

Asian Journal of Physical and Chemical Sciences

8(4): 1-13, 2020; Article no.AJOPACS.60593 ISSN: 2456-7779

## Reaction Kinetics of Iron Oxides in Ok Tedi Magnetite Skarn Ore

Mary Kama<sup>1\*</sup>, Kaul Gena<sup>1</sup> and Tindi Seje Nuru<sup>2</sup>

<sup>1</sup>Department of Mining Engineering, Papua New Guinea University of Technology, PMB Lae, Morobe Province, Papua New Guinea. <sup>2</sup>Teaching Learning Methods Unit, University of Technology PNG, Papua New Guinea.

## Authors' contributions

This work was carried out in collaboration among all authors. Author MK designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MK and KG managed the analyses of the study. Author TSN managed the literature searches. All authors read and approved the final manuscript.

#### Article Information

DOI: 10.9734/AJOPACS/2020/v8i430121 <u>Editor(s):</u> (1) Dr. Thomas F. George, University of Missouri, USA. <u>Reviewers:</u> (1) Rianti Dewi Sulamet-Ariobimo, Universitas Trisakti, Indonesia. (2) Roy M. Thomas, Cochin University of Science and Technology, India. Complete Peer review History: <u>http://www.sdiarticle4.com/review-history/60593</u>

**Original Research Article** 

Received 25 July 2020 Accepted 29 August 2020 Published 25 October 2020

## ABSTRACT

Magnetic skarn ore (MSO) is one of the major copper bearing ore extracted by the Ok Tedi Copper Mine in Papua New Guinea (PNG). Copper minerals are recovered by flotation while the iron not associated with copper are discarded as tailings. The objective of this investigation was to determine the iron ore reduction kinetics for the Ok Tedi MSO and ascertain if it can be processed to produce sponge iron for a mini steel plant in Papua New Guinea. SEM-EDAX analyses of the Ok Tedi MSO indicated 10.1% C, 30% O, 0.6% Mg, 1.1% Si, 21.1% S, 0.8% Ca and 36.2 % Fe. Most of the iron is in sulfide form. Both naturally occurring and roasted sinters of Ok Tedi MSO samples of different particle sizes were reduced by charcoal carbon at three different temperatures and seven different reduction times. Analyses of the reduced products indicated a metallic iron content of more than 65 wt. % on average. Results showed that there was no significant difference in reduction between fluxed and control materials. Only a slight increase in kinetics with reduced particle size, hence the reaction rate constant (K) did not vary much within the temperatures investigated. Reaction kinetics increases with increasing reduction time at 900 °C. Therefore, more iron reduction is observed with particles of 106  $\mu$ m size. In addition, the results also confirmed that the reduction energy used was higher at 800 °C and lower at 1000 °C. In conclusion, iron reduction can be improved but close monitoring of temperature and reduction times are essential to determine the reaction kinetics of the Ok Tedi MSO.

Keywords: Skarn ore; sponge iron; tailings; flotation; roasted sinter; hematite; magnetite; wustite; reaction kinetics.

## 1. INTRODUCTION

Most mines in Papua New Guinea (PNG) mine large quantities of iron in the form of sulfides, carbonates, oxides and sulfates that are eventually disposed off as tailings. The Ok Tedi MSO contains a significant amount of hematite, magnetite, siderite, ilmenite and pyrite that can be a source of iron. The mineralogical compositions of Ok Tedi MSO reveals more iron minerals than copper, yet all iron containing minerals are collected in the tails from the main copper production stream. Therefore, this study is conducted to investigate the possibility of producing direct reduced iron (DRI), or sponge iron, from the MSO. Such sponge iron may serve as the feedstock for electric arc/induction furnace based mini steel plants in PNG.

Iron ore reduction kinetics (IORK) has been widely investigated in the past years. However, studies were never done on the iron ores available in PNG. A comprehensive study was carried out by this investigation to establish the various parameters that influence the IORK of Ok Tedi MSO.Such parameters include; the of the iron oxide chemistry [hematite (Fe<sub>2</sub>O<sub>3</sub>)/magnetite (Fe<sub>3</sub>O<sub>4</sub>)], particle size, porosity of pellets, temperature, and reduction time etc [1]. Similarly, in carbothermic reduction, the physical and chemical qualities of carbon are important influencing factors. It is therefore very essential to characterize the reducibility of locally available iron ore with locally available coconut charcoal for the production of sponge iron [2,3,4,5,6,7]. Good quality lime/limestone for fluxing is essential together with good porosity of the Ok Tedi MSO so locally available sugar cane juice was used as the binder to form pellets of samples for the tests.

