganese ore samples for DTA and TGA studies. I also express my deep sense of gratitude towards Dr. H. M. Jayasheela for his help and support for the present studies.

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