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ALTERING FERROUS SULPHATE TO SYNTHETIC GOETHITE

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ABSTRACT

Catalyst is required in any reaction. Coal liquefaction is one of the processes to have need of it. The most common catalyst used in the process is ferrous based catalyst. It is very influenced by pyrhotite, which may be occurred from goethite while goethite can be composed of any iron sources. The research had the use of ferrous sulphate as the main iron source, which was reacted with caustic soda. Parameters on molar ratio of the $FeSO_4.7H_2O/NaOH$ *were 0.2 and 0.33, reaction time applied were 3.5; 6.5 and 17.15 hours, oxygen flow rates of 100; 200; 300; 400 and 500 cc/minute were also observed. The best result was achieved at 0.2 molar ratio of the* $FeSO_4.7H_2O/NaOH$ *within 6.5 hours by oxidation process that was containing pure goethite, while 100 cc/minute of oxygen rate was enough for the process to be happened.*

Keywords : ferrous sulphate, synthetic goethite, catalyst, coal liquefaction

INTRODUCTION

Generally, catalyst is required to support the reaction in any chemical process. Catalyst is required to promote reaction with shorter route, which is the way of reaction in smallest activation energy compared to non catalyzed reaction process. So, it is fastening the reaction time and inert in the process (Anon, 2007).

One of the processes requiring catalyst is coal liquefaction. Ferrous based catalyst is the most common interest in the process, because it is cheap and easy to use. The catalyst can be altered from limonite, pyrite and laterite (Kaneko et al, 2000; Cugini et al, 1994). Activity of coal liquefaction is very influenced by pyrhotite ($Fe_{1-x}S$), which is stated from goethite [FeO(OH)] content in the catalyst. It can be observed by sulphidation process.

Goethite is the Fe-oxide that occurs in soils and has yellowish brown colour. It also appears in dark brown or black in high concentration. Thermodynamically, goethite is the most stable of all Fe-oxide. Various conditions, such as cool temperature, moisture content of soil and the presence of organic matter comparatively support the formation of goethite than hematite. In suitable condition, goethite can be composed of any Fe source (Anon, 2006). If ferrous content mineral has been exposed in ambient condition, then the ferrous mineral will be oxidized to form goethite and to result iron-hat. For an example, pyrite becomes goethite by weathering, with the chemical reaction as follow

$4\ FeS_2 + 15\ O_2 + 10\ H_2O$ '! $4\ FeOOH + 8\ H_2SO_4$.

Goethite deposit is rarely found naturally in earth, thus a synthetic process can be applied by chemical reaction of ferrous chloride or ferrous sulphate that is resulted from leached pyrite or synthetic chemical materials. Goethite formation, which is converted from ferrous sulphate of leached pyrite is completed by pyrite dissolution followed by oxidation to form ferrous sulphate. The dissolution is leaching process for sulphide mineral. While synthetic chemical reaction of impure commercial grade to formed goethite procedure was mentioned by Cabral-Prieto et.al (1998), which is occurred in aqueous solution at room temperature.

The present experiment is to study general characterization of synthetic goethite from commercial ferrous sulphate, while the aim of this research is to find optimum operation condition of goethite formation applied for ferrous sulphate extracted from pyrite. Another experiment to produce goet-

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hite from ferrous sulphate had been done by Kaneko (1997), who had synthesized the ferrous sulphate by precipitation method in aqueous solution. Procedure of Kaneko adopted in Figure 1.

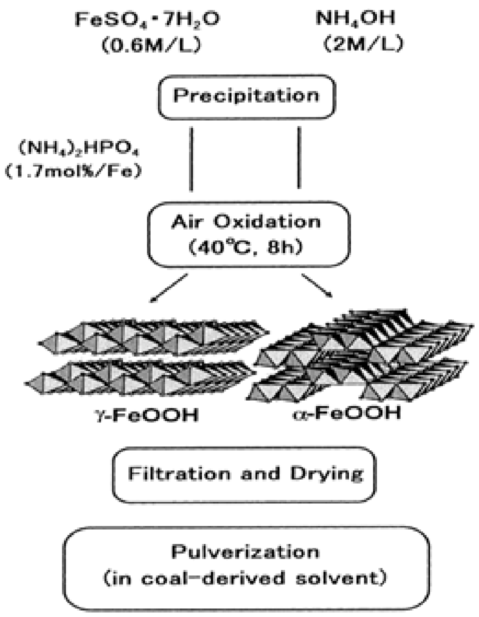

Figure 1. Scheme of Kaneko's Procedure on Goethite Formation

METHODS

Synthetic goethite was formed from impure ferrous sulphate and sodium hydroxide pro-analysis grade reagent. They were mixed as much as 0.33 molar of ferrous sulphate to 1 molar of sodium hydroxide. The mixing steps were as follows (Sariman et. al., 2006):

a. 20 grams of each reagent was diluted to 100 mL of water.
b. Sodium hydroxide solution was slowly added into stirred ferrous sulphate solution with oxygen bubbling at room temperature. The mixing colour of solution was become red-brown.
c. After mixing, the oxygen bubbling was continued for 3.5; 6.5; and 17.15 hours. The bubbling rate was not measured yet.

