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EFFECT OF SILICA AND FERRIC OXIDE ON THE OXIDATION OF SYNTHETIC IRON PYRITE IN STATIC AIR

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ABSTRACT

Thermoanalytical techniques (DTA, TG), chemical and X-ray diffraction methods have been combined to study the course of oxidation of synthetic iron pyrite in presence of silica and ferric oxide in static air. The direct oxidation of pyrite to ferric oxide, interaction of pyrite with ferrous sulphate and also the decomposition of sulphates were enhanced in presence of the additives. There is no reaction between iron pyrite and the additives. The catalytic effect is also not due to moisture or phase transition in silica or ferric oxide.

INTRODUCTION

The catalytic effects of silica and ferric oxide in the oxidation of both natural and synthetic iron pyrite have been reported earlier during process development studies in fixed bed /1,2/.

The present investigation combines thermoanalytical techniques (DTA, TG), chemical and X-ray diffraction methods to follow the courses of reaction of synthetic iron pyrite in presence of the additives, silica and ferric oxide, in static air and nitrogen atmosphere.

EXPERIMENTAL PROCEDURE

Synthetic iron pyrite was prepared by passing dry hydrogen sulphide over ferric oxide at 400 °C for 2 h. Silica was prepared by heating silica gel (BDH) at 1000 °C. Ferric oxide was obtained by precipitating the hydroxide from ferric chloride solution with ammonia and heating at 450 °C for 4 h. X-ray analysis confirmed the samples as quartz and α-Fe_2O_3.X-ray diffractometer, Philips make (PW 1140) was used with iron radiation and Mn filter. DTA in static air atmosphere was carried out in a Stanton Redcroft thermal analyser (model 673-4) using platinum sample holder, and heating rate 10 °C/min. DTA and TG in nitrogen atmosphere were done in a fabricated unit using for DTA, platinum sample holder and 10 °C/min heating rate, and for TG, quartz bucket and heating rate of 5 °C/min. The courses of the reactions were also followed by arresting the thermal analysis runs near important thermal peaks and analysing the samples by X-ray diffraction and chemical methods.

RESULTS AND DISCUSSION

The DTA curves of synthetic iron pyrite alone and also admixed with silica and ferric oxide are shown in Fig. 1. The DTA curve of synthetic FeS_2 shows endothermic peaks at 73, 90, 490, 550 and 743 °C and exothermic peaks at 144, 330 and 610 °C. The direct oxidation of pyrite to both ferrous sulphate and ferric

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oxide is predominant up to 330 °C. The formation of more amount of ferric oxide at 360 – 450 °C is due to the reaction of pyrite with ferrous sulphate /4/. The subsequent endothermic peaks are due to decomposition of ferrous (490, 550 °C) and ferric sulphates (743 °C). The probable reactions are:

$$FeS_2 + 3O_2 = FeSO_4 + SO_2 \quad (1)$$

$$2FeS_2 + 11/2\, O_2 = \alpha\text{-}Fe_2O_3 + 4\, SO_2 \quad (2)$$

$$FeS_2 + 5\, FeSO_4 + 3/2\, O_2 = 3\gamma\text{-}Fe_2O_3 + 7\, SO_2 \quad (3)$$

$$6\, FeSO_4 = Fe_2SO_4)_3 + 2\, \alpha\text{-}Fe_2O_3 + 3\, SO_2 \quad (4)$$

$$Fe_2(SO_4)_3 = \alpha\text{-}Fe_2O_3 + 3\, SO_3 \quad (5)$$

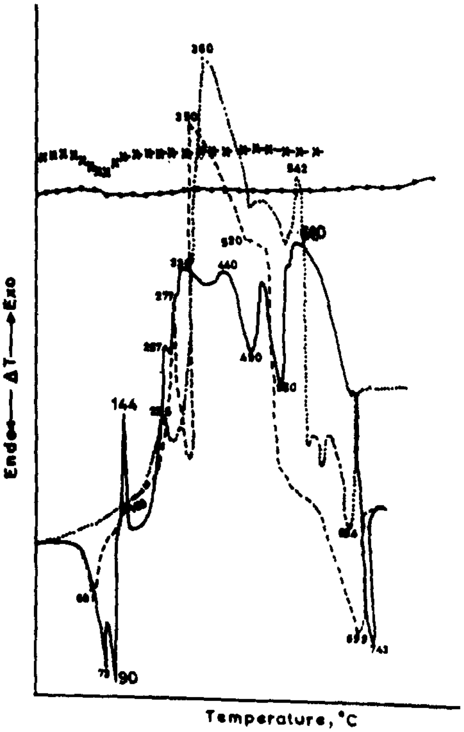

Fig. 1: DTA of synthetic iron pyrite mixed into additives in static air

———— FeS_2

- - - - - $FeS_2 + Fe_2O_3$ (20 %)

. . . . . $FeS_2 + SiO_2$ (30 %)

