Nickel Laterite Reduction Using Bioreductor from Coconut Shell Charcoal: An Approach to Create Zero Carbon Cycle in Nickel Pig Iron (NPI) Production

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Abstract—Nickel is an indispensable material in metal industries. As the third biggest country possessing nickel laterite resource, Indonesia has strategically inherited 15% of nickel laterite in the world. Nickel Pig Iron (NPI) is one of nickel products involving massive high-grade metallurgical coke consumption that is commonly being used to recover nickel from low grade lateritic ore. Concerning on the carbon dioxide emission, replacement of the coke using bioreductor has been developing by some researchers. One of the alternatives is coconut shell charcoal that has been studied and developed. Producing around 3 million tons of coconuts by 2014, Indonesia owns a high potential to provide bioreductor. Study on the optimization of the bioreductor performance has been conducted by exploring several variables, i.e., temperature (in the range of 800 – 1000 oC), composition of the bioreductor (from ratio 1:3, 1:4, and 1:5), and particle size of the samples. As for a comparator, anthracite was chosen to represent the metallurgical coke with its high fixed carbon content. XRD and gravimetry were applied to justify the phenomenon as well as to predict the kinetics of the nickel laterite reduction. By replacing the metallurgical coke, indeed the creation of zero carbon cycle can be realized in the nickel pig iron processing. Moreover, providing the abundance to the next generation can be established.

Keywords—environment; laterite; nickel; reduction; sustainable

I. INTRODUCTION

Nickel is a transition element which has properties of ferrous and nonferrous metal properties [1]. Approximately 65% of nickel are used to manufacture stainless steel, while another 12% consumed to super-alloy or nonferrous alloy industries [2]. Nickel deposit comes in association either with iron (nickel laterite) or sulfur (nickel sulfide). About 58% of nickel demand is supplied by sulfide ores, although 78% of nickel deposit lies in laterite ores [3].

Nickel laterite is not used as main nickel source, possibly because of its low nickel content and complex mineralogy which disabling its feasibility to physical beneficiation [4]. Indonesia, however, has abundant deposits of laterite ores with 15% possession in the world [3]. Breakthrough comes in 2005 when China began to produce Nickel Pig Iron (NPI) which is a product targeted at stainless steel industries, containing both nickel and iron [5].

Massive high-grade metallurgical coke consumption is commonly being used to produce NPI from laterites which consequently produce enormous carbon dioxide emission. Concerning on the carbon dioxide emission, replacement of the coke using bioreductor has been developing by some researchers. Recently in 2015, Chen et al. studied the reducing mechanism within laterite production using torrefacted biomass [6].

Producing around 3 million tons of coconuts by 2014, Indonesia owns a high potential to provide bioreductor [7]. Based on this fact, this study tried to explore coconut shell charcoal performance in reducing nickel laterite. As for a comparator, anthracite was chosen to represent the metallurgical coke with its high fixed carbon content. XRD and gravimetry were applied to justify the phenomenon as well as to predict the kinetics of the nickel laterite reduction.

II. MATERIALS AND METHODS

A. Laterite Ore

Laterite ore was obtained from Pomalaa, South East Sulawesi, Indonesia. XRF analysis (Thermo Scientific Niton XL3t) shows that the sample has high Fe and Si content (Table 1). XRD analysis shows a pattern (Fig. 1)
which suggests that the ore is mainly composed of clinochlore (Al2H8Mg5O18Si3), lizardite (H4Mg3O9Si2), and goethite (FeHO2).

### TABLE I. XRF RESULTS OF NICKEL LATERITE SAMPLE

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</thead>
<tbody>
<tr>
<td>36</td>
<td>45</td>
<td>1.53</td>
<td>6.69</td>
<td>0.18</td>
<td>0.6</td>
<td>1.21</td>
<td>1.49</td>
</tr>
</tbody>
</table>

**Fig. 1. XRD pattern of nickel laterite sample**

**B. Reductors**

Anthracite ore was obtained from LIPI Lampung, Indonesia. Coconut shell charcoal was obtained from Jalan Kaliurang, DI Yogyakarta, Indonesia. Proximate analyses of the reductors are given in Table 2.

### TABLE II. PROXIMATE ANALYSIS OF ANTHRACITE AND COCONUT SHELL CHARCOAL

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>2.5</td>
<td>2.3</td>
<td>7.4</td>
<td>87.9</td>
</tr>
<tr>
<td>Coconut Shell</td>
<td>3.7</td>
<td>6.0</td>
<td>13.2</td>
<td>77.2</td>
</tr>
</tbody>
</table>

**C. Sample Preparations**

Both laterite and reductors were crushed and screened using standard ASTM sieve screen to obtain particle size of -100+120 mesh. Meanwhile, oversize of coconut shell charcoal was also screened to obtain particle size of -60+80 mesh. Laterite and reductant were mixed together with reductant: laterite ratio of 1:4 while the coconut shell charcoal sized -100+120 mesh was also mixed with ratio of 1:3 and 1:5. Mixture of 5 grams was taken, added by 3 mL of distilled water, and then shaped into ball pellet. Pellet was dried at 90°C for 2 hours, and then continued at 110°C for 3 hours.

**D. Reductions**

Muffle furnace with heating rate of 20°C/min was used to reduce the pelletized samples. Muffle was heated into the desired temperature and then 15 pellets within 5 ceramic crucibles were charged into the muffle. Each of ceramic crucibles represents reducing time of 5, 15, 30, 60, and 120 minutes. Once the reduction process reached the designated time, the representing crucible was taken out of the furnace and the samples within were cooled to room temperature inside enclosed compartment to prevent re-oxidation of samples.