The oxidized material samples were filtered and dried in an oven. Then, the samples were analysed by using X-Ray diffraction (XRD) to reveal the mineral contents. The XRD patterns provide information about optimum reaction time of the highest value of total Fe content with less impurity for the next experiments.

The searched optimum time of the best result was observed for 0.2 molar concentrations ratio of $FeSO_4.7H_2O$ to NaOH with 2 (two) conditions of oxygen bubbling rates, measured and measureless. The measurement rates were 100; 200; 300; 400 and 500 cc/minute. Beside impure ferrous sulphate, pure analysis of ferrous sulphate was also tried to be used as feed and reacted in 0.2 molar concentrations at optimum time obtained at previous experiment.

RESULTS AND DISCUSSION

The method was adopted from procedure of Cabral-Prieto et.al (1998). He used 0.2 and 0.33 molar concentration ratio of $FeSO_4.7H_2O$ to NaOH. Goethite presents in moist condition, so oxidation is required. The oxidation rate was measured at 0.5, 0.17, 0.083, 0.05, 0.025, 0.017, 0.013, 0.01 cc/s respectively for various oxidations time from 20 to 120 minutes. The formation of synthetic goethite from sulphated medium depends on molar concentration of reactants and oxygen flow rate applied.

First experiment was undertaken at approximately steady oxygen flow-rate, so optimum time for the reaction was observed for 3.5; 6.5; 17.15 hours. The extreme range of oxidation between 6.5 and 17.15 hours are to prove the statement if the oxidation rate increases then total reaction time will be shorter. So, when the oxidation time is set to be steady then the result can be observed for different oxidation time including the extreme one. The results of goethite and gangue minerals obtained for GTNaO2 at 0.33 molar concentrations ratio is shown in Figure 2. Figure 2 present the mineral content of the product resulted in XRD pattern, the patterns are in the same intensity, but to compare them easily, the charts are combined. Gangue minerals in products (namely pyrite, jarosite, thermonatrite, clinochrysotile, fayalite, and andradite) are promoted from the mineral contents in raw material. Table 1 provides information of experiment condition and analysis result of the experimental products.

The oxidation time parameter gave the best result at 6.5 hours at steady oxygen flow-rate. It could be observed that the product contains only one gangue mineral (namely andradite) and the recovery of the product was 49.8% with 42.7% Fe content. Experiments were continued with 0.2 molar concentration ratio of the $FeSO_4.7H_2O$ to NaOH in 6.5 hours of oxidation time. Raw materials consist of two types that are pure analysis and impure ferrous sulphate. According to XRD pattern both show goethite, the GTNa-0.2 has higher recovery of 56.7% with 35.5% Fe content.

The best molar concentration ratio of the $FeSO_4.7H_2O$ to NaOH for GTNa is 0.2, because it produces only goethite without any gangue minerals. While in previous experiment by Cabral-Prieto *et.al* (1998) showed that the best molar ratio was 0.33. This phenomenon can be occurred because of difference of raw material and oxidation rate.

Figure 3 shows the oxidation rate of 100-500 cc/minute with 0.2 molar concentration ratio of $FeSO_4.7H_2O$ to NaOH. The experiment was held in 6.5 hours as an optimum reaction time. Overall reaction time will be shorter if the oxidation rate increases (Cabral-Prieto et al, 1998), meanwhile the results of all oxidation rate produce goethite without any gangue minerals. So, in order to minimize the oxygen consumption, the process can be applied at 200 cc/minute of oxidation rate in 6.5 hours.

Table1. Experiments condition, Total Fe and XRD result of products

Code	Oxidation time (h)	Molar concentration ratio $FeSO_4.7H_2O$/NaOH	Ferrous sulphate Initial Weight (grams)	Final Products Weight (grams)	Recovery of final produt (%)	Total Fe (%)	XRD result
GTNaO2	3.5	0.33	20	5.67	28.35	48	Goethite, Pyrite and Jarosite
	6.5		15	7.47	49.8	42.7	Goethite and Andradite
	17.15		20	9.36	46.8	35.7	Goethite, Clinochrysotile, and Fayalite
GPNa-0.2	6.5	0.2	20	7.47	37.35	31.3	Goethite and Thermonatrite
GTNa-0.2	6.5			11.34	56.7	35.5	Goethite