Chemistry of the Ok Tedi MSO was characterized by microscopic analyses of polished sections for its mineral assemblage in the starting material. Mineral compositions for both starting material and finished products were determined by X-Ray Diffraction (XRD) techniques. Elemental compositions were determined by Scanning Electron Microscopy (SEM) – Electron Dispersive X-Ray Analyzer (EDAX) techniques. Thus, distribution of minerals and elements in the starting material and finished products of both samples not only revealed the chemistry and reducibility kinetics of the various materials, but also the effects of certain parameters on the reduction rates of the iron oxides.

### 2. LITERATURE REVIEW

Iron is one of the most abundant elements which constitute about 4.6% mass of the earth's crust. In nature, iron does not occur in its elemental state but rather as compounds. The major sources of iron are magnetite ( $Fe_3O_4$ ) which contains 72.4 wt.% iron followed by hematite (Fe<sub>2</sub>O<sub>3</sub>) which contains 70 wt  $\overset{\circ}{\%}$  iron in stoichiometric proportions [2,3]. Magnetite is generally more difficult to reduce than hematite due to its poor porosity, however magnetite is typically favored due to its higher iron content. That is magnetite exhibits polarity on its surface as it is a ferromagnetic substance with tightly packed atoms of iron and oxygen, thereby requires a lot more heat to remove the high oxygen content during reduction than hematite. Since the targeted end product is metallic iron, a high iron content material is an advantage; and a grade of iron suitable to produce sponge iron would be  $\geq$  65 wt. % in the starting material [4].

The reduction of iron oxides in a direct reducing system occurs by both solid and gaseous reductants such as solid carbon from charcoal and CO gas [3]. Hence the metallic iron produced from the direct reducing system is termed 'direct reduced iron' (DRI). The 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) [3]. These reactions are represented by the chemical equations below:

$3Fe_2O_3 + C$	$\longrightarrow$	$2Fe_3O_4 + CO$	$\Delta H = 118.82 kJ/mol$
$Fe_3O_4 + C$	$\longrightarrow$	3FeO + CO	∆H = 209.26 kJ/mol
FeO + C —	$\longrightarrow$	Fe + CO	$\Delta H = 156.50 \text{ kJ/mol}$

The CO gas produced in the above reactions participates in further reducing the iron oxides. A substantial amount of heat is required to complete the reduction process, since the various stages of reactions are homogeneously endothermic [3].

Stages of Iron Oxides Reduction by CO gas;

3Fe <sub>2</sub> O <sub>3</sub> + CO -	$\longrightarrow$ 2Fe <sub>3</sub> O <sub>4</sub> + CO <sub>2</sub>	ΔH = - 53.80 kJ/mol
$Fe_3O_4 + CO -$	$\longrightarrow$ 3FeO + CO <sub>2</sub>	$\Delta H = 36.68 \text{ kJ/mol}$
FeO + CO —	$\longrightarrow$ Fe + CO <sub>2</sub>	$\Delta H = -18.68 \text{ kJ/mol}$
C + CO <sub>2</sub>	> 2CO	$\Delta H = 172.58 \text{ kJ/mol}$

That means as long as the solid carbon is present in the reaction mixture, carbon gasification reactions and reduction of iron are occurring simultaneously [8].

The reduction of iron oxide to metallic iron proceeds through various kinetic steps which controls the overall reaction rate. Different rate controlling factors which control the overall rate of reduction are discussed in Table 1 by a summary of mathematical expressions for the different steps (Baliasingh & Mishra, 2008).

