DTA STUDIES ON PREPARATION OF $MnSO_4$ BY REACTING PYRITE AND PYROLUSITE AT HIGH TEMPERATURES

P. Narayanchar, P. Basaveswara Rao and *M. Aneesuddin*

REGIONAL RESEARCH LABORATORY, HYDERABAD– 500 007, INDIA

The preparation of $MnSO_4$ by reacting pyrolusite at high temperatures with SO_2 generated from pyrite was followed by DTA, and the process conditions were optimized to fix the minimum time and temperature of reaction required to obtain the maximum yield of pure $MnSO_4$ from stoichiometric amounts of reactants in a natural draught of air. The presence of MnO and Fe_3O_4 in the reaction products, detected by DTA, indicates that the SO_2 is initially oxidized to SO_3 by reducing MnO_2, Mn_2O_3 and Fe_2O_3 to MnO and Fe_3O_4. SO_3 finally attacks MnO to form $MnSO_4$. When an intimate stoichiometric blend of pyrite and pyrolusite is heated at temperatures ranging from 873 K to 973 K for 3 hrs, about 93% of the Mn is converted to iron-free $MnSO_4$.

When intimate mixtures of pyrite (FeS_2) and pyrolusite (MnO_2) are reacted at high temperatures, about 80% of the Mn is converted to $MnSO_4$ in a period of 7 hrs [1]. A higher yield (92%) is obtained when MnO_2 is directly reacted with SO_2, but the amount of SO_2 used is high [2]. In view of this, the DTA technique was used to study the changes that take place in pyrite and pyrolusite during their reaction at high temperatures, and optimization studies were undertaken to fix the minimum time and temperature of reaction at which the maximum yield of pure $MnSO_4$ could be obtained.

Experimental

Materials

Pyrite containing 72% FeS_2 (– 300 mesh BSS) and pyrolusite containing 76% MnO_2 (– 300 mesh BSS) were used.

DTA: A Leeds & Northrup DTA unit provided with Pt–Pt 10% Rh thermocouples and a Robert–Grimshaw ceramic sample holder was used in a static atmosphere with calcined alumina as the reference material. The rate of heating was

maintained at 3 deg·min^{-1} for the reactants (wt. 50 mg) to simulate the conditions of roasting, and at 12.5 deg·min^{-1} for the products (wt. 300 mg).

Reaction set-up

To estimate the amount of $MnSO_4$ formed at different temperatures, pyrite and pyrolusite taken in gooch crucibles (height 4.5 cm and diameter 3.5 cm) were reacted in a vertical tubular furnace (height 25 cm and diameter 5 cm), plugged at both ends with ceramic blocks, having a 3 mm hold for inlet of the thermocouple (top) and a natural draught of air.

In the first set of experiments, 1.1 g of pyrite was used to generate the stoichiometric amount of SO_2 to convert 100% of the Mn present in 1.5 g of pyrolusite to $MnSO_4$. In the second set, 4.4 g of pyrite was used to generate excess SO_2 for reaction with 1.5 g of pyrolusite. In these sets, the gooch crucible containing pyrolusite was kept over a similar gooch crucible containing pyrite and heated.

In the third set, stoichiometric amounts of pyrite (1.1 g) and pyrolusite (1.5 g) were thoroughly blended together and heated in a gooch crucible. In the fourth set, stoichiometric amounts of the reactants were heated at 873 K (a) in an ordinary crucible, (b) in a gooch crucible through which air was circulated using an air circulation pump, and (c) in a gooch crucible as in set no. 3, but with variation of the duration of the reaction.

Small ceramic beads were placed at the bottom of the gooch crucibles to prevent the material from falling down, and also distributed uniformly throughout the mass of the reactants for the easy and uniform accessibility of air and SO_2. The crucibles, kept over a ceramic tripod placed on the bottom plug of the furnace, were heated at 40 deg·min^{-1} to the desired temperature, and then maintained at this temperature for 3 hrs.

