THE MAGNETOKINETICS OF OXIDATION OF PYRITE (FeS$_2$)

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ABSTRACT

The oxidation of pyrite has been so far studied by standard methods such as TGA and DTA, whereas we have used a new magnetokinetic approach for studying such oxidation processes. The kinetics are followed using a vibrating sample magnetometer as a probe to quantify the magnetic parameters of the intermediate and final reaction products, as a continuous function of time at specific temperatures, and as a function of their particle size and superparamagnetic properties. The technological relevance of our work stems partly from the possible magnetic separation of pyrite from coal after its oxidation (or reduction) to ferri- and antiferromagnetic compounds. The results of such magnetokinetic studies are presented and capabilities of the magnetokinetic technique are exemplified in terms of unique results, which elude standard TGA and DTA techniques.

INTRODUCTION

Iron sulfide (pyrite), FeS$_2$, grows in large cubic crystals[1] with space group symmetry Th^6 - Pa^3 with four formula units per unit cell. The metal ions are coordinated to six sulfur ions which are located at the corners of a distorted octahedron. The S ions are tetrahedrally coordinated to three Fe and another S ion. The cell constants are a = 5.4189Å, S-S = 2.14Å Fe-S = 2.26Å.

FeS$_2$ is a semiconductor being p or n type depending on its stoichiometry which has been found to range from 1.960 to 2.003 (S/Fe) ratio[2]. It has been concluded from band structure calculations correlated with optical data that FeS$_2$ is an ionic indirect gap semiconductor[3] with a band gap[4] of 0.9 ev. There is a minimum in the conduction band density of states which is associated with its yellow color. The magnetic susceptibility of FeS$_2$ has been studied[5] and shown to be almost temperature-independent down to 4.2°K. Its measured susceptibility of 10.1 x 10^{-6} emu/g at 295°K has been explained by the Van Vleck paramagnetic term and the diamagnetism of the core. Hulliger et al[6] explained the absence of magnetic moment of Fe on the basis of a low spin state 3d ^{6}. Mossbauer studies have been reported by many workers[7-12]. Herler and co-workers[7-8] reported that the isomer shift is characteristic of the covalency bond of FeII compounds. The quadrupole splitting of 0.62 mm/sec[12] has been explained in terms of the near 8° distortion in Fe-S octahedron. The magnetic properties and Mossbauer spectra are now being reexamined in our laboratory.

There have been many studies[13-18] of the oxidation and reduction kinetics of pyrite. These studies have involved the use of standard TGA and DTA instrumentation to follow the reactions. There has been considerable speculation as to whether or not oxidation of pyrite occurs in a one or two step process. Spektor et al[22] have reported that pyrite oxidation in air starts at 285°C and that in the initial stage of slow heating in air, Fe$_2$SO$_4$ is formed. Other workers have shown that pyrite oxidizes in a single step to αFe$_2$O$_3$ starting at about 425°C. Confusion as to the exact process of the oxidation is not surprising since the history of the mineral and heating rate could have a large effect. Physical properties such as thermal expansion, electrical conductivity[23] and external striations[24] which have been classified as positive or negative depending on whether the striations are parallel to the [001] on the (100) and (210) faces or perpendicular to the [001] have been shown to vary depending on the history of the mineral.

In this paper we discuss the kinetics of oxidation of pyrite using a novel magnetokinetic technique in contrast to the conventional techniques of DTA and TGA discussed before. The magnetokinetic approach was developed particularly because the reaction products exhibit a fascinating array of magnetic properties. It has been found that the oxidation is limited to the formation of αFe$_2$O$_3$ and γFe$_2$O$_3$. αFe$_2$O$_3$ is a pyro-antiferromagnetic material having a Morin temperature[19] of 250°K with a net spontaneous magnetization at room temperature of about 0.4 emu/g. It has also been shown that this spontaneous magnetization may be changed depending on the thermal history and degree of crystallinity of this compound. γFe$_2$O$_3$, a ferrimagnetic defect spinel has a magnetization[21] of 73.5 emu/g.