## Table 1. Mathematical Expressions of Rate equations representing different ratecontrolling steps

Equation	Rate controling step	Dependent variable
$1 - (1 - f)^{1/3} = kt$	Chemically Controlled	Temperature
- ln (1-f) = kt	Chemically Controlled	Temperature
$[1 - (1 - f)^{1/3}]^2 = kt$	Diffusion Controlled	Agitation
$1 - 2/3f - (1 - f)^{2/3} = kt$	Diffusion Controlled	Agitation
K $[1-2/3f - (1-f)^{2/3}] + D/r_0[1-(1-f)^{1/3}] = kt$	Mixed Controlled	Temp. & Agitation

Since the direct reduced system deals with solid to solid carbothermal reduction reactions, the reaction kinetics is slow due to its 'boundary layer diffusion' mechanism. Thus, it is chemically controlled and depends upon temperature and gaseous partial pressures. Hence, the mechanism of phase boundary reaction control involves the chemical reaction at the wustite-iron interface. In this rate controlling factor, the rate of reduction per unit area of the remaining iron oxide is found to be constant with time [7].

During oxidation roasting, the iron sulfides decompose at temperatures 600-1000°C to form

11

sulfur dioxide and iron oxides. This process is called 'pyrite dead roasting' [5]. The variation between these ranges of temperatures depends on the process and mineralogical composition. The iron oxides produced can be reduced by solid carbon and CO. However, sulfur is not completely removed during roasting and is still contained in the roasted product [9].

The following chemical equations represent the pyrite dead roasting reactions where the predominants of the reactions depend on partial pressure of oxygen and temperature.

$2FeS_2 + \frac{11}{2}O_2$	$\longrightarrow$ Fe <sub>2</sub> O <sub>3</sub> + 4SO <sub>2</sub>	$\Delta H = -1666 \text{ kJ/mol}$
3FeS <sub>2</sub> + 8O <sub>2</sub>	$\longrightarrow$ Fe <sub>3</sub> O <sub>4</sub> + 6SO <sub>2</sub>	∆H = -2381 kJ/mol

Since these roasting reactions are strictly exothermic reactions, a considerable amount of heat is generated within the system [9].

Pellets of the iron oxides samples were preferred for faster reducibility due to high porosity, good bed permeability (spherical) with low angle of repose giving minimal segregation, uniform chemical composition and high strength to withstand higher temperature with easy handling and transportation. Binders can be organic substances, such as Dextrin, Starch, glucose and Alginate, or inorganic, such as Bentonite, Cement, Lime, Calcium hydroxide [4]. Charcoals from burnt coconut shells are a preferred source of high purity carbon compared to wood charcoals for iron reduction process [8].

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 [6,7.8, Terkel, nd; Misra, nd; 10]. 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.

#### **3. EXPERIMENTAL PROCEDURE**

Two Ok Tedi MSO samples of different grades are compared, naturally occurring and roasted. The reducing agent used was coconut charcoal with particle size of 150 µm and composition of 98% carbon. The fluxing agent used to simulate real operation was lime of 95% CaO. It has the ability to increase the basicity and decrease the slag viscosity and hence remove the impurities [11].

About 9 kg of naturally occurring Ok Tedi MSO samples were ground and screened to produce three sets of particle size samples: 250  $\mu$ m, 106  $\mu$ m and 53  $\mu$ m.

## 3.1 Naturally Occurring Ok Tedi MSO

Several 30 g samples were then produced containing 30 wt. percentage charcoal. Ratio of

charcoal to iron contained in the sample was about 1:1, which was sufficient to increase the metallization of iron during the reduction process [11].

The impact of fluxing agents typically used for the downstream smelting process was also investigated. In all, 126 samples were prepared for both oxidized and naturally occurring MSO, characterized and reduced for all sizes and temperatures used in this investigation. Table 4 has the data for the samples and parameters used in the reduction test work.

All samples were made into pellets using 5 wt. percentage sugarcane juices as the binder since the green ball formation was sufficient to withstand the drying temperature at that composition. Then the pellets were weighed into 50 mL porcelain crucibles. All fluxed and control samples were compared bv reduction isothermally at temperatures 800°C, 900°C and 1000°C for periods of 10, 20, 30, 40, 50, 60 and 90 minutes. Losses of mass were recorded and plotted to observe the kinetics of reactions by weight measurements. Analyses were carried out by XRD and SEM-EDAX.

