

# Effects of temperature on the direct reduction of Southeast Sulawesi's limonite ore

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**Abstract.** Mining industry is one of the most important industries for the improvement in people's value in daily lives. Indonesia has abundant mineral resources. Nevertheless, these minerals are still in the depths of the earth and need to be explored so that the minerals are on the surface of the earth. In addition, it is necessary to also extraction process to be more efficient in the next process. Therefore, the method of mineral extraction needs to be further developed to obtain optimal results with the best use of energy but at the most competitive cost. In this study, the objective is to know the effect of reduction temperature on the increase of nickel contents in nickel laterite process using a pyrometallurgy extraction which will be performed in the varying temperature of 700°C, 800°C, 900°C, and 1000°C. The mixture contains coal reducer which will reduce iron metal and supposedly increase the nickel contents in nickel laterite ore. Moreover, Na<sub>2</sub>SO<sub>4</sub> will be added as a constant variable where the sulfur in Na<sub>2</sub>SO<sub>4</sub> is known to help extracting the nickel laterite. The tests include XRD, AAS, and proximate and ultimate test from coal. The result of this study shows that 700°C is the optimum temperature in doing the nickel laterite reduction. Apart from some factors that affect the final result, it is only at the temperature of 700°C that the nickel contents facing an increase from 1.16% to 1.18% after being reduced in a muffle furnace for an hour.

## 1. Introduction

Metallic minerals inside the soil can be considered raw and needs further processes, so that it can be utilized properly. One of the processes is extraction which is a method of purifying the metal by separating it between the valuable minerals and the impurities. The process can also increase the content of valuable metal inside the minerals or unrefined ore. This study will discuss nickel, which its demands keep in rising around the world, and its mining process which cost less energy because it can be found easily on the soil surface.

The majority of the world's nickel demands are supported by nickel sulfide deposit [1]. It also needs to be known that the nickel sulfide deposit is only 28% of the total world's deposits, and the rest of 72% is nickel laterite. One of laterite types is limonite ore which has low-grade of nickel



content. Indonesia's nickel deposit in the form of laterite oxide is estimated to reach 12% of world's nickel laterite deposit. In its function, nickel is widely used as an element that contributes to the manufacture of stainless steels, catalysts, and special steels, such as tool steel and protective steel [2].

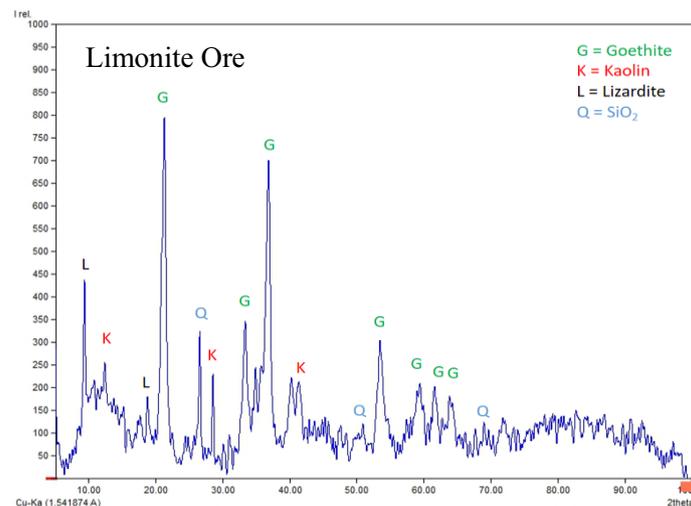
Until this day, a low-grade nickel ore, like limonite, was still couldn't be processed effectively. Whereas, the volume of nickel limonite usually was 2-3 times bigger than the volume of saprolite. With this condition, the usage of limonite as a nickel sources through the extraction process to increase the grade of nickel inside, would be more possible. Limonite ore contains some of metallic elements like nickel, cobalt, and also ferrous with almost same grade like ferrous ores in common, which is around 60% of ferrous inside a limonite. In everyday life, we could see the application of nickel e.g. for stainless steel making, catalyst, and also in making of specific steel (like tool steel and shield steel) [3].

There are some factors that affect the effectiveness in increasing nickel content in laterite ore i.e. the pellets formation process where the weight and the diameter will affect the percentage of adding  $\text{Na}_2\text{SO}_4$  as a chemical element for leaching process, and the temperature where the oxidative roasting and the reduction of nickel laterite is done. From those factors, an experiment has been done in varying situations and previous measures. In this study, the author will try to do nickel laterite extraction in order to increase the nickel content using some variables that have been mentioned above. The reduction temperature and condition when reducing the laterite will be the prime variable in this study.