EXPERIMENTAL

A vibrating sample magnetometer (made by the Princeton Applied Research Laboratory) has been modified[25] to carry out in-situ reactions isothermally up to 600°C. Pyrite from Rico, Colorado was crushed and sieved to give particles in the range 250 - 90 µm. A sample of crushed pyrite (0.100 ± 0.001) was placed in a gold sample tube in which a glass wool bed was inserted. Dry nitrogen was passed at a flow rate of 150 ml/min directly through the sample holder in the furnace until the desired reaction temperature was attained. Nitrogen gas was allowed to flow for an additional 15 min before passing dry air at the same flow rate. Magnetization was measured as a continuous function of time at a constant magnetic field of ~4000 Oe. The parameters varied were the particle size of pyrite and reaction temperature. Exploratory results obtained for temperature, between 400 - 500°C are discussed in the next section.

RESULTS AND DISCUSSION

In Figure 1 typical results on the magnetization per gram of the sample is plotted as a function of time during the oxidation of pyrite with three particle size distributions (250 - 180; 180 - 125 and 125 - 90 µm) at a constant reaction temperature of 450°C. It is interesting to note that in each case, the magnetokinetic curve shows a peak in magnetization, which occurs during the initial stages of the oxidation of pyrite. These peaks represent a smaller percentage of the total net magnetization as particle size is decreased. These peaks have been attributed to the formation of γFe$_2$O$_3$ on the surfaces of pyrite particles. This is reasonable since a relatively small amount of pyrite is expected to have reacted at this point and the fact that the calculated magnetization based on initial weights taken are much too large to be accounted for in terms of the formation of αFe$_2$O$_3$, which is antiferromagnetic. The decrease in this initial peak is due to the change of γFe$_2$O$_3$ → αFe$_2$O$_3$ which starts at about 427°C[21] with complete conversion at 510°C.
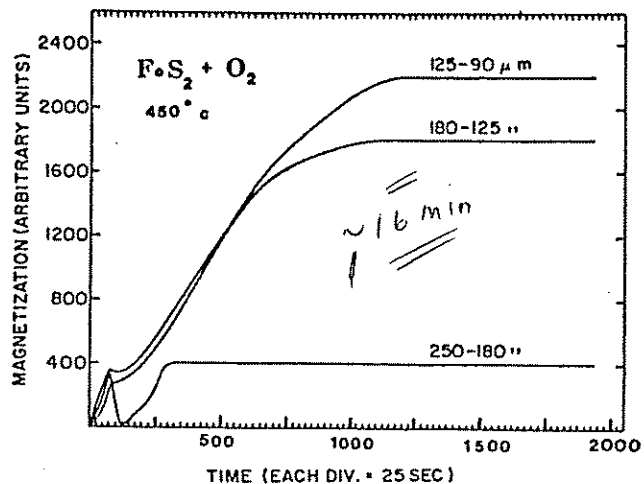
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Figure 1. Magnetization per gram of pyrite during oxidation at 450°C as a function of time for three particle size distributions.

Figure 2. Magnetization of the pyrite sample cooled to ∿25°C after reaction as a function of reaction temperature and particle size.

Another interesting feature of the magnetokinetics curves is that the slopes of the curves after reaching the peaking effect (that is, above 100 secs and up to the point of approaching constant magnetization) increases with decreasing particle size. Results of all exploratory runs between 400 – 500°C are summarized in Figure 2. Here the magnetization (emu/g) of the sample, cooled to room temperature after the completion of the reaction is plotted as a function of reaction temperature for various particle sizes. The general trend indicates that the oxidation of smaller particles yields larger net magnetization for the reaction product at room temperature. Kopp and Kerr[14] in their study of the DTA of pyrite noticed that the exothermic peaks in their analysis were shifted towards lower temperatures with decreasing particle size. These authors[14] explained this in terms of the increased surface area available for oxidation with decreasing particle size. Other workers[26,27] have attributed this type of behavior to a decrease in crystallinity with smaller particle sizes. The most striking feature of Fig. 2 is the peaking up of net magnetization (measured at room temperature) for reactions carried out at 450°C, the net magnetization increasing for smaller particles. Schoenlaub[17] noted in his TGA studies on the oxidation of pyrite that there was an unusually sharp break in the curves at 445°C. He suggested that the boiling of sulfur at this temperature may have some significance. We believe that the composition and magnetic properties of the product(s) at this temperature are also significant. Samples reacted at 450°C which gave the largest net magnetizations have been separated magnetically into two fractions. X-ray powder patterns have identified these as αFe_2O_3 and γFe_2O_3 which supports the magnetokinetics data. Chemical mechanisms responsible for this peaking effect in reaction temperature are still under investigation.