#### 3.2 Oxidation roasted Ok Tedi MSO

About 2.2 kg of Ok Tedi MSO samples of each sized fractions were weighed into 4 x 400 mLclav "G" pots. Each pot contains 550 g of samples so the transfer of heat through the particles is uniform and all sample particles are subjected to oxidation. In all, a total of 12samples - 4 pots per size were oxidation roasted at 1000°C in a fusion furnace for 1 hour to increase the grade of iron. The fusion furnace operates on a maximum 1060°C temperature at and minimum temperature at 300 °C. Its application is for fusion and roasting of ores, however, its temperature control has low tolerance.

The roasted sinters were cooled overnight and losses of masses were recorded. After roasting and cooling, the sinters of same particle size were combined and total masses were recorded together with the loss of masses in Table 2. Sample preparation and formation of pellets for both control and fluxed samples were the same as for naturally occurring Ok Tedi MSO samples. That is, the recipe and compositions were same for both ore to compare the grades of iron oxides. Also the steps in comparing both fluxed and control samples by isothermal reduction are identical. Finally, the same instrumental techniques were used to determine the mineral and element compositions of the oxidation roasted and isothermal reduced products.

## 4. RESULTS AND DISCUSSION

Microscopic analysis of the polished sections of naturally occurring Ok Tedi MSO showed that most of the iron is locked in the form of sulfides as pyrites, chalcopyrite and bornite. Some iron is locked with carbonate which is in the form of siderite. Others are locked in magnetite and minor composition in biotite. Magnetite has the highest composition, followed by siderite and iron sulfides. Gangue minerals are mostly Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, which are constituents of the rock forming mineral of biotite. The XRD analyses shown in Fig. 2, confirms the mineral phases depicted by the micrograph in Fig. 1. The data from the SEM- EDAX analyses shown in Table 5 support the XRD results.

The XRD analyses of the oxidizing roasted MSO for the finer size (easy to visualize) is shown in Fig. 3 and the EDAX results for all sizes are shown in Table 6. It seems from the results that most of the iron, originally in the form of sulfides and carbonates were being converted to iron oxides during roasting. As a consequence, the iron content was upgraded by about72 wt. % for all particle sized samples used. The sulfur content was not completely eliminated although drastically reduced, the oxygen content was slightly reduced due to oxidation of sulfur, and the carbon content was completely eliminated. However, there were still traces of impurities in the roasted sinters. These results were confirmed by the EDAX analyses in Table 5.

Table 2. Oxidation roasting samples size, masses before and after roasting and the loss of mass

Samples & size	Sample Mass (g)	Mass of Roasted sinters (g)	Loss of mass (g)
250 μm	2200	1786.9	413.1
106 µm	2200	1812.3	387.7
53 µm	2200	1804.7	395.3

	Naturally occurring MSO	Oxidized MSO	Reducing agent – coconut charcoal carbon	Flux - CaO	Pellet binder - sugar cane juice
Mass (g)	30	30	10	1.5	1.5
Particle size (µm)	250, 106 & 53	250, 106 & 53	106	106	-
Wt. %	100	100	30	5	5
Purity - %	-	-	98	95	-

#### Table 3. Samples and materials used in the test work



chalcocite (Cu<sub>2</sub>S), covelline (CuS), bornite (Cu<sub>5</sub>FeS<sub>4</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), pyrite (FeS<sub>2</sub>), biotite ([K (Mg, Fe) <sub>3</sub> (AlSi<sub>3</sub>) O<sub>10</sub> (OH, F) <sub>2</sub>]) chalcopyrite(CuFeS<sub>2</sub>), siderite (FeCO<sub>3</sub>),

Fig. 1. Micrograph showing the mineral phases of Ok Tedi MSO

Kama et al.; AJOPACS, 8(4): 1-13, 2020; Article no.AJOPACS.60593

Samples	Number of Control samples	Number of fluxed samples	Reduction Temperatures (°C)	Reduction Times in minutes
Naturally occurring MSO	7 per size per temperature = 63	7 per size per temperature = 63	800,900 & 1000	10, 20, 30, 40, 50, 60 & 90
Oxidized MSO	7 per size per temperature = 63	7 per size per temperature = 63	800,900 & 1000	10, 20, 30, 40, 50, 60 & 90
Total	126	126	3	7