## 2. Materials and method

### 2.1. Materials

Limonite ore samples used in the study carry out initial characterization by XRD test. Figure 1 provides the XRD test result of nickel ore. From the data in figure 1 it can be seen that the Fe contents in the nickel limonite sample were considered as high. As for the nickel contents, about 1.16% in nickel limonite which is a low-grade ore, have fitted the required range of 0.8% - 1.5%. Based on the composition phase in nickel limonite sample that was used, some phases could be seen, such as goethite ( $\text{FeO}(\text{OH})$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), lizardite ( $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ ), and quartz ( $\text{SiO}_2$ ). This study was in accordance with Connor and his colleagues' research [4] that inside the nickel laterite, which has not been reduced yet, contains many goethite, kaolinite, and lizardite. Moreover, in the solution, Fe was oxidized and settled as a ferric-hydroxide and eventually formed some minerals like goethite, hematite, magnetite, and limonite near the surface.



**Figure 1.** XRD pattern of initial nickel lateritic ore.

While for the quantity test, the AAS test is performed to see the Fe and Ni contents in the limonite

ore. The AAS test result can be seen in Table 1.

Beside the limonite, coal as a reductor was also tested with proximate and ultimate test to see the composition of the coal. The test results can be seen in Table 2.

**Table 1.** Atomic absorption spectroscopy analysis of iron, nickel, and cobalt content from limonite ore.

Element	Content (%)
Fe	41.46
Ni	1.16
Co	0.08

**Table 2.** Proximate and Ultimate Analysis of Coal.

Parameter	Content (% adb)	Standard Method
Proximate Analysis		
Moisture in air dried sample	7.26	ASTM D.3173
Ash	15.87	ASTM D.3174
Volatile Matter	16.44	ASTM D.3175
Fixed Carbon	60.43	ASTM D.3172
Ultimate Analysis		
Carbon	64.02	ASTM D.5373
Hydrogen	3.11	ASTM D.5373
Nitrogen	0.60	ASTM D.5373
Total Sulphur	0.08	ASTM D.4239
Oxygen	16.32	ASTM D.3176

## 2.2. Experiment

The process included the sample preparation (initial characterization and ball milling), the reduction, and the final characterization. The sample preparation included preparing nickel laterite ore type limonite that was going to be used. After the laterite ore has been prepared and already measured to the required size and quantity, the sample then was mixed with the coal reducer using ball milling method. After that, the sample was ready for the extraction process to increase the nickel content in laterite ore using muffle furnace. The carbothermic process or what is usually called the reduction was done with the approximate temperature of 700 to 1000°C. Then, it was followed by the sample characterization using XRD and AAS tests and analysis.

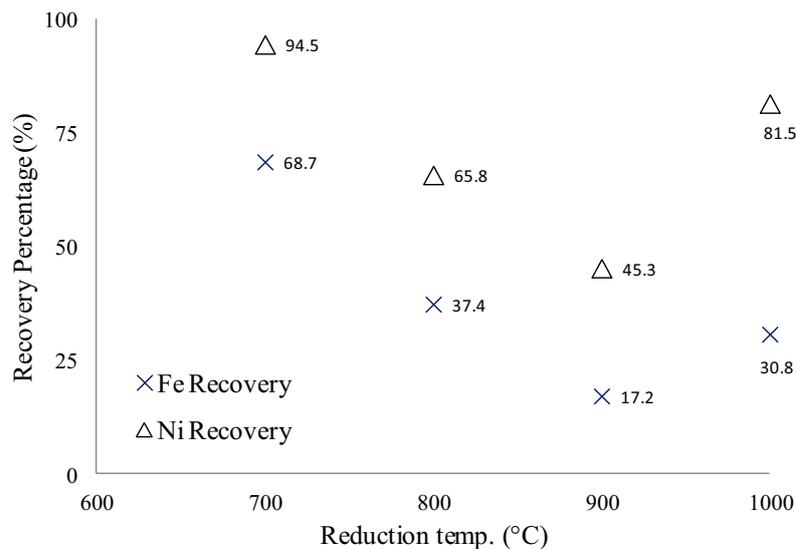
## 3. Result and discussion

In the making of pellets, nickel limonite was mixed with coal reducer using a ball mill. After the nickel limonite and coal reducer have been mixed properly, sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and bentonite, as the binders, were added. Then, pellets were made with the weight of 10 grams each. In this study, the reduction temperatures were 700°C, 800°C, 900°C, and 1000°C. Each reduction process in each temperature was held for an hour. Then, the obtained product was analyzed using XRD and AAS, as shown in table 3 and figure 2.