Product analysis

Products obtained at different temperatures were leached in water to recover water-soluble sulphates, and the amount of $MnSO_4$ in the washings was determined chemically. In the case of the second set, the amount of water-soluble Fe in th lower crucible was determined as $FeSO_4$. The insoluble residues from sets no. 2 a⌐ ⌐ 3 were dried at 110° and subjected to DTA to ascertain qualitatively the presence c unreacted oxides of Mn and FeS_2, respectively. SO_2/SO_3 could not be estimated i⌐ view of possible interference with the residence time of the gases in the crucibles

Results and discussion

DTA of reactants

The DTA curve of pyrolusite (Fig. 1a) indicates two endothermic peaks between 803 K and 873 K and between 1173 K and 1248 K, due to the reduction of MnO_2 to Mn_2O_3, and of Mn_2O_3 to Mn_3O_4, respectively [3].
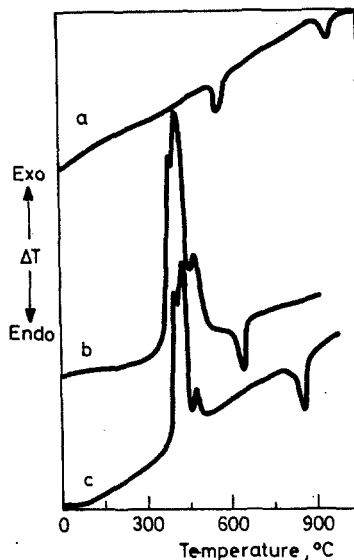

Fig. 1 DTA of reactants: a) pyrolusite, b) pyrite, c) mixture of pyrolusite and pyrite

The DTA curve of pyrite (Fig. 1b) shows an intense exothermic effect between 573 K and 793 K, corresponding to the formation of oxides and sulphates of iron. The endothermic peak between 873 K and 923 K is due to the decomposition of $FeSO_4$ via $[Fe_2(SO_4)_3]_2 \cdot Fe_2O_3$ to Fe_2O_3 and SO_3 [4].

The exothermic effect in the DTA curve of the intimate stoichiometric blend of pyrite and pyrolusite (Fig. 1c) is more or less identical to that observed for pyrite (Fig. 1b), except that the reaction is completed earlier, at the lower temperature of 768 K. Peaks for the reduction of MnO_2 to Mn_2O_3 and for the decomposition of $FeSO_4$ are absent. The endothermic peak starting at 1053 K records the decomposition of $MnSO_4$ [5].

Estimation of MnSO$_4$ and FeSO$_4$

It is evident from the DTA pattern (Fig. 1c) that FeS$_2$ and MnO$_2$ react in the presence of air to form MnSO$_4$ between 573 K and 768 K, but increase of the amount of reactants would increase the temperature at which the reaction would end. With this in view, pyrite and pyrolusite were reacted at temperatures ranging from 573 K to 1073 K at intervals of 50 deg in the reaction set-up described above, and the MnSO$_4$ formed at each temperature was determined.

In the case of stoichiometric amounts of reactants (Table, set no. 1), the amount of MnSO$_4$ formed increases with temperature up to 973 K; it is slightly less at 1023 K; and it then drops to a considerably lower value at 1073 K. Similar results were obtained when excess SO$_2$ was reacted with pyrolusite (Table, set no. 2). However, the amount of MnSO$_4$ in set no. 2 is higher at temperatures ranging from 773 K to 1073 K, which is due to more SO$_2$/SO$_3$ being available for reaction.