Table 4. A summary of samples and parametersused for reduction test work







Fig. 3. XRD analyses of oxidation roasted Ok Tedi MSO sample of particles size 53  $\mu m$  at  $1000^{\circ}C$  for 1 hour

Element	С	0	Mg	Si	S	Ca	Fe	Cu	
% mass	10.1	29.95	0.59	1.06	21.12	0.8	36.22	<0.1	

Table 5. SEM-EDAX analyses of Ok Tedi MSO

Table 6. SEM-EDAX results for roasted Ok Tedi MSO at 1000 °C for 1 hour

		Element (% mass)									
Particle size (µm)	Fe	0	S	Si	Ca	Mg	Cu	Mn	AI	Κ	Ρ
53	60.5	24.4	2.4	5	2.9	2	0.9	0.5	0.6	0.2	0
106	62.6	23.2	4.1	4	2.7	1.4	1	0.5	0.5	0.1	0
250	61.2	22	4.5	3.7	2.2	1.1	0.8	0.4	0.4	0.1	0.1



# Fig. 4. XRD results for fluxed sample of particle size 53 μm reduced at 900 °C for 60 minutes. (naturally occurring MSO)

XRD results in Fig. 4 for fluxed samples show an abundance of metallic iron, magnetite and hematite HP, and iron (III) oxide. Slight reoxidation may be possible with abundance of hematite and reduction of iron oxides was retarded in showing transition of hematite to iron (III) oxide. Hence, skipping formation of wustite to form metallic iron could mean the gases ratios were not at equilibrium although the carbon was completely used up in the process.Fig. 5 shows transition of iron compounds with some graphite peaks for the control sample. These results indicate complete reactions with clear formation of the iron oxides peaks for fluxed samples than the control samples. However, the XRD results in Fig. 5 agree with the EDAX results in Table 7.

Table 7 shows data of the EDAX analyses for 53  $\mu$ m particles (a-to d) reduced for 30 minutes and

60 minutes for both the control and the fluxed samples of naturally occurring Ok Tedi MSO. Also included in (e) is the EDAX result for particle size 106 µm of the control sample reduced for 90 minutes. The result showed that the carbon was depleted under the reducing conditions of (e), subsequently upgrading the iron content by 50%. Thus, an increase in particle size and reduction time correspondingly increases the reduction of the iron oxides. Incomplete reduction is evident for particles of size 53 µm in both 30 and 60 minutes at 900 °C, possibly due to the particles being too fine to react with carbon. Fluxing did notinfluence the reduction of iron oxides much as there was still unreacted carbon in the reduced products.



Fig. 5. XRD results for control sample of particle size 53  $\mu m$  reduced at 900 °C for 60 minutes. (naturally occurring MSO)

		Element (% mass)												
Sample type/ time (min)	#	С	Fe	0	Ca	S	Si	Mg	К	AI	Cu	Mn	Ρ	Na
Control/30	а	43.3	28.9	19.7	1.4	2.3	2	0.8	0.4	0.3	0.5	0.2	0.1	0
Fluxed/30	b	39.8	29.9	19.6	3.9	2.6	1.9	0.6	0.5	0.3	0.5	0.2	0.1	0
Control/60	с	35.7	35.4	20.6	1.6	2.2	2.1	0.8	0.4	0.4	0.6	0.3	0.1	0
Fluxed/60	d	35.3	34.3	19.8	3.8	2.4	2	0.7	0.5	0.3	0.6	0.2	0.1	0
Control/90	е	-	54	35.2	4.4	4	2.4	-	-	-	-	-	-	-

Table 7. SEM-EDAX results for naturally occurring Ok Tedi MSO reduced at 900 °C



Fig. 6. XRD results for fluxed sample of particle sizes 53  $\mu m$  reduced at 900 °C for 60 minutes (oxidized MSO)



Fig. 7. XRD results for control sample of particle sizes 53 µm reduced at 900 °C for 60 minutes (oxidized MSO) С