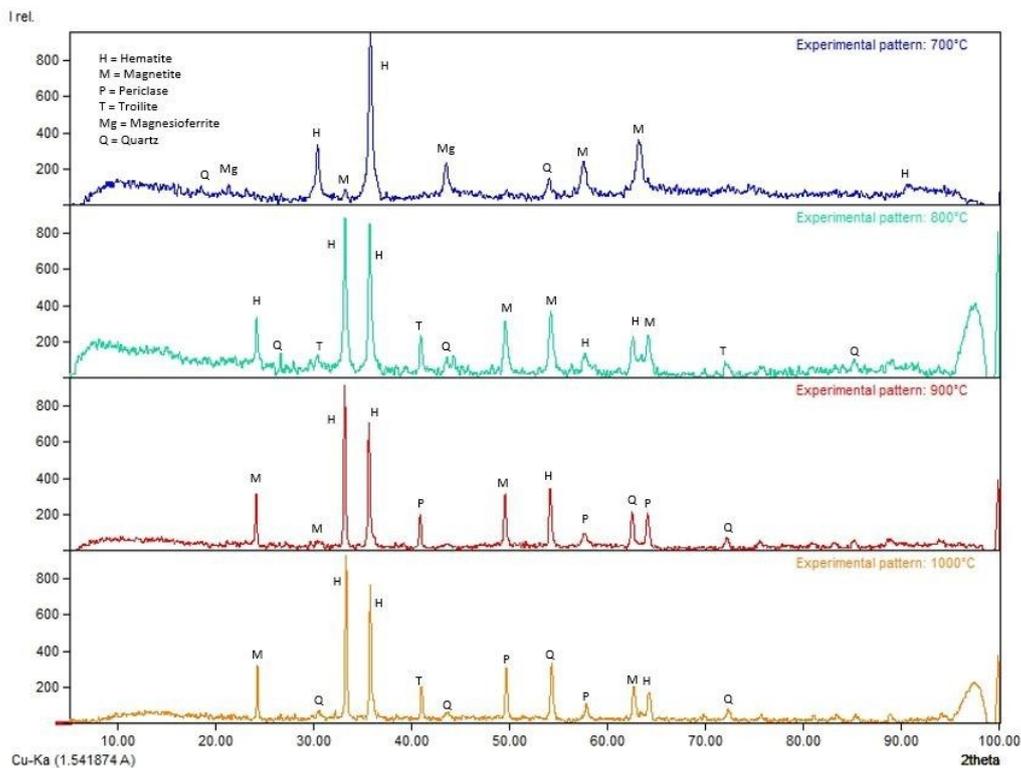
In the nickel laterite extraction research performed by M. Valix and colleagues [5], it was mentioned that starting at temperature above 600°C is the most optimum temperature in the nickel limonite reduction and held for about 30-60 minutes. The recovery calculation showed that the temperature of 700°C was the optimum temperature in increasing the nickel contents in the reduction result sample.

**Table 3.** Comparison of nickel and iron content of limonite between ore and after reduction samples.

Element	Ore	After reduction				Unit
		700°C	800°C	900°C	1000°C	
Fe	41.46	30.57	16.67	7.61	13.49	% w/w
Ni	1.16	1.18	0.82	0.56	1.00	% w/w
Co	0.08	0.07	0.06	0.05	0.06	% w/w

**Figure 2.** Result of Nickel Recovery in a graphic (Reduction Temp. vs Recovery Percentage).

However, there was no significant increase in nickel contents at all four temperatures. Only at the temperature of 700°C that the nickel contents increased by 0,02% and the recovery of 94,5% occurred because of these following possible reasons. In the nickel laterite extraction research performed by Xueyi Guo and colleagues [6], it is mentioned that starting at temperature above 600°C is the most optimum temperature in nickel limonite reduction and being held for about 30-60 minutes, but unfortunately, it took too long holding time on this research. First, the reduction process took place in the muffle furnace was too long. In each temperature of 700°C, 800°C, 900°C, and 1000°C, the nickel spent approximately 5 hours of reduction in the muffle furnace. This certainly made the reducer, which should reduce the Fe and was expected to increase the nickel content, drained out before it was properly reduced. The heating Fe was also too long that cause the metals to re-oxidize, which probably happened when the temperature was declined after being held for an hour. Consequently, those factors made the coal reducer drain out, the Fe re-oxidize inside the sample, and the nickel metallization obstruction. Besides, the magnetic elements inside the nickel limonite sample that were not separated made it possible for impurities to exist in the sample and eventually decrease the valuable minerals contents that were expected to be obtained.



