Kinetics study of carbon raiser on the reduction of nickel laterite from Pomalaa, Southeast Sulawesi

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Abstract. As one of the top ten on nickel laterite ore resources in the world, Indonesia must have been initiating the nickel processing in total amount of about 1.5 million tonnes. In regard to the low nickel laterite processing, one of the possible product is nickel pig iron (NPI) needed for the stainless steel industries. In this study carbon raiser that is waste from oil industries was used to replace metalurgical coke. The kinetic of nickel laterite reduction using carbon raiser was studied and compared with anthrasite coal. In this work, the author conducted the reduction of nickel laterite ores by both carbon raiser and anthrasite coal as reductant, in air and CO_2 atmosphere, within the temperature ranged from 800°C and 1000°C. Two models were applied, sphere particle geometry model and Ginstling-Brounhstein diffusion model, to study the kinetic parameters. The results indicated that type of reductants and reduction atmosphere greatly influence the kinetic parameters. The obtained values of activation energy were varied between 17.44-18.12 kcal/mol.

1. Introduction

Nickel is one of the most important materials in the world. 66% of nickel consumption used for stainless steel making, while the others 18% used in other alloy making, and the rest used for other purposes. There are two main nickel sources, sulfide ore and laterite ore. At least, 60% of nickel demand is supply by sulfide ore besides 80% of nickel deposit lies on laterite ore [1]. Laterite is a highly weathered material rich in secondary oxides of iron, aluminium, or both. In addition, laterite often contains minor amounts of nickel, cobalt, and chromium [2]. One of the reasons that laterite ore is not used as the main nickel source is because of its low nickel content but recently China as the biggest stainless steel producer had found a way of utilizing laterite ore. They used it to produce nickel pig iron (NPI), as a substitute for pig iron in the stainless steel making process, using blast furnace or rotary kiln – electric furnace (RKEF). One of the important processes in NPI making is the reduction process. In the conventional NPI production, coal was used as a reductant.

There have been several studies of nickel laterite reduction. But to the best of our knowledge, very few works have been presented on studying the kinetic of nickel laterite reduction. The kinetic study of nickel laterite reduction using gaseous reductant shows that the reduction mechanism was diffusion controlled [3] but the kinetic study of nickel laterite reduction using solid reductant has not been studied yet. Therefore, this present work investigated the kinetic of nickel laterite reduction using solid reductant. The effect of using various kind of reductant to the kinetic parameter was also studied.

2. Materials and Methods

Anthracite coal, and carbon raiser was used as a reducing agent. Laterite, anthracite coal, and carbon raiser were provided by Indonesian Institute of Sciences. All of the materials above were crushed using mortar and then screened to get the desired size (-100+120 mesh). Laterite was characterized by

XRD (Shimadzu 7000), XRF (Thermo Scientific Niton XL3t). The proximate analysis of reductants was done by PAU UGM.

2.1. Pelletization

Laterite, starch, and anthracite charcoal were mixed together with laterite/reductant/binding agent ratio of 4:1:0.3. Then 5 mL of distilled water was added to the mixed sample and shaped into a ball pellet using hand. The pellet was dried at 110°C for 5 h. Using the same procedure, another pellets were made with carbon raiser as a reductant.

2.2. Reduction of the pellets

The pellets were roasted using two different atmospheric conditions, air and CO_2. Muffle furnace was used for air atmospheric roasting and tube furnace was used for CO_2 atmospheric roasting with CO_2 flow rate of 3 L/min. The pellets were roasted at temperature of 800, 900, and 1000°C with roasting time varied from 15 to 240 minutes. After the roasting process, the pellets were cooled and placed in desiccator. Thereafter, the pellets were crushed using mortar and were characterized using XRD (Shimadzu 7000).

2.3. Fraction of reduction reaction

To evaluate the kinetics parameters, the term fraction of reaction (*f*) was used. Eq (1) represents the formula for fraction of reaction. The equation was modified from the term used in iron ore reduction process [4]. The maximum weight loss of a pellet in Eq (1) was obtained from the maximum weight loss of laterite and reductant. The maximum weight loss of laterite was obtained from the total of removable oxygen from laterite. The total of removable oxygen from laterite is the oxygen binds to the iron and nickel.

$$f(t) = 100 \frac{\Delta W_t}{\Delta W_{max}} \tag{1}$$

where:
f = fraction of reaction.
ΔW_t = weight loss of pellet (g).
ΔW_{max} = maximum weight loss of pellet (g).