–·–·–·– Fe_2O_3

xxxxx SiO_2

Reactions (1), (2) are exothermic and reactions (3), (4), (5) are endothermic. The intensity of the exothermic peak at 350 – 360 °C is much enhanced in presence of both silica and ferric oxide (Fig. 1). In presence of the additives the amount of ferric oxide increased while that of ferrous sulphate got decreased (Table 2). This indicates that important observation was the formation of more ferric sulphate in presence of the additives (reaction (4)). The decomposition of sulphates (reactions (4), (5)) were also enhanced by the additives, as evident from the nature of the DTA peaks beyond 450 °C and also from product distribution. The decomposition peak due to reaction (5) was at 743 °C in case of the FeS_2 sample, whereas the same peak came at 634 °C and 699 °C in presence of silica and ferric oxide, respectively. The nature of thermal curves and production distribution were to some extent different in dynamic air /5/. Basic ferric sulphate in small amount was detected during oxidation of FeS_2 in static air and also in presence of Fe_2O_3.

Table 1. Solid phases identified at 360 °C

Sample	Phases identified
1	FeS_2, $FeSO_4$, α-Fe_2O_3, basic ferric sulphate
2	FeS_2, α-Fe_2O_3, $FeSO_4$, SiO_2
3	FeS_2, α-Fe_2O_3, $FeSO_4$, basic ferric sulphate

Table 2. Product distribution of iron compounds in the oxidation

Sample	Temp. /°C/	$FeSO_4$ /%/	$Fe_2(SO_4)_3$ /%/	Fe_2O_3 /%/	FeS_2 /%/
1	360	24.00	-	21.98	54.00
	450	22.70	3.20	56.50	17.50
2	360	16.75	-	27.74	55.50
	450	30.40	10.60	48.00	9.80
3	360	22.38	-	45.12	32.49
	450	13.69	21.62	57.48	7.20

Sample 1 FeS_2; Sample 2, FeS_2+SiO_2/30%/; Sample 3, FeS_2+Fe_2O_3/20%/

The thermal analysis of synthetic iron pyrite in presence of the additives in nitrogen atmosphere are given in Figs 2 and 3. The endothermic peaks in the DTA and corresponding weight loss peaks in TG were due to decomposition of iron pyrite to pyrrhotite. The X-ray analysis of the samples at 580 and 680 °C showed the presence of FeS and FeS_2 only. The decomposition of iron pyrite to pyrrhotite was enhanced in presence of the additives (Figs 2 and 3). The mixtures of FeS_2 and Fe_2O_3 (20 %) and FeS_2 and silica (30 %) were heated separately in a porcelain boat at 600 °C in nitrogen for 1 hour. The product contained only ferrous sulphide and iron pyrite as confirmed by X-ray and chemical analysis. There was no formation of ferroso ferric oxide contrary to previous report /3/. Hence, the effect of the additives was not due to any solid-solid chemical reaction. DTA of the additives alone (Fig. 1) were also carried out. α-ferric oxide did not show any thermal change and silica showed a small weight loss endothermic peaks at 100 °C due to loss of adsorbed moisture. Hence, the catalytic effect of the additives was not due to phase transition. The results indicate that iron pyrite is auto-catalysed by ferric oxide /2/ and the catalytic effect of silica and ferric oxide may be by increased adsorption of oxygen /2,5/.

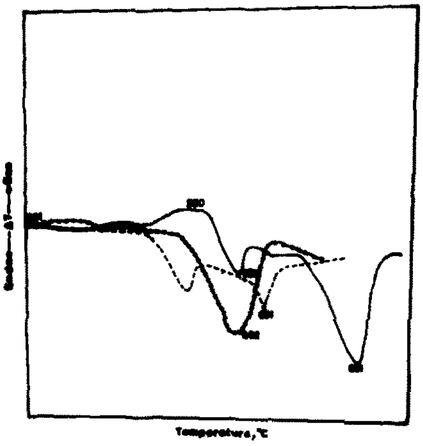

Fig. 2: DTA of synthetic iron pyrite mixed into additives in nitrogen atmosphere

———— FeS_2

------ $FeS_2 + SiO_2$ (30 %)

—·—·— $FeS_2 + Fe_2O_3$ (20 %)

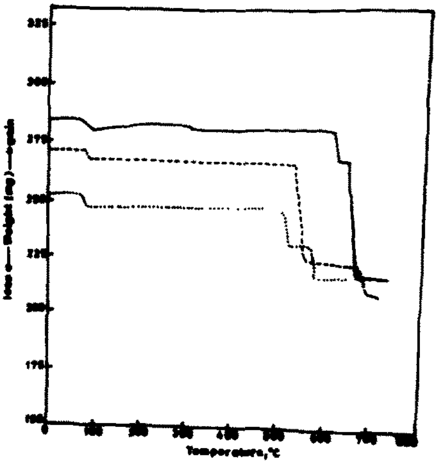

Fig. 3: TG of synthetic iron pyrite mixed into additions in nitrogen atmosphere

———— FeS_3

------ $FeS_2 + SiO_2$ (30 %)

•••••••••• $FeS_2 + Fe_2O_3$ (20 %

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