Mechanism of Oxidation of Iron Pyrites

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Summary Thermoanalytical techniques (DTA and DTG), chemical, and *X*-ray diffraction methods have been combined to study the course of oxidation of synthetic iron pyrites; pyrites is oxidised directly to ferrous sulphate, and no intermediate pyrrhotite is formed.

CONTRADICTORY views[1-4] regarding the mechanism of oxidation of iron pyrites (FeS_2) are expressed in the literature. Some workers[1,2] suggest that the oxidation of pyrites proceeds primarily through the formation of sulphates [$FeSO_4$, $Fe_2(SO_4)_3$] which later decompose to ferric oxide (Fe_2O_3) and sulphur dioxide (SO_2). Others[1,3,4] hold that the primary products of oxidation are the oxides (FeO, Fe_2O_3) which subsequently react with sulphur dioxide to produce sulphates. It is also believed that oxidation of pyrites is accompanied by thermal decomposition to pyrrhotite (Fe_nS_{n+1}, $n \geqslant 5$).

The present investigation combines thermoanalytical techniques (DTA and DTG), chemical, and *X*-ray diffraction methods to follow the course of oxidation of both synthetic and natural iron pyrites. Previous workers studied the oxidation and thermal characteristics only of natural samples of pyrites of various origins and hence containing different types of impurities. The present study is mainly confined to the synthetic sample to derive a generalised mechanism of oxidation which might also be applicable to natural samples of pyrites.

Synthetic pyrites was prepared[5] by heating an intimate mixture of ferric oxide, sulphur, and ammonium chloride at 340° for 2 h. The purified and dried sample contained 99·32% FeS_2.

The thermal analyses were carried out in a static atmosphere (air) at atmospheric pressure. [Preliminary studies showed that using a flow of air (20 litre/hr), either dried or un-dried, did not affect the oxidation of pyrites]. The heating rate in the thermal analyses was maintained at 10°/min. The DTA curves of pure synthetic pyrites showed exothermic peaks at 100 (50—120), 520 (400—540), and 650° (570—670) and endothermic peaks at 140 (120—220), 320 (220—400), 560 (540—570), and 750° (670—850). TG showed weight loss up to 320°, followed by weight gain up to 640° and then continuous weight loss up to 850°. DTG curves showed weight loss peaks at 225 (50—320) and 800° (640—850) and weight gain peaks at 480 (320—540) and 580° (540—640).

Synthetic pyrites was heated in a porcelain boat in a tubular furnace up to various temperatures in the range associated with important thermal changes. The samples were then cooled in a dry nitrogen atmosphere, and analysed by X-ray diffraction and chemical methods. The solid phases at different temperatures identified by X-ray diffraction are recorded in the Table.

TABLE

Temp.	Phases identified
130, 170, 260°	$FeSO_4$, FeS_2
390°	$FeSO_4$, γ-Fe_2O_3, FeS_2
450°	$FeSO_4$, γ-Fe_2O_3, α-Fe_2O_3
520°	$FeSO_4$, $Fe_2(SO_4)_3$, α-Fe_2O_3
590, 650°	$Fe_2(SO_4)_3$, α-Fe_2O_3

An appreciable amount of ferrous sulphate ($FeSO_4$) was formed even at 100°; the products up to 230° contained mainly ferrous sulphate and, up to 450°, this continued to be the major oxidation product. The composition of the oxidised sample at 450° was: 68·36% $FeSO_4$, 4·35% $Fe_2(SO_4)_3$, 5·22% FeO, 20·71% Fe_2O_3, and 1·50% unreacted FeS_2. The small weight loss at the initial stage in the TG was due to loss of moisture, loss of water from hydrated ferrous sulphate (formed by aerial oxidation of pyrites during sample preparation), and oxidation of pyrites to ferrous oxide. These processes predominated over direct oxidation of pyrites to ferrous sulphate (which is a weight gain reaction) at the initial stage of oxidation, which is perhaps the reason for a resultant decrease in weight. The exact reason for the observed weight loss at the initial stage of oxidation is being investigated. Ferrous sulphide (FeS) or pyrrhotite could not be detected, even in traces, during the oxidation of either natural or synthetic pyrites, contrary to previous reports.[1,2] It appears that the oxidation does not proceed through the simultaneous formation of ferrous oxide and its conversion into ferrous sulphate, since by this mechanism a large gain in weight should have been obtained up to 320° instead of the observed weight loss. Another important observation in support of the direct sulphation mechanism was that both synthetic and natural pyrites were oxidised to an efflorescence of hydrated ferrous sulphate even at room temperature when kept open to the atmosphere for a few hours. This is contrary to the general belief that pyrites is stable in air.[5] The maximum conversion of pyrites into ferrous sulphate was at 320—450°; this was supported by the strong exothermic trend and weight gain in the DTA and DTG curves, respectively. The formation of γ-Fe_2O_3 in the range 260—450° was perhaps due to the interaction of pyrites and ferrous sulphate;[2] this is an endothermic reaction accompanied by weight loss which might run parallel to direct sulphation of pyrites. γ-Fe_2O_3 was converted into α-Fe_2O_3.[5]

The mechanism which explains the product distribution quite satisfactorily up to 450° may be expressed in terms of the following principal reactions:

$$FeS_2 + 3\,O_2 = FeSO_4 + SO_2$$

$$FeS_2 + 5/2\,O_2 = FeO + 2SO_2$$

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

$$\gamma\text{-}Fe_2O_3 \longrightarrow \alpha\text{-}Fe_2O_3$$

Further, the decomposition of ferrous sulphate which started at 450° was complete at 560°; ferric sulphate [$Fe_2(SO_4)_3$], basic ferric sulphate [$Fe_2O_3{\cdot}2SO_3$],[1,6] and ferric oxide were identified as the products of decomposition. The exothermic peak at 650° and increase in weight up to 640° could be due to the reaction of ferric oxide, sulphur dioxide, and oxygen to form ferric sulphate.[3] The subsequent weight loss and endothermic peak were due to the decomposition of both normal and basic ferric sulphates. Basic ferric sulphate was found in the temperature range 500—700°. The thermal effects and nature of oxidation products of natural Amjore pyrites were similar to those of the synthetic sample.

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