Table 8. SEM-EDAX results	for reduced roasted	ା Ok Tedi MSO at 900 ବ	C

		Element (% mass)											
Sample type/ time (min)	#	С	Fe	0	Ca	S	Si	Mg	К	AI	Cu	Mn	Ρ
Control/30	f	41.2	31	19.9	1.6	1.6	2.3	0.8	0.4	0.3	0.6	0.2	0.1
Fluxed/30	g	38.6	30.1	20.9	3.7	2	2.2	0.7	0.6	0.3	0.6	0.2	0.2
Control/60	ĥ	41.6	30.4	20.1	1.5	1.7	2.2	0.8	0.5	0.3	0.5	0.2	0.1
Fluxed/60	i	36.5	32.2	20.8	3.8	1.9	2.1	0.7	0.5	0.3	0.6	0.2	0.1
Fluxed/90	j	0	56.2	32.4	4.2	4.6	2.7	0	0	0	0	0	0
Control/90	k	20.1	39.8	30.2	4.5	3.1	2.2	0	0	0	0	0	0

Figs. 6,7 showed XRD results of high wustite and metallic iron with less magnetite. Since the oxidized Ok Tedi MSO samples have high iron and less impurities, all haematites were reduced to magnetite and subsequently, to wustite and metallic iron. These conversions were evident in the XRD analyses. If the reduction time increases, then magnetite will likely get reduced to metallic iron.

Table 8 shows data for the EDAX analyses of reduced oxidized Ok Tedi MSO samples. The element compositions of particle size 53 µm reduced at 900 °C for 30 and 60 minutes are

 $\ln K = [-Ea/R] [1/T] + \ln A i.e. Ea = (\ln K - in A) \times RT$ 

K = Rate Constant (constant at a particular temperature)

Reduction Reactions occur in stages as follows:

 $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2(1-2a)$ 

labeled (f - i) and for 106 µm particles reduced at 900 °C for 90 minutes are labelled (j - k). Increased reduction time for fluxed 106 µm particles in (j) showed more reduction of iron. These results depict carbon dissolution of iron by unreacted carbon; therefore to increase reduction of iron the reducing times must be increased.

The reduction energy required for the reactions for each stage of carbothermic reduction of iron oxides were calculated for all reactions, using the Arrhenius equations as follows:

(1)

 $Fe_{3}O_{4} + CO = 3FeO + CO_{2}(2-2b)$ 

 $FeO + CO = Fe + CO_2 (3-2c)$ 

Reaction 2a proceeds before reactions 2b and 2c, therefore less reduction energy is required than the later reactions. Much higher reduction energy is required to dismantle the unreactive wustite core as sufficient reacting gas (CO) should pass through the same passage as the exiting gas (CO<sub>2</sub>) to reach the core for further reactions to occur. In order to maintain this balance of chemical reactions, the gasification reactions of supplying the CO must meet this requirement and this will only be achieved at sufficient reducing temperature and time. Hence, higher reduction energy is required as the reduction of iron oxides penetrates through to the core of the MSO particles. Arrhenius plot shows Ok Tedi MSO pellets (-425 + 53 µm) reduced by coconut charcoal carbonfor reaction 2b.

The mechanism of phase boundary reaction control for the MSO involves the chemical reaction at the wustite-iron interface and it is temperature dependent. In this rate controlling factor, the rate of reduction per unit area of the remaining iron oxide is found to be constant with time.

When counter diffusion of reducing gas and product gas on the reduced outer layer is sufficiently fast, the concentration of reducing gas at the reacting surface is effectively the same as its concentration at the particle surface. In such case, the rate of reaction at the wustiteiron interface would control the overall reduction rate [12]. For this reason, the kinetic model most applicable for determining the reaction kinetics for the MSO, according to Baliasingh & Mishra, 2008 is:

 $-\ln(1-f) = Kt$  (3)

Where,

t is the reduction time, f is the fraction converted, K is the rate constant.

The plots of  $-\ln (1-f)$  verses reduction time gives a straight line. Hence, the reduction rate of the iron oxides in the Ok Tedi MSO is determined by the reaction rate constant (K), which is the slope of equation 3: Fig. 8 shows the kinetic Plots for reduced naturally occurring Ok Tedi MSO for particle sizes 106 µm. Gradients of the lines for both fluxed and control samples at temperatures 800°C and 100 °Cwere reducing with increase in reducing time whilst it was steady for 900°C as time increases. Fluxing has no effect at this temperature.

