# Hydrothermal Production of Highly Pure Nano Pyrite in a Stirred Reactor

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**ABSTRACT:** *In this study, pyrite was produced by hydrothermal precipitation from the reaction between $FeSO_4$ and $Na_2S_2O_3$ at high pressure and high temperature in a stirred reactor. The solid product was purified by means of solvent extraction to remove sulfur. Powder was characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and thermal analyses. Results indicated that pyrite was produced as nanostructure with high purity.*

**KEY WORDS:** *Hydrothermal, Pyrite, Sulfur, Nanostructure, Stirred reactor.*

## INTRODUCTION

In recent years, nanostructure materials have been attracting considerable attentions because of their unique physical properties [1]. Pyrite (FeS2) is a good candidate as alternative absorber material for solar cells due to its very high optical absorption coefficient and its suitable band gap (Eg= 0.95 eV) for solar spectrum ($\alpha = 5\times105$ $cm^{-1}$ for $\lambda \leq 700$ nm) [2-4].

Another application of pyrite is in lithium batteries as a cathodic active material [5-8]. Recent development of lithium batteries have made them an important type of power sources for electric vehicles [9-10].

Traditionally, pyrite was produced by thermal sulfuration of iron and in aqueous solutions at different temperature and pressure by a number of investigators [11-16]. Pyrite is produced in aqueous solution according to following two pathways: (a) solvothermal and (b) hydrothermal synthesis [15-16].

In this study, formation of nano pyrite via hydrothermal process in a new way was investigated using FeSO4 and Na2S2O3 without adding sulfur in a stirred reactor, while in previous work sulfur was used as raw material in an autoclave [11]. Also effect of NaHCO3 was studied as an amphoter to prevent marcasite production. In addition, properties of product such as purity and structure were investigated.

## EXPERIMENTAL SECTION

### *Materials*

Iron sulfate ($FeSO_4$, E-Merck) and sodium thiosulfate ($Na_2S_2O_3$, E-Merck) were used as iron and sulfur sources without further purification. Sodium bicarbonate ($NaHCO_3$, E-Merck) as an amphoter and carbon disulfide ($CS_2$, E-Merck) as sulfur-extracting solvent were used. The distilled water was prepared in double water distiller.

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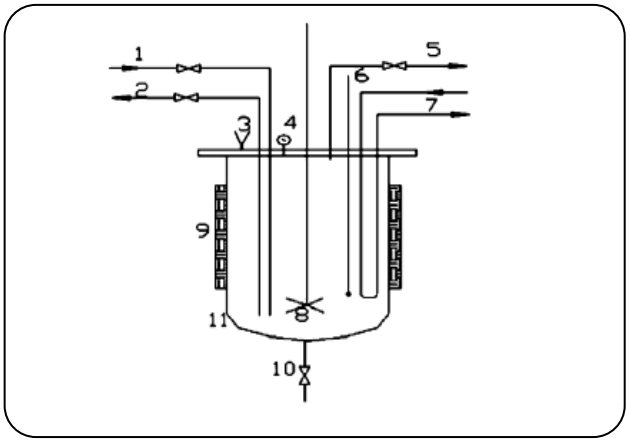


***Fig. 1: A schematic of the batch reactor set-up constructed and utilized in this research; 1: gas inlet, 2: sampling valve, 3: feed inlet, 4: pressure indicator, 5: gas vent, 6: thermocouple, 7: cooling coil, 8: stirrer, 9: reactor heating, 10: discharge valve and 11: reactor body.***

### *Pyrite production*

Experiments were carried out in 2000 mL stainless steel stirred reactor equipped with a temperature controller and a barometer (Fig. 1). Iron and sulfur solutions were prepared separately in 500mL distilled water, and were mixed in the reactor. The solution volume in reactor was kept constant at 1.00 ± 0.02 L. The Teflon-lined reactor was sealed and maintained at 180±1ºC. All reactions were carried out in 4 hours. Products were filtered, washed two times with boiling distilled water, and then dried in oven for 4 h at 60 ºC. The pH of the reaction solution was measured several times during experiment at room temperature.

To increase the pH of reaction solution, sodium bicarbonate was added to the reactor in another experiment with similar conditions.

### *Pyrite purification*

The produced pyrite contained elemental sulfur. A solvent extraction technique was used to remove the elemental sulfur. The extraction was conducted at room temperature with 100 mL $CS_2$ for several times. The suspension was agitated with a magnetic stirrer for 15 minutes. After that, product was filtered and then washed with boiling distilled water. Ultimately, the product was dried in oven for 4 hours at 60ºC. Following solid/liquid separation, the solvent was evaporated to leave sulfur residue and the amount of produced sulfur in these experiments was measured.

