PRODUCTION OF SPONGE IRON FROM THE OK TEDI PYRITE CONCENTRATES

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Abstract

The Ok Tedi Copper Mine in Papua New Guinea has accumulated large quantities of pyrite concentrates over time at Bige dam where they are disposed and buried below the water table. These pyrite concentrates contained substantial amount of iron which are of economic value. Therefore this study was done to investigate the possibility of extracting iron from the pyrite concentrates in the form of sponge iron for commercial purposes. The pyrite concentrates were analyzed by Scanning Electron Microscopy (SEM) – Electron Dispersive Analysis X-ray (EDAX) and the results showed; 29.6 % Fe, 11.8 % C, 23.5 % O, 0.1 % Mg, 1.2 % Al, 4.1 % Si, 28.1 % S, 0.6 % K, and 0.7 % Ca by mass. Oxidizing roasting tests were conducted on the pyrite concentrates to increase the grades of iron oxides prior to reduction tests by use of coconut charcoal carbon. The particle sizes of pyrite concentrate range in size from 150 µm to 106µm. Several reduction tests were conducted on the various roasted pyrite concentrates in a fusion furnace at varying temperatures and times. Sample masses were noted before and after the roasting processes. The pyrite concentrates were oxidized at temperatures and times ranging from 700 °C to 1000 °C and from 5 minutes to 40 minutes, respectively. SEM-EDAX analysis of the oxidized pyrite concentrates at 1000 °C and in roasting time of 40 minutes showed; 52.3 % Fe, 20.7 % S, 12.3 % O, 5.2 % C, 5.7 % Si, 3.4 % Ca, 0.3 % Cu by mass. Loss of mass during roasting were observed and recorded. Hence, the gravimetric results indicated that the roasting kinetics were marginally faster at 850 °C. Sulfur was not completely removed however iron content was appreciably upgraded. Products of the roasted pyrite concentrates at a temperature of 1000 °C and roasting time of 60 minutes were used in the isothermal carbothermic reduction process. About 30 g of roasted products were mixed with 30 % by mass of carbon and reduced at temperatures ranging from 900 °C to 1000 °C and reduction times ranging from 30 minutes to 120 minutes. Analysis of the reduced product sat 1000 °C in 120 minutes by SEM EDAX showed; 52.7% Fe, 4.7% C, 33.6% O, 0.7% Mg, 0.7% Al, 4.4% Si, 4.5% S, and 0.7% Ca by mass. Oxygen was not completely removed, but the iron content increased appreciably due to removal of sulphur. The results suggest that the pre-roasting of the pyrite concentrate needs to be carried out at temperatures between 850 – 900 °C with prolong time to completely remove sulfur. It also suggests that the final reduction temperature needs to be below 1000°C because CO_2 is unstable above this temperature. Therefore, it is necessary to adjust the temperature and time of reduction to prevent re-oxidation of the sponge iron produced. Reduction of iron oxide will occur more efficiently if the initial sulphur in the charge is low. Hence magnetic separation of the iron oxides may be tried to increase grade.

Keywords: Pyrite, Concentrates, Sponge Iron, Kinetics, Tailings.

INTRODUCTION

The sulphide copper ore of Ok Tedi mines contains considerable amount of pyrite (FeS_2), which usually passes into the tailing after concentrating the copper minerals. A pyrite plant is set up to concentrate the pyrites by floatation. At the moment, the pyrite concentrates are transported in a slurry form to Bige, where it is buried below the water table to prevent oxidation and generation of acid mine drainage. Thus, a large quantity of pyrite is accumulating at Bige, about 20 km from the mine site. Thereby, this investigation is carried out to explore the feasibility of recovering the iron value in the pyrite in the form of sponge iron or direct reduced iron (DRI). To produce DRI, it is important to study the reaction kinetics of the iron oxides contained in the pyrite concentrates. Sponge iron or DRI has emerged as an important feed material for steel making in many countries. Hence, economic production of DRI will not only solve the problem of disposal of huge quantities of pyrite but also open up the prospect of small scale electric arc or induction furnace based steel plants in Papua New Guinea.