Table 1 Percentage conversion of Mn to MnSO$_4$ and of Fe to FeSO$_4$ at different temperatures in 3 hrs

Temperature, K	Set no. 1 MnSO$_4$, %	Set no. 2 MnSO$_4$, %	Set no. 3 MnSO$_4$, %	Set no. 2 FeSO$_4$, %
573	3.98	3.54	8.57	2.30
623	10.24	7.96	16.22	2.80
673	13.69	20.31	59.29	5.11
723	30.53	26.70	93.13	7.71
773	31.87	38.42	93.56	4.87
823	39.86	47.05	92.42	4.61
873	51.36	51.69	93.24	—
923	52.90	55.71	90.65	—
973	53.26	59.13	93.12	—
1023	52.05	61.86	73.33	—
1073	11.25	38.80	56.02	—

When stoichiometric amounts of pyrite and pyrolusite are blended together intimately and reacted, the amount of MnSO$_4$ formed increases with temperature up to 723 K, and remains more or less constant up to 973 K, but it starts to decrease from 1023 K onwards (Table, set no. 3). The amount of MnSO$_4$ in set no. 3 is more than that in sets nos 1 and 2 at all temperatures; in the latter cases, an appreciable proportion of the SO$_2$/SO$_3$ released from the pyrite escapes without coming into contact with oxides of Mn. Further, unlike in set no. 3, where the formation of FeSO$_4$ does not take place (Fig. 1c), in sets nos 1 and 2, at temperatures below 873 K part of the sulphur is locked up as FeSO$_4$ in the lower crucible containing

pyrite, due to which SO_3 is available for reaction only after the decomposition of $FeSO_4$ beyond about 873 K.

In the present study, all the factors affecting the rate of evolution of SO_2/SO_3 [6] were more or less constant in each set of experiments, yet it is seen that the amount of $MnSO_4$ formed in general increases with increase of the temperature of roasting up to 973 K/1023 K. It therefore appears that the higher the temperature of roasting up to 973 K/1023 K, the greater is the degree of thermal shock and consequent cracking of the particles of FeS_2 and oxides of Mn. With elevation of the temperature of roasting, a progressively large surface of FeS_2 exposed to atmospheric oxygen reacts with it, abruptly releasing larger amounts of SO_2/SO_3, which in turn react with progressively large amounts of oxides of Mn.

The decrease in amount of $MnSO_4$ at 1023 K and beyond, may be due to the initiation of decomposition of $MnSO_4$ at temperatures below its actual decomposition temperature of 1053 K in the presence of other ingredients.

Water-soluble Fe as $FeSO_4$ was determined in all the samples of roasted pyrite of set no. 2. The Table, column 4, shows that the amount of $FeSO_4$ formed is generally low. It increases with elevation of the temperature from 573 K to 673 K, and then drops. At 873 K, it is totally absent. 873 K is therefore the minimum temperature at which iron-free $MnSO_4$ can be prepared.

In the case of an intimate blend of stoichiometric amounts of pyrite and pyrolusite reacted at 873 K for 3 hrs in an ordinary crucible (set no. 4a), 42.91% of the Mn in pyrolusite was converted to $MnSO_4$, and when a gooch crucible was used through which air was circulated (set no. 4b), 32.53% of the Mn was converted to $MnSO_4$. Both these values are less than that indicated in set no. 3 for reaction at 873 K for 3 hrs. In set no. 4a, the amount of air appears to be insufficient, and in set no. 4b, it appears that, due to the higher air velocity, a large amount of SO_2/SO_3 escapes without coming into contact with MnO_2. The availability, velocity and residence of the required amounts of O_2 and SO_2/SO_3 in the environment therefore appear to affect the amount of $MnSO_4$ formed.

When the time of reaction was reduced, all other experimental conditions being kept the same as in set no. 3, the amount of $MnSO_4$ formed in 2 hrs was 68.21%, compared to 93.24% in 3 hrs; a further increase of the time did not make much difference, as the amount of $MnSO_4$ formed in 4 hrs was 93.53%.

DTA of washed products

Residues of leached products of pyrolusite (set no. 2) were subjected to DTA (Fig. 2a). These water-insoluble residues contain only oxides of Mn which have escaped reaction with SO_2/SO_3.