### *Characterization*

Product was analyzed by XRD, SEM, DTA and TGA analyses. SEM image of pyrite blocks were collected on a Leica/Cambridge Instruments S360 SEM. XRD was carried out using a Philips PW170 based diffractometer (Cu $K_\alpha$ radiation, 35 kV, 40 mA). XRD patterns, in the range of 3–90° 2θ, were collected under air using the following settings: 0.1 mm receiving slit, 0.4 s/0.02° 2θ counting time. The TGA test was carried out with a TA Instruments module SDT 2960. TGA–DTA runs were recorded at a scan rate of 20º/ min up to 800ºC.

## RESULTS AND DISCUSSION

Some experiments were carried out in various ratios of sodium thiosulfate to iron sulfate. Results of experiments are summarized in Table 1. The amount of produced sulfur was increased by rising concentration of sodium thiosulfate. Results showed that the main undesirable product of this process (pyrite production via reaction between iron sulfate and sodium thiosulfate) is elemental sulfur.

Fig. 2 shows XRD patterns of the extracted product for various molar ratios of raw materials. As can be seen in this Figure, only product is iron disulfide, and sulfur has removed from product completely by solvent extraction. Also, this Figure indicates qualitatively that marcasite is present in the products obtained in experiments 1&2, even though their intensities are different. However, marcasite is vanished in high ratio of $Na_2S_2O_3$/ $FeSO_4$. Increasing concentration of $Na_2S_2O_3$ causes increase of pH value of reaction solution (Table 2). It is concluded that marcasite is formed in strong acidic media. Therefore, production of marcasite is decreased in high concentration of $Na_2S_2O_3$. Thus, it is concluded that molar ratios of raw material greater than 4, is sufficient to produce pyrite without any marcasite but it causes to produce high amount of sulfur.

It was assumed that adjusting pH of reaction solution (by adding an amphoter to solution) could cause lower amount of marcasite. For this reason, experiment No. 1 was repeated with adding $NaHCO_3$ as an amphoter. In detail, 0.2 gr $NaHCO_3$ was added to the reactor and pH was measured. It was found that pH of solution increased from 4.9 to 5.6. In this experiment pyrite was produced without marcasite (Fig. 3) and the amount of products (pyrite and sulfur) were approximately constant in comparison with experiment No. 1 (13.5 gr pyrite and 0.04 gr sulfur).

***Table 1: Summary of the experimental results for pyrite production at 180ºC.***

| EXP. No. | Amount of $FeSO_4$ (g) | Amount of $Na_2S_2O_3$ (g) | $Na_2S_2O_3$/ $FeSO_4$ (molar ratio) | Quantity of $FeS_2$ (g) | Quantity of sulfur (g) |
|---|---|---|---|---|---|
| 1 | 50 | 33.3 | 0.625 | 15 | 0.05 |
| 2 | 50 | 112 | 2.187 | 24 | 10 |
| 3 | 50 | 203.5 | 3.97 | 33 | 26 |

***Table 2: Changes of pH during reaction for different ratios of reactants.***

| $Na_2S_2O_3$/ $FeSO_4$ | pH at first hour | pH at second hour | pH at third hour |
|---|---|---|---|
| 0.625 | 2.8 | 1.9 | 1.7 |
| 2.187 | 3.7 | 2.4 | 2.1 |
| 3.97 | 5.5 | 3.9 | 3.5 |

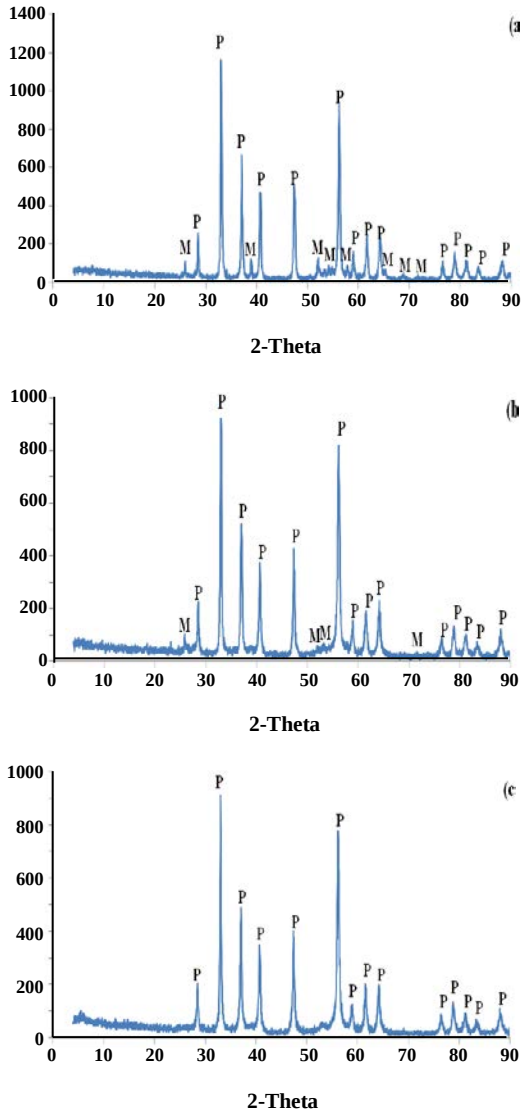


***Fig. 2: X-ray diffraction patterns of $FeS_2$ powder produced in various ratios of $Na_2S_2O_3$/$FeSO_4$ a) 0.625 b) 2.187 and c) 3.97 (P: pyrite, M: marcasite).***