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REVIEW OF LITERATURE

Roasting of pyrite oxidizes the iron sulfide to either iron sulfate or iron oxide. However, conversion of pyrite to ferrous sulfate occurs at low temperature (200 – 370 °C) only (Ferrow, Mania and Bosser, 2005). During roasting at high temperature range (600 – 1000 °C), iron sulfide is converted to iron oxides (Rosenqvist, 1983). The variation between these ranges of temperatures depends on the oxidizing process and mineralogical requirements. Apart from the thermo – gravimetric techniques, Mossbauer spectroscopy and magneto – kinetic measurements have been used to quantitatively assess the kinetics of roasting of pyrite (Prasad, Singru & Biswas, 1985). Since the targeted end product is metallic iron, a high iron content material is an advantage. Thus, a grade of iron suitable to produce sponge iron would be ≥ 65 wt. % in the starting material (Mohapatra & Patra, 2009). Reactions in a direct reducing system occur spontaneously in stages to form the DRI; that is the hematite is reduced by carbon to form magnetite, which is then reduced to wustite (FeO) and finally wustite is reduced to metallic iron (Fe) (Pati & Vinay, 2008). These stages of reduction reactions showed that as long as the solid carbon is present in the reaction mixture, carbon gasification reactions and reduction of iron are occurring simultaneously (Singh & Pande, 2009). Iron ore reduction

kinetics (IORK) deals with the rate at which iron oxide is converted to metallic iron by removal of oxygen. Hence, the rate of iron ore reduction influences the production rate, which ultimately determines the economic feasibility and the process technology involved. Therefore, close observation of the reactions between the gases and the solids together with the rates of reductions are of great importance. Factors affecting the rates of reduction such as the temperature, reduction time, particle size, pellet size, use of a fluxing agent, chemical nature of oxide, reactivity of reducing agent and the iron oxide/carbon ratio have been noted. More importantly are the different rate controlling factors such as the boundary layer control, phase boundary reaction control, gaseous diffusion control and the mixed control (Abril, 2002; Bandyopudhyay & Al Chatralosly, 1993; Singh & Pande, 2009; Sun, 1997). It is worth noting that the reaction rate is exponentially dependent on temperature therefore a slight change in temperature can significantly impact the rate constant and this is developed in the discussion section below.

Experimental Procedure

The Ok Tedi pyrite concentrate was analyzed by X – ray diffraction (XRD) and energy dispersive analysis in JEOL scanning electron microscope (SEM - EDAX). These analyses revealed that the pyrite concentrate contained FeS_2, carbonaceous matter and oxides of Al, Mg, Ca, Si and Fe. In the first step, samples of 30 g of pyrite concentrates (150 μm) each were roasted isothermally at temperatures 700 °C, 750 °C, 800 °C, 850 °C, 900 °C, 950 °C and 1000 °C respectively. Periods of roasting range from 5 minutes to 40 minutes in order to monitor the oxidation reaction by change of mass measurements. Hence, this process provided the study of conversion of pyrite to iron oxide at different times and temperatures. No attempt was made to recover SO_2 as the main thrust of this investigation was on the recovery of iron.

In the second step, an adequate quantity of pyrite was first roasted at 1000 °C for one hour to increase the grade of iron oxide. The objective of high temperature roasting was to ensure that the sulfides are converted to oxides completely. Several samples of 30 g oxidized sinters were mixed homogeneously with 30 % by mass charcoal. These samples were reduced isothermally at temperatures 900 °C, 950 °C and 1000 °C. Periods of time of reduction range from 30 minutes to 120 minutes. Losses of mass were recorded. The XRD and SEM – EDAX analyses of the oxidized and reduced products of the pyrite concentrates were conducted and the results were recorded.

RESULTS AND DISCUSSION

Although the XRD pattern is not showing the carbon compounds, it is suspected that large proportion of carbon may be in the form of siderite ($FeCO_3$). It may be reasonably suspected from the EDAX analysis that considerable quantity of iron oxide remained mixed up with the pyrite, even though the XRD pattern suggested that the main gangue material is Al_2O_3. The XRD pattern of the Ok Tedi pyrite concentrate is shown in Figure 1.