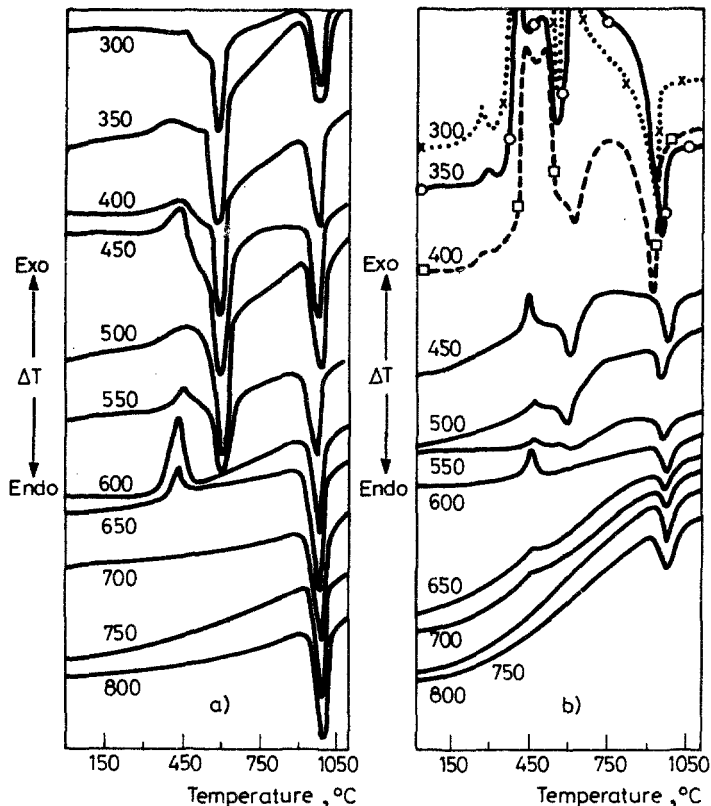The DTA patterns of samples roasted at temperatures ranging from 573 K to

Fig. 2 DTA of products after leaching-out of $MnSO_4$: a) set no. 2, b) set no. 3

823 K show an endothermic peak starting at about 813 K, due to the reduction of unreacted MnO_2. The DTA curves of all the samples exhibit an endothermic peak starting at about 1173 K, due to the reduction of Mn_2O_3 to Mn_3O_4, indicating the presence of unreacted Mn_2O_3 in samples roasted at temperatures ranging from 873 K to 1073 K.

The DTA curves of samples roasted at temperatures ranging from 573 K to 923 K show an exothermic effect between 573 K and 783 K, ascribed to the presence of MnO [7]. Its absence in samples roasted at temperatures beyond 923 K may be due to its complete oxidation by air during roasting.

The residues of leached products of blended pyrite and pyrolusite (set no. 3) were also subjected to DTA (Fig. 2b). The DTA patterns of the reaction products between 573 K and 673 K show a small exothermic peak starting at about 498 K, due to the oxidation of Fe_3O_4 to Fe_2O_3 [8], the intensity of which decreases with the elevation of temperature up to 673 K, beyond which it is absent. The second intense

exothermic peak starting at about 573 K indicates the presence of unreacted sulphides of Fe. This exothermic peak is immediately followed by an endothermic peak due to the reduction of unreacted MnO_2 to Mn_2O_3. The large endothermic peak starting at about 1053 K is due to the combined effect of the decomposition of a small amount of $MnSO_4$ formed from unreacted FeS_2 and MnO_2 during the DTA, and the reduction of unreacted Mn_2O_3 to Mn_3O_4. The DTA curves for samples roasted at 723 K and above are similar to the corresponding curves in Fig. 2a.

The amount of $MnSO_4$ in sets nos 2 and 3 shows an increase with elevation of the temperature of roasting (Table), and therefore the amount of unreacted oxides of Mn leached out is expected to decrease as the temperature of roasting is raised, but this is not reflected by the intensities of the DTA peaks (Figs 2a, b). This non-coordination may be due to non-uniform changes in the particle size and the shape of reactants during roasting, leaching and drying.