2.4. Kinetic models

The experimental data (*f*) were applied to the following mathematical models :

Sphere Particle Geometry Model [5]

$$1 - (1-f)^{1/3} = kt \tag{2}$$

where:
   t = time (s).
   k = kinetic constant (1/s).

$$k = k_0 exp\left(-\frac{E_a}{RT}\right)$$

where :
   k_0 = pre-exponential factor (1/s).
   E_a = activation energy (kcal/mol).
   T   = reduction temperature (K).
   R   = universal gas constant (kcal/mol/K).

Ginstling-Brounhstein Diffusion Model [5]

$$1 - \frac{2}{3}f - (1-f)^{2/3} = kt \tag{3}$$

3. Results and Discussion

3.1. Material characterization

The chemical compositions of nickel laterite used in this research was showed in the Table 1. The laterite was dominated by Fe and Si element and based on the analysis of the XRD pattern using Match! 2 software (Figure 1), the main mineral composition of the laterite was goethite (FeOOH), lizardite $(Mg_3(Si_2O_5)(OH)_4)$, clinochlorite $((Mg,Fe^{2+})_5Al(AlSi_3O_{10})(OH)_8)$, and quartz (SiO_2). The proximate analysis of the reductants was done by PAU UGM and the results was showed in the Table 2. The results showed that all of the reductants used had different characteristics. Anthracite coal had the highest fixed carbon content and the lowest ash content while carbon riser had the lowest fixed carbon and volatile matter content.
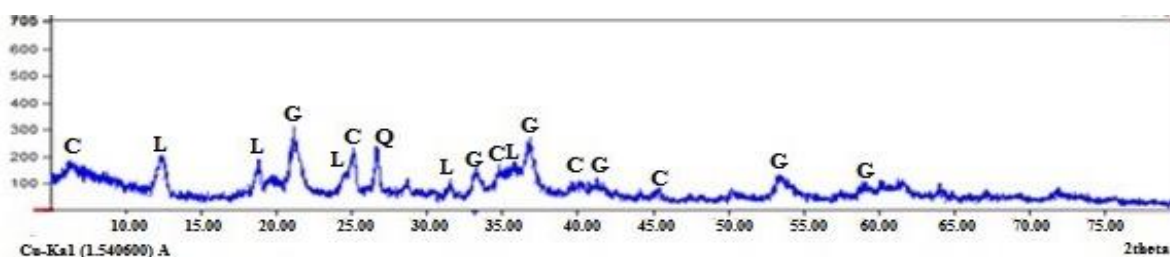
Table 1. Main Components of Laterite from Pomalaa, Southeast Sulawesi

Components	SiO_2	Fe_2O_3/Fe[*]	NiO/Ni[*]	MgO	Al_2O_3	Na_2O	Cr_2O_3
(wt.%)	26,94	43,83/30,60	3,19/1,73	12,67	5,13	2,73	1,63

[*] Analyzed using XRF Metal

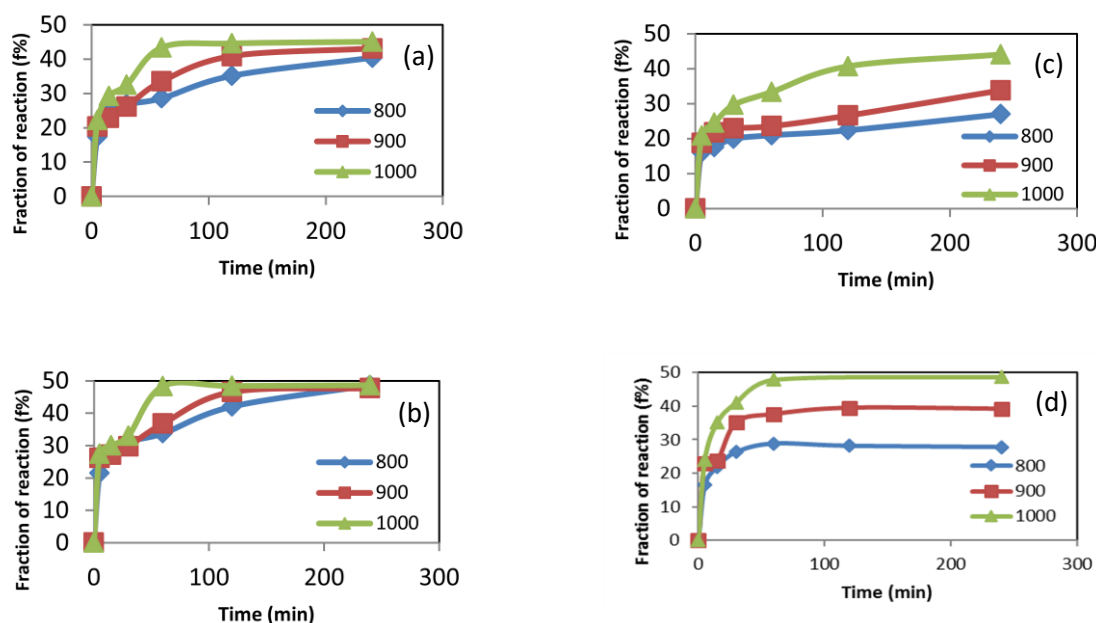**Table 2.** Proximate Analysis of Reductans (%wt)