Table 1. EDAX analysis of the pyrite concentrate

The EDAX data is provided in Table 1

Element	C	O	Mg	Al	Si	S	K	Ca	Fe
% Mass	11.77	23.53	0.69	1.19	4.14	28.05	0.59	0.69	29.59

During oxidation roasting, the expected reaction was $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$. Evolution of SO_2 was noted by the pungent smell. The degree of conversion (α) was calculated by the mass differences as follows:-

$$\alpha = \frac{W_0 - W_t}{W_0}$$

Where W_0 = initial mass of charge, W_t = mass of charge at time t
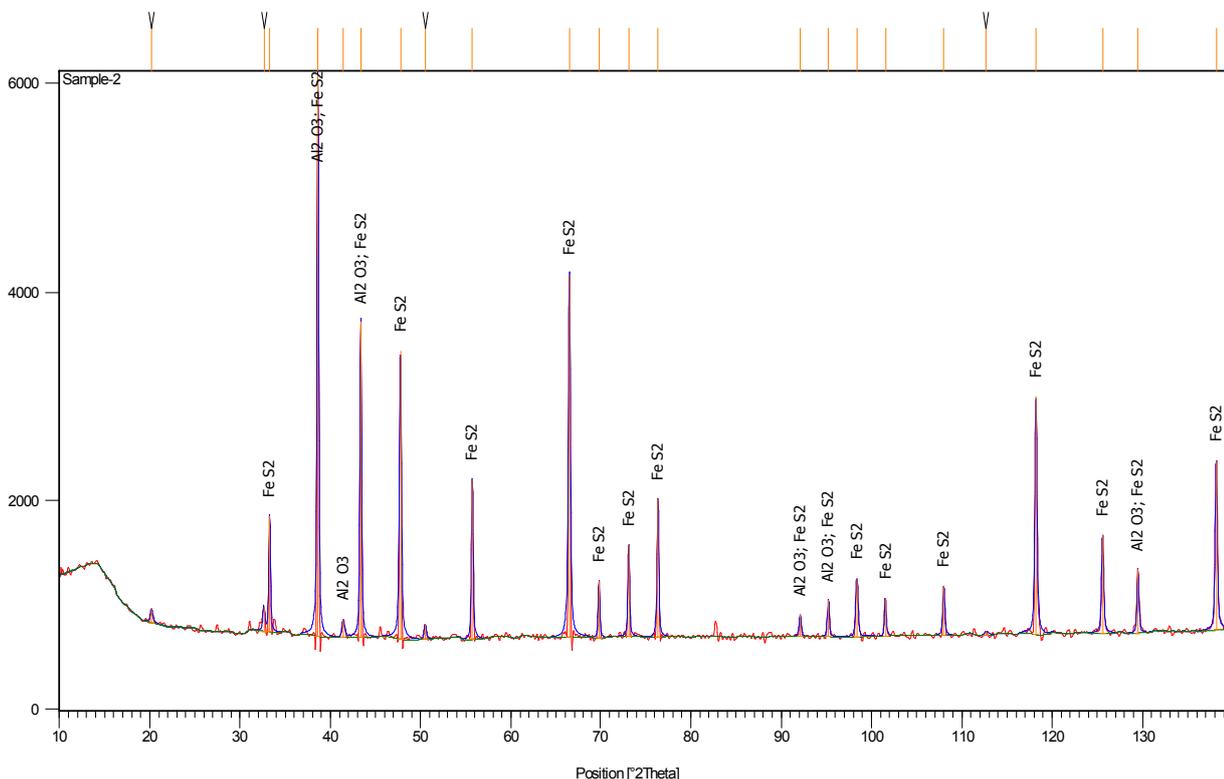
Figure 1 – XRD pattern of Ok Tedi pyrite concentrate