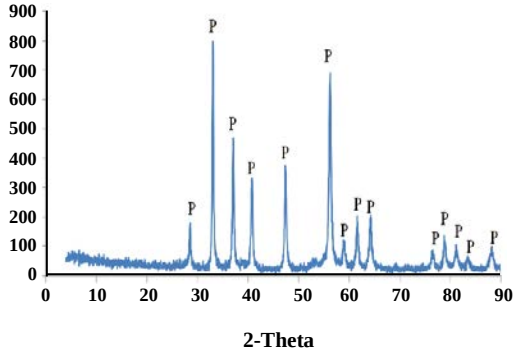


***Fig. 3: X-ray diffraction pattern of $FeS_2$ powder produced with adding $NaHCO_3$ in 0.625 molar ratio of $Na_2S_2O_3$ /$FeSO_4$ (P: pyrite).***

As demonstrated by the SEM image presented in Fig. 4, the pyrite particles were formed as nanostructures. Scanning Electron Microscopy (SEM) micrograph of obtained pyrite showed fine and clearly particles in spherical shape.

The produced sample of pyrite was investigated using ThermoGravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). Results were presented in Figures 5 and 6. The main aim of drawing TGA & DTA figures is to characterize synthesized pyrite and compare with commercial sources. For this purpose, fabric sample was chosen arbitrary and pretreated according to solvent extraction procedure. Figure 5 shows that the synthesized sample is decomposed at 675°C while natural sample is decomposed at 631°C. In addition, Fig. 6 shows produced sample has lower weight loss than fabric sample during TGA analysis. This fact indicates improvement of thermal properties in the synthesized pyrite. This is an advantage to utilize in thermal batteries.

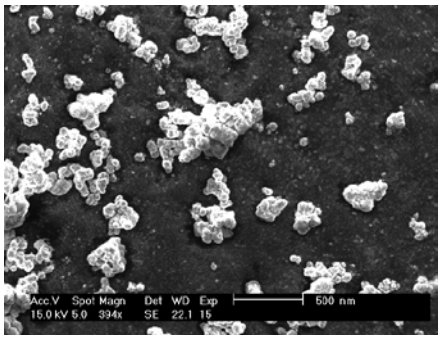


***Fig. 4: The SEM images of $FeS_2$ produced at 180 °C with adding NaHCO.***

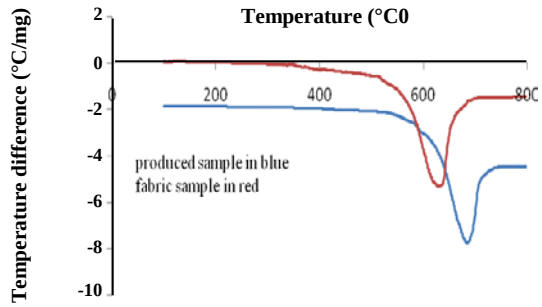


***Fig. 5: DTA thermograms of pyrite samples.***

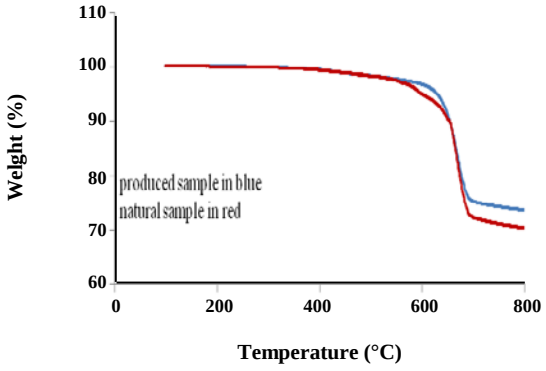


***Fig. 6: TGA thermograms of pyrite samples.***

## CONCLUSIONS

In this paper, pyrite was produced with good crystallization using hydrothermal method. Results indicated that formation of marcasite as an unwanted production occurred in low amount of pH. To adjust pH of reaction solution, $NaHCO_3$ was used and results showed that pyrite was produced without marcasite. SEM analysis indicated that pyrite particles were in nano size. Ultimately, improvement of thermal properties of the synthesized pyrite was demonstrated by thermal analyses.

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