Reductor Type	Moisture	Volatile matter	Ash	Fixed Carbon
Anthracite coal	2,3	7,4	2,5	87,9
Carbon riser	4,7	12,6	13,5	69,2

Figure 1. XRD pattern of initial laterite ore [Q: quartz; L: lizardite; G: goethite]

3.2. Fraction of reaction

Experimental data which were the sample mass from time to time converted into fraction of reduction reaction (*f*). The maximum weight loss from a pellet made with one type of reductant is different from a pellet made with the other type of reductant because the ash content of a reductant is different from the other reductant. The maximum weight loss of the pellet is 80.4% for the sample made with anthracite coal, and 73.5% for the sample made with carbon raiser. Figure 2 shows the graphical representation of fraction of reduction vs time.

From the experimental data, fraction of reaction value was already reached a constant value before reached its maximum value at certain time. The maximum value of fraction of reaction was 48%. It could happen because the reduction reaction has stopped. The reason of it could be two things. The first reason is the ratio between laterite and reductant was not high enough which makes the reductant has already used up before could reduce the minerals completely. The second reason is there are a
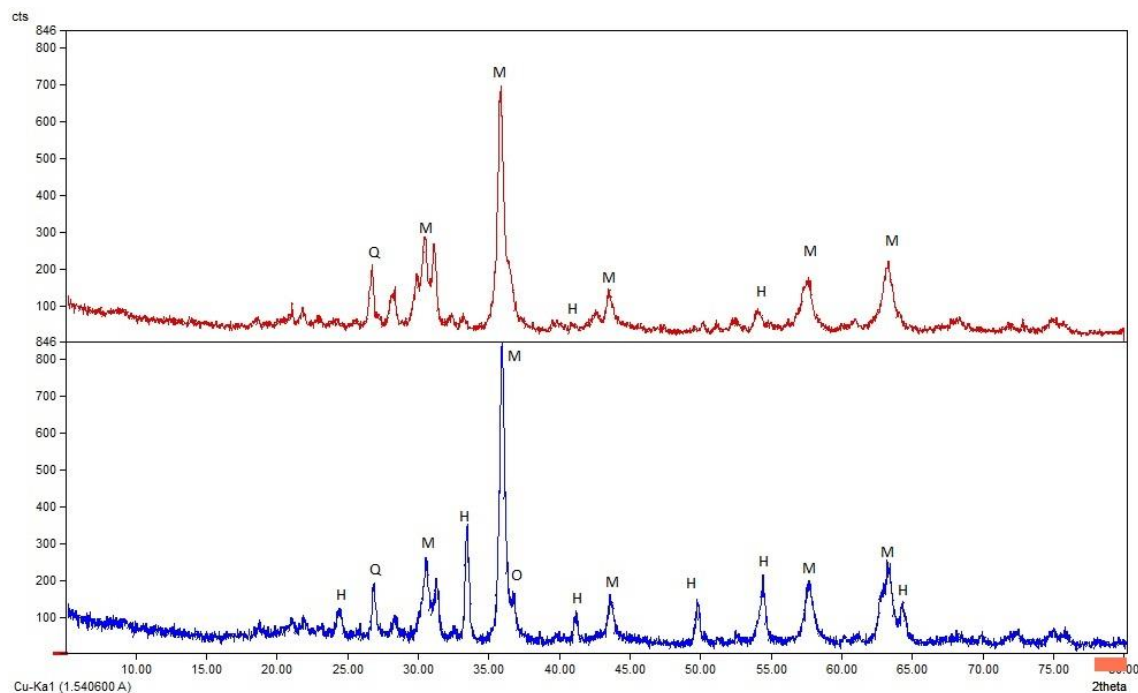
reaction between iron oxide and quartz which form fayalite ($FeSiO_4$) [6]. Fayalite has relatively low melting point (1100^oC) [7] and already melt during the reduction process which makes the porosity of the pellet decreased. The decreasing of porosity of pellet could prevent reducing gas diffusion. On the other hand, fayalite could also act as a nucleating agent on iron metal forming process. During the reduction process, iron metal layer formed around the surface of fayalite and prevent the contact of reducing gas. The fraction of reaction reached a constant value faster at higher temperature. It could happen because the reaction rate is faster at higher temperature. The reaction has stopped even when CO gas is used as a reductant instead of using solid reductant like in this study [3]. It concluded that the second reason was better at explaining why the reaction has stopped. The reduction reaction was fast at the early stage of the reduction process because at the early stage, the devolatilization of the reductant occurs alongside the dehydroxylation of the minerals in the laterite which makes the weight loss of the sample is very high.