A slight increase in oxidation for temperatures between 700 °C to 1000 °C was noted within the time periods used, as shown in Figure 2. No change in the degree of conversion was observed after 30 minutes. Thereby, maybe a much higher temperature with a longer period of roasting time is required for complete conversion of the sulfides.
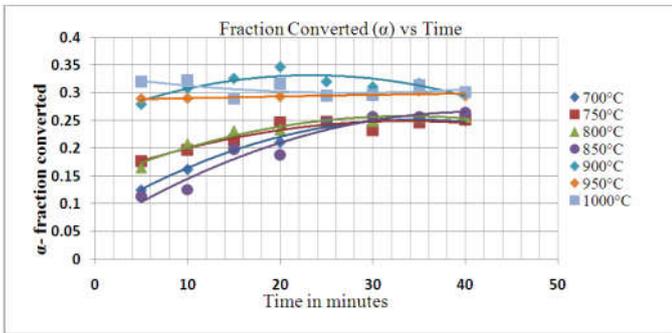
Figure 2. Degree of conversion is plotted against time for the roasted pyrite concentrate

Since the reaction kinetics is slow due its 'boundary layer diffusion' mechanism, the conversion of pyrite to iron oxide is chemically controlled and depends on oxidation temperature and O_2 partial pressure. In this controlling factor, the rate of oxidation per unit area of the pyrite was found to be constant beyond 30 minutes. Therefore, the first order kinetic model (-ln (1-f) = Kt) is used to explain the reaction kinetics of converting the sulfides to oxides in the pyrite concentrates. This model is used to calculate the values plotted in Figure 3. Hence the reaction rate constant (K) is determined from the slopes of lines and are provided in Table 2.

In using $-\ln(1 - f) = Kt$, where f is the fraction converted,

t is the oxidation time, and
K is the reaction rate constant
A slight increase in the rate reaction constant (K) at 850 °C was noted within the time periods used.
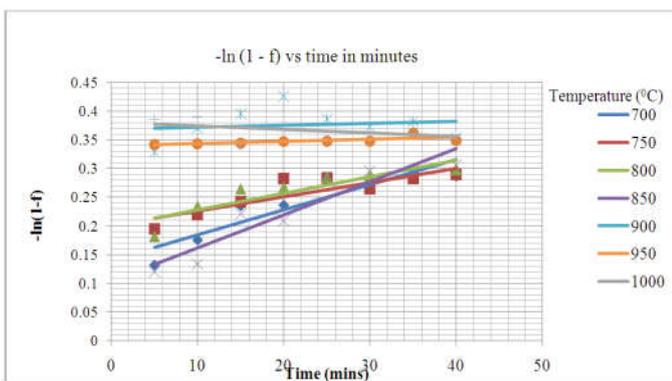
Figure 3. ln (1-f) verses oxidation time in minutes for Ok Tedi pyrite concentrates

Table 2. Reaction rate constants (K) determined from the plots in Figure 3

Temperature (°C)	Reaction rate constants (K)
700	4.37×10^{-3}
750	2.49×10^{-3}
800	2.90×10^{-3}
850	5.76×10^{-3}
900	3.19×10^{-4}
950	3.83×10^{-4}
1000	-6.28×10^{-4}

The roasted pyrite concentrates were analyzed by SEM – EDAX and the results are provided in Table 3 for the respective temperatures used in the oxidizing process. From these EDAX data, one can observe that the results confirm the gravimetric plots in Figure 2 and the reaction rates in Table 2. That is, % mass of Fe and O increase slightly with a marginal decrease in C and S, as oxidizing times increases under oxidation temperature of 850 °C. Apparently, % mass composition of Fe and O slightly decrease with a slight increase in C and S, as oxidation time increases at 1000°C. Under the oxidizing conditions investigated, sulfur was only slightly reduced and not completely eliminated. That means some iron is still in sulfide form. Therefore, further investigations under the oxidation temperature of 850 °C with longer time periods of roasting may be required to establish the reaction kinetics of complete conversion of sulfides. Besides, Si and Ca in the slag composition of the oxidized products slightly increase in % mass with increase in temperature. A gradual increase in loss of mass occurs from 30 minutes to 90 minutes of reduction at 1000 °C, according to figure 4. These losses of mass may be linked to oxidizing of carbon and sulfur and reduction oxides in the charge. A net gain of mass was observed after 90 minutes to 120 minutes so this could be due to re-oxidation of the products. Reduction roasting at 900 °C and 950 °C showed a steady increase in loss of mass from 30 minutes to 120 minutes.
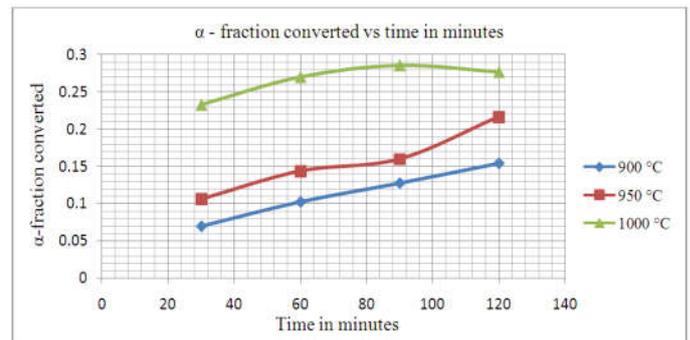
Figure 4. Fraction of oxides converted verses reducing times for the reduced oxidized Ok Tedi pyrite concentrates