Calculations based on Wiedemann's Law[28] for the reaction products yielding the highest net magnetization (450°C, 120 – 90 μm) yields a conversion of 8.75% of oxidized pyrite to γFe_2O_3. Hence, it seems reasonable to propose the following reactions of the oxidation of pyrite:

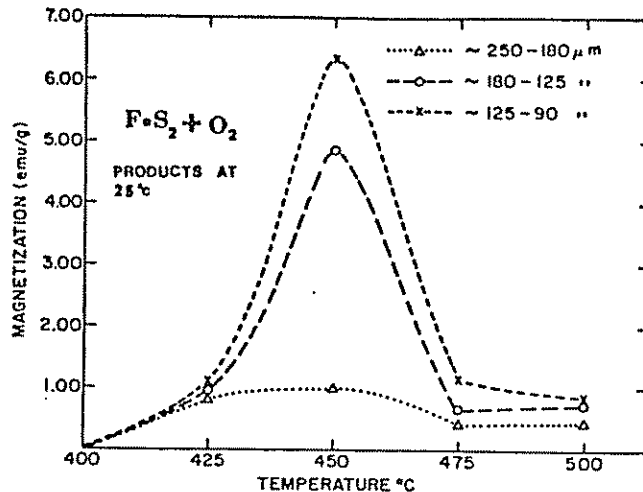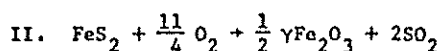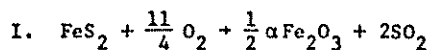$$\text{I. } FeS_2 + \frac{11}{4} O_2 \rightarrow \frac{1}{2} \alpha Fe_2O_3 + 2SO_2$$

$$\text{II. } FeS_2 + \frac{11}{4} O_2 \rightarrow \frac{1}{2} \gamma Fe_2O_3 + 2SO_2$$

As shown in Figure 2 the extent to which equation II enters the reaction kinetics is a function of particle size and reaction temperature. Figure 3 is a plot of maximum magnetization of the initial oxidation peaks vs. reaction temperature. These calculations are based on the initial weights taken. These curves again indicate that the temperature of 450°C is most favorable for the reaction to take place according to equation 2. Experiments to ascertain the possible effects of topotaxy and various partial pressures of O_2 are being conducted to determine their effects on the magnetokinetics of oxidation of pyrite.

We further plan to take into consideration the possible formation of Fe_3O_4 and FeS during the oxidation of pyrite.
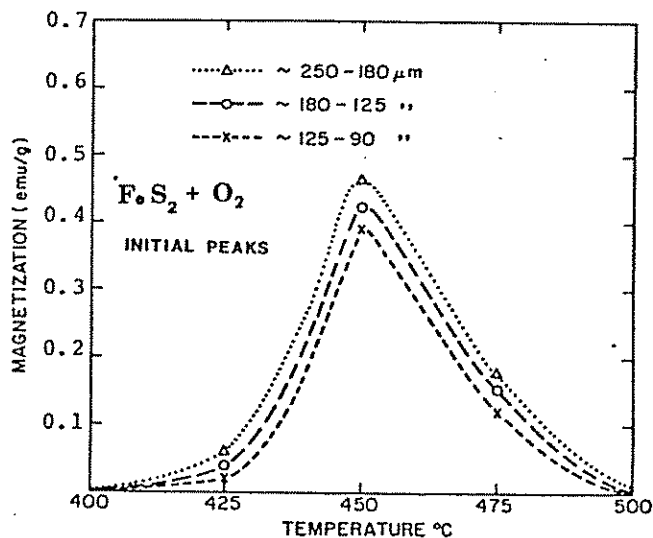

Figure 3. Maximum magnetization at the initial oxidation peaks for the pyrite sample (Figure 1) as a function of reaction temperature and particle size.

Further details of magnetokinetic studies on the oxidation and reduction of pyrite, now in progress, will be published separately.

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