Table 9 shows data for the reaction rate constants for all particle sizes of reduced naturally occurring Ok Tedi MSO samples. The K values are higher for the control samples for all sizes at 900°C and 1000°C than the fluxed samples. Comparing the control and fluxed samples of the median sized particles, there is consistency in their K values. However, they are inconsistencies when comparing the finer and coarser particle sizes. Note that K values depict the reduction rates of the iron oxides.

Fig. 9 shows the kinetic plots for the reduced oxidized Ok Tedi MSO for particles 106  $\mu$ m. The gradients of the lines for the oxidized MSO depict the same as those in Fig. 9, however fluxed sample of the median size seem to perform higher than the control sample. Nevertheless, the K values in Table 10 indicated otherwise that rates of reduction for both are equal.

Table 10 shows K values for the reduced oxidized Ok Tedi MSO for all sizes. The results indicated that fluxing has no effect at higher temperature and has some effect at lower temperature. However, rates of reduction are not steady for both temperatures. Nevertheless, fluxing affect reduction rates for larger and smaller particles as revealed by the K values for both samples. The reaction rates for the median particle sizes for both samples were not affected by fluxing.

Table 9. K values for reduced natural	ly occurring Ok Tedi MSO samples
---------------------------------------	----------------------------------

Temperature	Particle siz	e 53 μm	Particle size 106 µm		Particle size 250 µm	
(°C)	К		K		К	
	Control	Fluxed	Control	Fluxed	Control	Fluxed
800	1 x 10 <sup>-3</sup>	8 x 10⁻⁴	8 x 10 <sup>-4</sup>	1.4 x 10 <sup>-3</sup>	1.2 x 10 <sup>-3</sup>	1.1 x 10 <sup>-3</sup>
900	2.6 x 10 <sup>-3</sup>	1.8 x 10 <sup>-3</sup>	2.1 x 10 <sup>-3</sup>	2.1 x 10 <sup>-3</sup>	1.7 x 10 <sup>-3</sup>	2 x 10 <sup>-3</sup>
1000	2.5 x 10 <sup>-3</sup>	1.3 x 10 <sup>-3</sup>	2.3 x 10 <sup>-3</sup>	1.3 x10⁻³	1.3 x 10 <sup>-3</sup>	1.2 x 10 <sup>-3</sup>

Kama et al.; AJOPACS, 8(4): 1-13, 2020; Article no.AJOPACS.60593







Fig. 9. In (1-f) verses reduction time for reduced roasted Ok Tedi MSO samples

Temperature	Particle size 53 μm Κ		Particle size 106 μm K		Particle size 250 μm K	
(°C)						
	Control	Fluxed	Control	Fluxed	Control	Fluxed
800	8 x 10⁻⁴	5 x 10⁻⁴	6 x 10⁻⁴	6 x 10⁻⁴	2 x 10 <sup>-4</sup>	6 x 10⁻⁴
900	2.7 x 10 <sup>-3</sup>	3.5 x 10 <sup>-3</sup>	1.6 x 10 <sup>-3</sup>	1.6 x 10 <sup>-3</sup>	1.3 x 10 <sup>-3</sup>	1.5 x 10 <sup>-3</sup>
1000	1.1 x 10 <sup>-3</sup>	9 x 10⁻⁴	1.1 x 10⁻³	7 x 10⁻⁴	9 x 10⁻⁴	1.3 x 10 <sup>-3</sup>

Table 10. K values for reduced roasted Ok Tedi MSO samples

## 5. SUMMARY AND CONCLUSION

The kinetic data show that reaction rate is exponentially dependent on temperature to certain duration of reduction as in the case of 1000 °C. Thereby, the increase of 900 °C to 1000 °C did not increase K dramatically according to the kinetic model plots and the Arrhenius plots. However, the increase in temperature from 800 °C to 900 °C does increase the reaction rate constants slightly and so in concluding, the overall rate of reduction appears to be controlled by  $C/CO_2$  reaction or carbon gasification reaction. Therefore, the IORK of Ok Tedi MSO is limited to further investigations within reducing temperature of 900 °C.