Hence, the reduction net reaction may be summarized as $Fe_2O_3(s) + C(s) = Fe(s) + CO(g)$. However, actual reduction of Fe_2O_3 to Fe takes place in several stages. Simultaneously, any CO_2 formed is quickly converted at 1000 °C to CO by the solution loss reaction $CO_2(g) + C(s) = 2CO(g)$. Both direct reduction by carbon and indirect reduction by carbon monoxide are possible at 1000 °C. Also, CO_2 is unstable above 1000 °C.
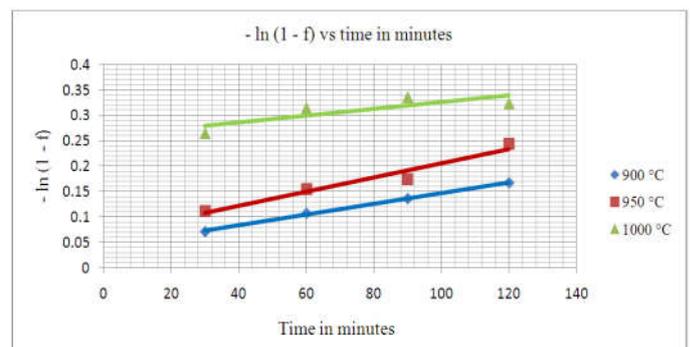
Figure 5. shows –ln (1 - f) = Kt plots for the reduced oxidized Ok Tedi pyrite concentrates

Table 3. EDAX results for Ok Tedi pyrite concentrates oxidized at respective temperatures

Oxidizing Temperature °C	time (min)	Element % Mass							
		C	Fe	O	Ca	S	Si	Al	Cu
850	10	10.4	45.6	12.0	1.7	27.2	3.1	-	-
	20	5.4	52.7	12.1	1.4	24.1	3.9	0.1	0.3
	40	5.2	55.8	12.5	1.5	21.0	4.0	0.1	-
900	10	5.6	55.3	13.5	1.3	20.3	3.9	0.1	-
	20	-	56.3	15.1	2.2	20.0	6.0	0.1	0.3
	40	-	57.1	15.2	2.9	19.0	5.8	0.1	-
950	10	-	58.3	12.9	1.6	22.4	4.4	-	0.3
	20	4.6	56.4	11.9	1.6	20.7	4.7	0.1	-
	40	16.1	45.4	13.9	2.1	17.7	4.7	0.1	-
1000	10	5.1	56.7	11.6	1.8	20.3	4.4	-	-
	20	6.1	53.3	11.1	2.5	22.1	4.9	-	-
	40	5.2	52.3	12.3	3.4	20.7	5.7	-	0.3
1060	60	6.2	50.7	12.8	2.7	20.5	7.0	0.1	-

Table 4. Reaction rate constants (K) determined from the plots in Figure 5

Temperature (°C)	Reaction rate constants (K)
900	1.10×10^{-3}
950	1.40×10^{-3}
1000	7.0×10^{-4}

Table 5. EDAX results for oxidized Ok Tedi pyrite concentrates reduced at respective temperatures