Figure 2. Fraction of reaction as a function of time of the laterite with anthracite (a), and carbon raiser (b) in air atmospheric condition and with anthracite (c), and carbon raiser (d) in CO_2 atmospheric condition.

There was a slope change on the fraction of reaction vs time data on 0-5 minutes and 5-60 minutes reduction duration. This could happen because there were changes of reduction mechanism between these two periods. In the early stage of reduction, the process will follow the reaction controlled mechanism and after that the process will follow diffusion controlled mechanism [3]. The changes of slope in the previous study happened at 20 minutes reduction duration [3], but in this study, the changes happened at 5 minutes duration time. It could happen because the reaction happened in this two study is different. The changes of slope happened in the very early stage of the reduction. These early changes made the evaluation of kinetic parameters could only be done starting at 5 minutes reduction time.

The maximum value of fraction of reduction was almost the same (around 47%) for both reductions happened in air and CO_2 atmosphere, but based on the XRD analysis of the reduced sample, the mineral phase of both sample was different. The comparison of XRD pattern of the reduced samples was shown in Figure 3. The reduction in CO_2 atmosphere proceeds more complete compared with reduction in air atmosphere based on the loss of hematite and magnetite peaks. It could happen because there is oxygen in the air atmosphere reduction which could oxidized the reduced mineral in the sample.
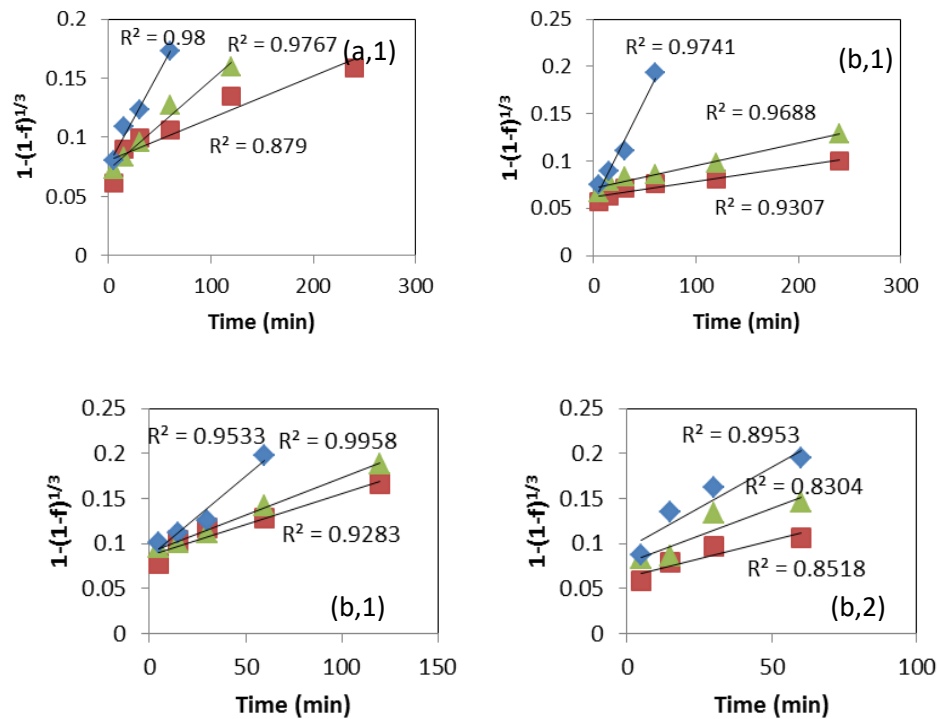
Figure 3. XRD pattern laterite roasted in air condition (a) anthrasit (b) carbon raiser at 1000^oC for 240 minutes. [Q: quartz; O: olivine; H: hematite; M: magnetite]
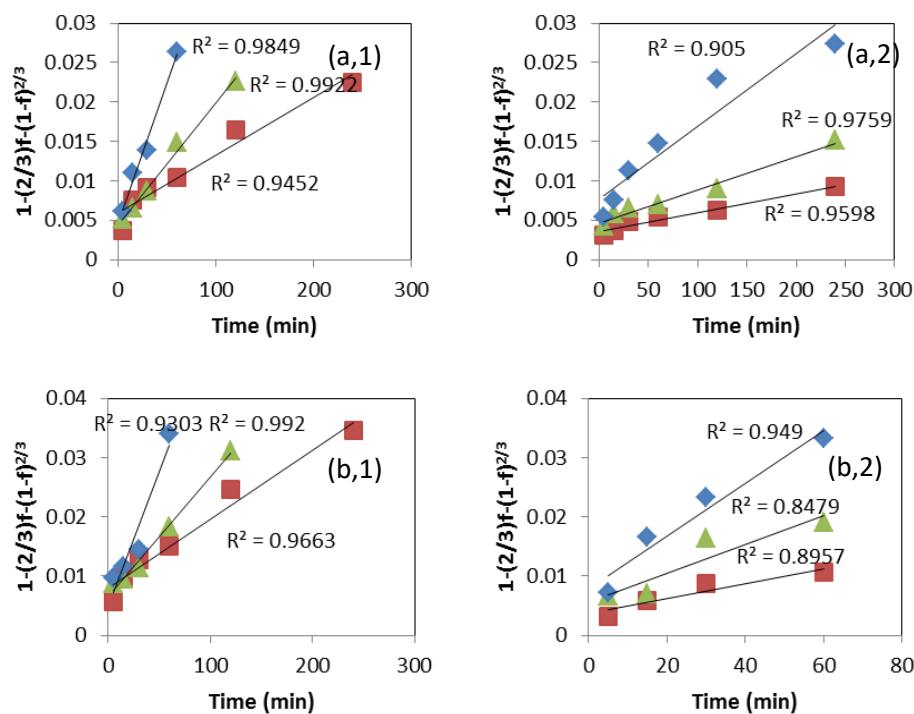
3.3.   Kinetic analysis