Oxidizing roasting of Ok Tedi MSO certainly upgraded the iron oxide grade to above 60% Fe by mass in composition however the reduction of the iron was slow such that the reduction rates of both samples of Ok Tedi MSO proceeded at the same rates for all temperatures. Grades of iron oxides of Ok Tedi MSO do not have much influence on the reduction rates within the conditions used in this study.

Slight differences in reduction rates were noted with the smaller size particles (-106+53  $\mu$ m and - 250+106  $\mu$ m). Fluxing with calcium oxide does influence the reduction of Ok Tedi MSO particles of size  $\geq$  +250  $\mu$ m.

Reducing temperature of  $1000^{\circ}$ C proved to be unstable in the fusion furnace at the reducing time of 60 minutes, thus reduction of wustite was almost impossible because there weren't enough CO in the furnace to speed the reduction due to unstable CO<sub>2</sub> and re-oxidation resulted. That means CO<sub>2</sub> was unable to diffuse through the porous layer of iron and outward from the exterior surface of the particle to the bulk gas boundary, instead reacts with the iron.

To conclude, 900 ℃ is the reducing temperature for Ok Tedi MSO and the reducing time can exceed the maximum reducing time of 90 minutes used in this study. Since all mechanisms of the rate controlling steps require adequate time to complete all processes for high production of metallic iron, prolong time is required to carefully study the IORK of the iron oxides in the Ok Tedi MSO.

## DISCLAIMER

The products used for this research are commonly and predominantly use products in our

area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

## ACKNOWLEDGMENTS

The authors thank the Ok Tedi Mining Ltd Metallurgical team for the supply of MSO samples taken from the mine pit. They also extend their gratitude to the PNG University of Technology for using their facilities to carry out the investigations. Besides, they also appreciate the technical assistance provided by Mr. Philip Pirah of Mining Engineering department, Mr. Philip Badawol of Applied Sciences department and Steven Vauta from National Analysis and Testing Laboratories Services (NATLS).

#### **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

#### REFERENCES

- Wu C, Chen H, Hong W, Li D, Liang P, Fang J, Lai C. Magnetite chemistry and implications for the magmatic-hydrothermal ore-forming process: An example from the Devonian Yuleken porphyry Cu system, NW China. Chemical Geology. 2019; 522:1-15.
- Bohn CD. et al. The kinetics of the reduction of iron oxide by carbon monoxide mixed with carbon dioxide. Al Ch. E Journal. 2010;56(4):1016-PO29.
- Pati RR, Vinay M. Reduction behavior of iron ore pellets - A thesis, Department of Metallurgy &Materials Engineering – Rourkela; 2008.
- Mohapatra B, Patra D. Study of reduction behavior of iron ore lumps – A thesis, Department of Metallurgy & Materials Engineering – Rourkela; 2009.
- Lloyd WA. A study on the kinetics of iron oxide reduction. University of Minnesota; 1954.
- 6. Abril ER. Kinetics of iron oxide reduction by coal. Lab. Am. Appl. Res. 2002;32:2.
- Bandyopudhyay D, Al Chatralosly. A study on the kinetics of iron – oxide reduction by

solid carbon. Steel Research. 1993;64: 340-345.

- Singh AK, Pande OP. Preparation and Characterization of sponge iron. A Thesis. School of Physics and Material Science. 2009;7-12.
- 9. Runkel M, Sturm P. Pyrite roasting, an alternate to sulfur burning. The Southern African Institute of Mining and Metallurgy-Sulfur and sulfuric acid conference. 2009;6-8.
- 10. Sun SS. A study of kinetics and mechanisms of iron ore reduction in

ore/coal composites – A thesis, McMaster University; 1997.

- 11. Potnuru S, Kumar M. Studies on physical properties and reduction-swelling behavior of fired hematite iron ore pellets A thesis, Department of Metallurgical & Materials Engineering Rourkela; 2012.
- Srinivasan NS. Reduction of iron oxides by carbon in a circulating fluidized bed reactor. Powder Technology volume124, pp. 28-39, Division of Materials Engineering, Lund University, Sweden; 2002.

© 2020 Kama et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history: The peer review history for this paper can be accessed here: http://www.sdiarticle4.com/review-history/60593