Reducing Temperature °C	time (min)	Element % Mass								
		C	Fe	O	Ca	S	Si	Al	K	Cu
900	30	57.6	22.5	9.0	0.8	8.0	1.8	-	0.3	-
	60	48.2	29.0	10.1	0.9	9.3	2.2	-	0.3	-
	90	44.7	29.0	12.5	1.0	9.4	3.2	0.0	0.2	-
	120	35.7	34.9	13.6	1.0	10.9	3.6	0.1	0.2	-
950	30	48.1	28.4	10.1	0.9	9.3	3.0	0.0	0.2	-
	60	38.4	33.7	11.8	1.1	10.8	3.8	0.0	0.2	-
	90	47.7	29.1	8.8	1.0	10.6	2.4	0.0	0.2	0.1
	120	35.7	34.1	12.3	1.3	12.6	3.7	-	0.3	-
1000	60	27.7	26.2	28.8	1.3	11.6	2.6	0.9	0.4	-
	90	6.0	50.0	13.4	2.7	20.4	7.4	0.1	-	-
	120	4.7	52.7	33.6	0.7	4.5	4.4	0.7	-	-
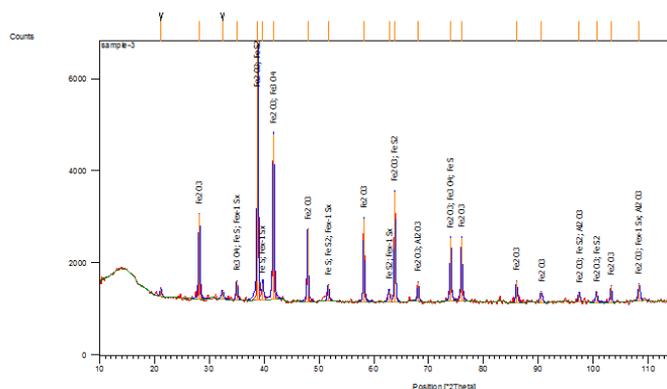
Figure 6. XRD pattern of oxidized pyrite concentrate reduced at 1000 °C for 90 minutes
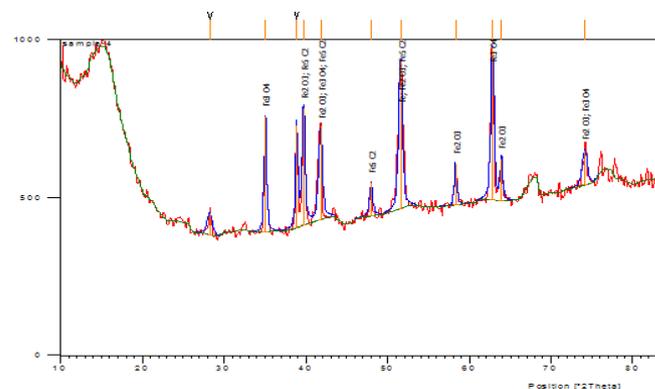
Figure 7. XRD pattern of oxidized pyrite concentrate reduced at 1000 °C for 120 minutes

Reaction rate is slightly faster at 900 °C to 950 °C and with prolong reduction time will most likely increase metallization. On the hand, reaction rate is much lower at 1000 °C, may be due to re-oxidation of the metal produced. The EDAX results may be matched with the XRD patterns given in Figure 6. It clearly indicates that various iron sulfide phases are still present along with the oxides (Fe_3O_4 and Fe_2O_3). When this incomplete oxidized product was reduced at 1000 °C for 120 minutes, the emergence of iron (Fe) phase could be detected in Figure 7. Results of EDAX analyses confirm the XRD data of the oxides still present in considerable quantity. In addition, a carbide phase (Fe_5C_2) had also formed. Indeed the reduced sinter produced in 120 minutes had a sponge iron like appearance.

Conclusion

The real challenge was to increase the degree of metallization to meet the requirement of sponge iron production. However, the limited test work has provided the following information:-

1. Effective oxidation roasting of the pyrite may be carried out at 850 °C. However, a prolonged treatment may be necessary to completely convert the sulfides to oxides.

2. Reduction of iron oxide will occur more efficiently if the initial sulfur in the charge is low. Hence, magnetic separation of the iron oxides may be tried.

3. Effective reduction of the oxidized pyrite may be carried out between 900 °C and 950°C. Prolong reduction time will most likely increase the metallization of sponge iron.

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