Note: GP = pure analysis ferrous sulphate, GT = non pure ferrous sulphate

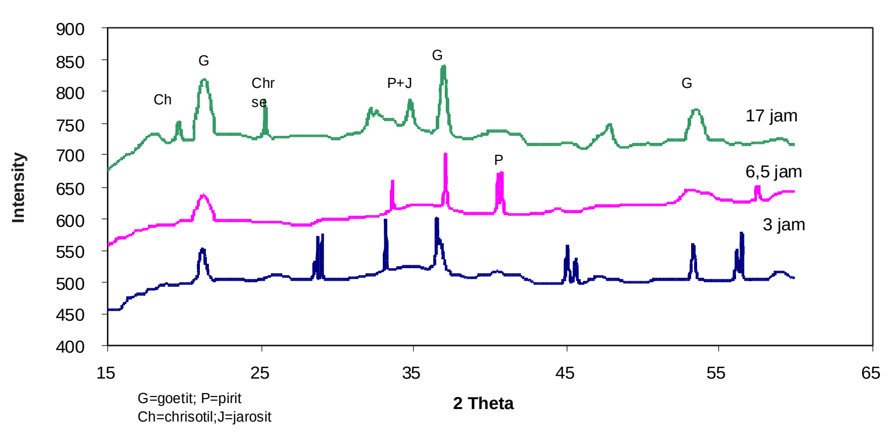

Figure 2. The XRD patterns of sample GTNaO2 caused by the length of oxidation time

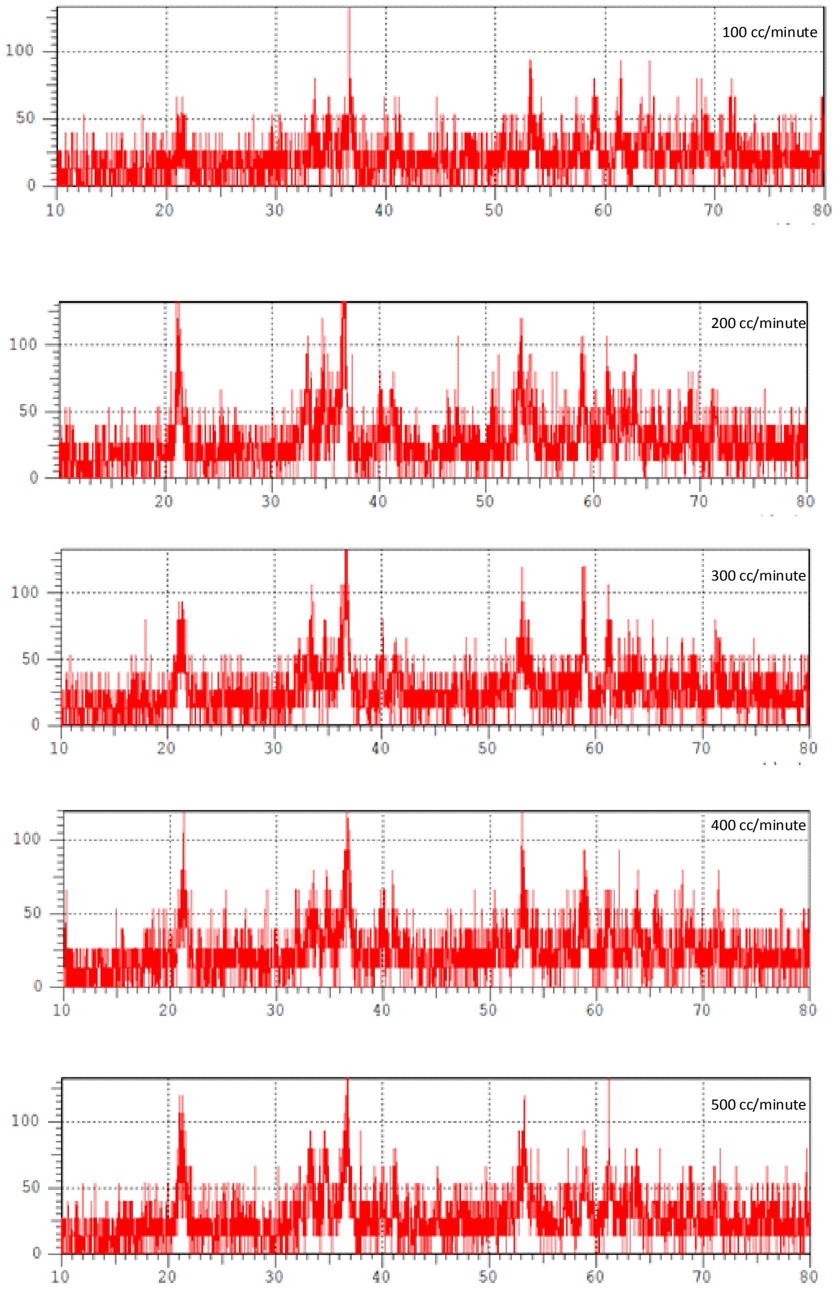

Figure 3. XRD patterns for 100 – 500 cc/minute of oxygen bubbling rate

CONCLUSIONS AND SUGGESTION

1. Goethite can be produced from impure commercial grade of ferrous sulphate.

2. The best condition to produce goethite is 0.2 molar ratio of the $FeSO_4.7H_2O/NaOH$ at 6.5 hours of reaction time with high oxidation rate.

3. Oxidation rate of 100-500 cc/minute yields goethite without any gangue mineral, so the process can be occurred with oxygen flow rate of 200 cc/minute to minimize oxygen consumption

4. The research is necessary to be continued by measuring oxidation rate in order to optimize the oxygen consumption.

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