**E. Measurements**

Pelletized samples were weighted before and after reduction at room temperature. As for XRD, one ceramic crucible containing 2 pellets were charged inside muffle furnace and heated for 2 hours. Certain pellets with highest mass loss percentage were chosen to represent certain data points. The chosen pellets were then grounded to be analyzed by XRD.

### III. RESULTS AND DISCUSSION

**A. Comparison of Reduction by Anthracite and Coconut Shell Charcoal**

Fig. 2 and Fig. 3 shows the XRD patterns of nickel laterite reduced by anthracite coal and coconut shell charcoal at different reduction temperatures. Magnetite (Fe3O4) peak increased as the temperature of reduction rises, which means the reduction reaction of iron bearing mineral proceed more complete. It is also shown in these figures that peaks found in both laterite reduced by anthracite and coconut shell charcoal were similar, which means that reduction by anthracite and coconut shell charcoal follows similar mechanism. Furthermore, magnetite intensity of laterite reduced by coconut shell charcoal was higher in both temperatures, which means that coconut shell charcoal may has better capability to reduce laterite than anthracite.
Fig. 2. XRD pattern of nickel laterite reduced by anthracite coal at 1000°C (a) and 800°C (b) for 2 hours

Fig. 3. XRD pattern of nickel laterite reduced by coconut charcoal at 1000°C (a) and 800°C (b) for 2 hours

B. B. Reduction Mechanism

There are several reactions which may occur in the pellet while it was heated as shown in the equations below.

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 \quad (1) \\
CO_2 & \rightleftharpoons CO + 0.5 O_2 \quad (2) \\
CO + Me.O & \rightarrow CO_2 + Me.O - I \quad (3) \\
C + Me.O & \rightarrow CO + Me.O - I \quad (4)
\end{align*}
\]

Equation (1), (3), (4) shows the oxidation-reduction reaction which occurs in the pellets. Equation (3) and (4) specifically points out the reduction of metal oxides (Me.O) which may occur either by gaseous carbon monoxides, or by solid carbon. Equation (2) is an equilibrium reaction which occurs in the gaseous state within muffle furnace. As reaction involving solid pellets will affect the mass of pellet, gravimetry will be applied to study the phenomenon.

Fig. 4 shows that varying reductor particle size did not significantly affect the reduction percentage, which means that reduction phenomenon was not affected. As we know, when the size of carbon was bigger, then the surface contact between carbon and laterite should be smaller. But, data shows that reduction was not affected, which means that most reduction of laterites follows reaction (3) not (4). This finding was different from coal-based reduction [8], in which reaction (3) and (4) occur simultaneously. Possibly, the reason for this phenomenon was because bioreductor did not provide good solid-solid interaction, in which makes laterite and reductor did not dissolve each other.

Varying particle size should also affect the pores needed by O2 and CO to diffuse through pellet. However, as carbon was burned when comes into contact with O2 and only constituting one-fourth of the pellets, it turns out laterite was blocking the diffusion, not the solid carbon.

Fig. 5 also shows that varying composition did not affect the reduction percentage. However, mass loss of pellet definitely was affected, as a reduction percentage was calculated as mass loss divided by sum of maximum reduction and maximum combustion. This finding may conclude that reactions (1) and (3) have intercorrelation, which means that reaction (1) cannot proceed without oxygen supplied by (3) and reaction (3) cannot proceed without CO provided by (1) and equilibrium dependencies. However, as reduction percentage in the pellet was provided by both reduction and combustion, mass loss by reduction in one of those experiments may be higher than others. X-ray diffraction data will be necessary to finalize the conclusion of hypothesis mentioned above.
C. Reduction Kinetics

Kinetics of reduction was evaluated by Ginstling-Brounshtein model [9], as reaction (1) and (3) have inter-correlation and are diffusion controlled was being assumed. In this kinetics model, slopes of $\Omega$ versus time were calculated to determine the kinetics. Table 2. shows that higher temperature will produce higher diffusion kinetics. This also corresponds with XRD data mentioned before.

$$\Omega = 1 - 2/3 r - (1-r)^{2/3} \quad (5)$$
$$\Omega = kdt \quad (6)$$

Where, $r$ represents reduction percentage and $kd$ denotes diffusion reaction rate constant.

### TABLE III. DIFFUSION RATE CONSTANT (KD) FROM GINSTLING-BROUNHSTEIN REGRESSION

<table>
<thead>
<tr>
<th>Reduction Temperature [°C]</th>
<th>Time [minutes]</th>
<th>$\Omega$</th>
<th>$k_d * 10^4$ [min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>5</td>
<td>0.0153</td>
<td></td>
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<tr>
<td></td>
<td>15</td>
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<td>60</td>
<td>0.0431</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>5</td>
<td>0.0204</td>
<td>6.9248</td>
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<tr>
<td></td>
<td>15</td>
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<td></td>
<td>30</td>
<td>0.0380</td>
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<tr>
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</tr>
<tr>
<td>1000</td>
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<td>0.0341</td>
<td>10.1062</td>
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<td>15</td>
<td>0.0421</td>
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<tr>
<td></td>
<td>30</td>
<td>0.0626</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0886</td>
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</table>

IV. CONCLUSIONS

Reduction carried out in this experiment concludes that reduction was not affected by particle size of reductor nor reductor compositions. Reduction however, proceeds better with higher temperatures, both in kinetics and yield. However, in this research, data on ratio will be able to be better comprehended if the yield of reduction was analyzed by better instrumentation. BET test of pellets was also an option to better understand the progression of surface area within pellets while being reduced.

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REFERENCES