For the kinetic analysis of the experimental results, the kinetic model equations (2) – (3) have been applied to the experimental data for the temperatures of 800, 900, and 1000^oC. The graphical representation of the fitting of experimental data to the kinetic model were shown in Figure 3 and Figure 4.

   Based on the simulation, both models could represent the reduction process well enough because the error in the data fitting process was small enough for both model applied. However, based on literature study, the diffusion model was considered as the model that could represent the process. It also fitted with the reason why the reaction stopped at a certain time. The kinetics parameters obtained from evaluation of the data using diffusion model was listed in Table 3. The variation of activation energy means that the reaction mechanism happened is different for each reductant and atmosphere condition. The reaction mechanism differences happened because the reactions which took place consist of various step such as carbon oxidation, reducing gas diffusion, and reduction reaction hence the reaction was very complex.

Figure 4. Applications of the sphere particle geometry model to the experimental data of sample reduced with anthracite coal (a), and carbon raiser (b) in air atmosphere (1) and CO_2 atmosphere (2) at temperature of reduction of 800 (■), 900 (▲), and 1000°C (♦).

Figure 5. Applications of the Ginstling-Brounhstein diffusion model to the experimental data of sample reduced with anthracite coal (a), and carbon raiser (b) in air atmosphere (1) and CO_2 atmosphere (2) at temperature of reduction of 800 (■), 900 (▲), and 1000°C (♦).

Table 3. The value of Activation Energy (E_a) dan k_0 from Simulation of Ginstling – Brounhstein Diffusion

Reductant Type	Atmosphere			
	Air		CO$_2$	
	k_0 (1/min)	Ea (kcal/mol)	k_0 (1/ min)	Ea (kcal/mol)
Anthracite coal	0.3182	17.4445	0.1083	18.1217
Carbon riser	0.5366	18.1169	0.5714	18.0832

4. Conclusion

From the results the following conclusions were drawn:

1) Carbon raiser is potential to replace coking coal in the NPI production.
2) Both model applied were good at representing the experimental data, but Ginstling-Brounhstein diffusion model was considered better at representing the process because it has relatively smaller error and was supported by literature study.
3) From applying Ginstling-Brounhstein diffusion model, the obtained value of activation energy was varied around 17.44 kcal/mol to 18.12 kcal/mol depends on the type of reductant and the reduction atmosphere used.

Acknowledgements

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