**Figure 3.** XRD pattern of nickel laterite after the Reduction at 700°C-1000°C.

The reduction temperature of 700°C was the only temperature that was capable of increasing the nickel contents. It can be seen in the XRD test result in Figure 3. It shows that hematite phase ( $\text{Fe}_2\text{O}_3$ ), was reduced quite a lot and it changed most of the hematite into magnetite ( $\text{Fe}_3\text{O}_4$ ). According to a research by J. Lu and colleagues [7], goethite phase that existed in nickel laterite since the beginning was going to undergo some dehydroxylation at the temperature around 300°C and being reduced to become a hematite. Afterwards, hematite began to reduce to become magnetite at the temperature of 500°C. As for magnesioferrite ( $\text{Fe}_2\text{MgO}_4$ ), it was formed by the reduction of MgO and reacted to Fe. Even so, the quartz phase was not yet being reduced because the minimum temperature of silica reduction was 1200°C which was mentioned by Samadhi [8].

At the temperature of 800°C, hematite phase was still the dominant one. Then, it was followed by troilite, magnetite, and quartz phases. This means that hematite phase has not been reduced properly into magnetite. The phase formed after the reduction from 700°C and above was magnetite which was the result of hematite reduction. For troilite ( $\text{FeS}$ ) phase, after being added by  $\text{Na}_2\text{SO}_4$  which contains sulfur element combine with a long duration of heat, made the Fe face a breakdown or an expansion with  $\text{Na}_2\text{SO}_4$  that made the sulfur easily react with other metals inside the nickel laterite ore. Nevertheless, quartz phase was only reduced under 1200°C, so that the quartz phase would still be formed.

The XRD test result at the temperature of 900°C decreased the magnetite contents from about 13%, from temperature of 800°C, to  $\pm 6\%$ . Nonetheless, in periclase (MgO) phase, the contents which were 7.2%, was increasing compared to the initial sample. It might happen because the reduction was done imperfectly. The periclase has not been fully reduced and it reacted with other elements in nickel laterite. As what has been seen before at temperature of 700°C, the MgO phase has reacted and reduced better, so that it formed magnesioferrite ( $\text{Fe}_2\text{MgO}_4$ ) phase. In nickel laterite ore that contained high periclase (MgO) and low magnetite (Fe) reduction samples like the one in XRD test at the temperature of 900°C, the nickel reduction was very low. That was due to the tendency of the nickel to replace the magnesium in magnesium silicate which can be seen in Johnny et al. research [9]. Also, the quartz ( $\text{SiO}_2$ ) phase was still formed although it continued to decrease compared to the XRD result at 700°C and 800°C.

In the temperature of 1000°C the nickel and iron contents which were previously decreasing from 700°C to 800°C and 900°C, showed an increase at 1000°C. However it was still lower than the initial sample and the reduction sample at 700°C. The same result appeared in the XRD test also where the content of magnetite and quartz phases were increasing compared to the previous sample at 900°C. Meanwhile, the formation of plenty MgO decreased the Ni reduction, so that Ni reacted with magnesium silicate. Moreover, troilite (FeS) reappeared at the temperature of 1000°C eventhough only a small amount of it. For quartz phase, the contents were quite many and kept on increasing as the theory said that this phase will be reduced when the temperature hits 1200°C.

#### 4. Conclusion

Nickel laterite ore was not properly reduced because the test result shows that the nickel contents do not increase significantly. Even though the reduction was not performed well enough from the four different temperatures, the temperature of 700°C was the most significant one since Ni content has increased from 1.16% to 1.18% and gained the highest nickel recovery of 94.8%. The XRD test result showed that reduction at 700°C was able to reduce hematite (Fe<sub>2</sub>O<sub>3</sub>) into magnetite (Fe<sub>3</sub>O<sub>4</sub>) quite well in terms of the magnetite content that was formed.

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