$MnSO_4$ in set no. 3 is more than that in set no. 2, due to which the amount of unreacted oxides of Mn recovered after washing will be less. Further, unreacted oxides of Mn are contaminated with products of oxidation of pyrite. This accounts for the lower intensities of all the peaks for the oxides of Mn (Fig. 2b), as compared to Fig. 2a.

Conclusion

When $FeS_2(SO_2)SO_3$ and MnO_2 react at temperatures ranging from 573 K to 1073 K in the presence of air, part of the FeS_2 remains unreacted up to 673 K, unreacted MnO_2 is present up to 823 K, Mn_2O_3 present from 873 K to 1073 K, while Fe_3O_4 can be detected in samples roasted between 573 K and 673 K, MnO between 573 K and 973 K, and Fe_2O_3 at all temperatures. SO_2 from the oxidation of FeS_2 coming into contact with MnO_2, Mn_2O_3 and Fe_2O_3 at high temperatures is oxidized to SO_3 by reducing the above oxides to MnO and Fe_3O_4. It is this SO_3 that reacts with MnO to form $MnSO_4$. The presence of MnO and Fe_3O_4, indicated in the DTA curve of the products of reaction between FeS_2 and MnO_2, lends support to this proposed mechanism.

The amount of $MnSO_4$ formed increases with (1) elevation of the temperature up to 973 K to 1023 K; (2) increase in the amount of SO_2/SO_3 available for reaction with oxides of Mn; (3) greater contact of the reactants; (4) a lower velocity of oxygen and SO_2/SO_3 in the environment of the reaction; and (5) increase in time up to 3 hrs.

The highest conversion, of about 93% of the Mn, to $MnSO_4$ free from Fe as impurity, is obtained when an intimate blend of stoichiometric amounts of pyrite

and pyrolusite is reacted at temperatures between 873 K and 973 K for 3 hrs in a gooch crucible containing ceramic beads uniformly distributed in the reactants, through which a natural draught of air is allowed to pass.

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Zusammenfassung — Mittels DTA wurde die Darstellung von $MnSO_4$ aus Pyrolusit und aus Pyrit dargestelltem SO_2 untersucht und die Verfahrensbedingungen optimiert, um eine minimale Reaktionszeit und Temperatur zum Erreichen einer maximalen Ausbeute an reinem $MnSO_4$ aus in stöchiometrischem Verhältnis vorhandenen Reaktanden im normalen Luftstrom zu bestimmen. Eine durch DTA nachgewiesene Gegenwart von MnO und Fe_3O_4 unter den Reaktionsprodukten zeigt, daß SO_2 unter Reduktion von MnO_2, Mn_2O_3 und Fe_2O_3 zu MnO und Fe_3O_4 zuerst zu SO_3 oxidiert wird. Abschließen reagiert SO_3 mit MnO zu $MnSO_4$. Mehr als 93% Mn wird zu eisenfreiem $MnSO_4$ umgesetzt, wenn man eine innige Mischung aus Pyrit und Pyrolusit 3 Stunden lang bei einer Temperatur zwischen 873 und 973 K hält.

Резюме — Методом ДТА проведено изучение условий получения сульфата марганца реакцией взаимодействия двуокиси серы, получаемой из пирита, с пиролизитом при высоких температурах. Определно минимальное время и температура реакции, необходимые для получения максимального выхода чистого сульфата марганца, исходя из стехиометрических количеств реагентов, находящихся в естественной воздушной тяге. Обнаруженное методом ДТА наличие в продуктах реакции окиси марганца и окиси трехвалентного железа показывает, что двуокись серы первоначально окисляется до трехокиси серы с восстановлением двуокиси марганца, окисей трехвалентного марганца и железа соответственно до окиси двухвалентного марганца и Fe_3O_4. Наконечной стадии реакции трехокись серы взаимодействует с окисью марганца с образованием сульфата марганца. Около 93% марганца превращается до свободного от железа сульфата марганца, когда близкие к стехиометрическому составу смеси пирита и пиролюзита нагреваются при температурах от 873 до 973 K в течении трех часов.