Preliminary study on the use of rice husk as a reducing agent in iron sand reduction

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Abstract. Titanium is a valuable mineral that has many advanced functions in our daily lives. This has caused the demand for this mineral to increase over the years. Researchers have long studied the use of reduction methods using coal in increasing titanium content in iron sand before further processing. Considering the sulfur content in coal which causes various excess problems in the reduction process, then in this experimental study we tried to examine the potential of rice husk as a reduction agent in the iron sand reduction process. This study includes several stages, namely roasting and reduction processes with or without the addition of Na₂SO₄, and magnetic separation. The weight ratio of iron sand and rice husk used in this study was 10:1, while the reduction process was carried out at a temperature of 700°C for 60 minutes, followed by the magnetic separation process. Characterization of samples was carried out using XRD and ICP-MS. And the final results obtained after magnetic separation showed that the Ti content in the product tail was higher than the Ti content in the concentrate, which was 0.692% and 0.221% respectively.

Keywords: Iron sand, rice husk, reduction, titanium.

1. Introduction
In Indonesia, Titanium is one of the chemical compounds that have a large number of sources. Titanium is used in many applications in daily life. It is because the characteristic of Titanium is really forceful. Titanium is as strong as steel but much less dense. Titanium is mainly used in spacecraft, aircraft, and missiles. Due to their high tensile strength to density ratio, high corrosion resistance, and the ability to withstand the extreme temperatures, titanium is used for several advanced applications such as sensor[1], photovoltaic[2], and medical applications [3].

It has been observed that Iron sand is the part of metal mining material with the sedimentation process of sand-sized material containing iron element. It contains many oxide compounds, such as ilmenite (FeTiO₃), magnetite (Fe₃O₄), hematite (Fe₂O₃), and many more [4].
Pyro-metallurgy is the method that used in this study. it is very necessary to use redactor agent to be able to do the reduction process. Initially the reduction agent commonly used in this process is the use of coal, but its use causes serious pollution impacts to the environment as well as the limited resources to be renewed.

To solve the environmental issue, the mining and industrial sectors associated with the metal processing are expected to reduce coal consumption due to the decreasing the non-renewable energy consumption and greenhouse gas emissions. The alternative way that can be implemented to break this issue is using biomass energy or waste from natural resources to replace the role of coal as a reducing agent, such as rice husk.

2. Experimental method

2.1 Materials

To support this research process, there are some equipment required including furnace, thermocouple, digital scale and also followed by XRD and ICP-MS at BATAN for characterization process. Then, the materials that used in this study were iron sand from West Java as the raw material, rice husk as the redactor agent as well, bentonite for palletizing process and Na$_2$SO$_4$.

From the XRD result as described at Figure 1, the iron sand ore has hematite, magnetite, and magnesium titanate phases.

![Figure 1. XRD analysis results of initial sample of iron sand.](image)

ICP-MS is also done to investigate the quantitative data of the initial sample method, and the result as shown in Table 1 indicated that the percentages of the Fe and Ti that consisted in the initial condition of the iron sand. It clearly proved that there is Ti content in that sample even the percentage is really small.

| Element | Fe  | Ti  |
|---------|-----|-----|
| Content (%) | 51.772 | 2.872 |

Table 1. The contents of Ti and Fe elements in iron sand ore are measured using ICP-MS.
2.2 Experiment
The samples were prepared with each of them were crushed up to #150. Before we add the Na$_2$SO$_4$, we did the initial characterization test to know the phase and the contention of the raw iron sand. After sample preparation finished, iron sand and bentonite and Na$_2$SO$_4$ were homogenized and mixed into 2 sample with the ratio ratio: 10:1:0 and 10:1:1 respectively. Then after that, the crucible was used for purpose of roasting process, at 700°C for 1 hour. And finally, the main process which is the reduction process was done before the XRD and ICP-MS for the characterization step were finished.

3. Results and discussion
The ICP-MS test results on samples that have undergone a roasting process, as shown in Table 2, show an increase in Fe and Ti levels. This is presumably caused due to reduced water content, volatile matter and other oxides such as Ca and Na oxides. This phenomenon is in line with the results obtained in previous studies where the roasting process is carried out on iron ore [5], [6] or limonite ore [7].

Table 2. The contents of Ti and Fe elements in iron sand after roasting process that measured by using ICP-MS.

| Element | Fe    | Ti    |
|---------|-------|-------|
| Content (%) | 52.659 | 4.786 |

![Figure 2. XRD analysis results of sample after reduction without Na$_2$SO$_4$.](image)

The reduction process, which is the main step of this experiment proceed the characterization of the initial sample of iron sand to purposed or to order to know the changes in the compounds form that occurs after the reduction at temperature 700°C with reduction time in 1 hour. The sample is separated into two, sample 1 with the addition of Na$_2$SO$_4$ and sample 1 without the addition. And after the magnet separation, the purposed to collect the powder which stayed on the contact surface of the magnetic separator and it also called as the concentrate the results showed in the qualitative and quantitative result.
Figure 3. XRD analysis results of sample after reduction with Na$_2$SO$_4$.

From the XRD result between sample with and without addition of Na$_2$SO$_4$ as seen in Figure 2 and 3, the results show the similar pattern in both of hematite and magnetite phases and they are still presenting the highest peak of the phase. Those phases would contain the Fe and Ti within the sample. Compare to the result of the quantitative result shows the result of Ti Content and Fe with this following Table 3.

| Sample                        | Fe (%) | Ti (%) |
|-------------------------------|--------|--------|
| Iron ore without Na$_2$SO$_4$ | 33.12  | 1.49   |
| Iron ore with Na$_2$SO$_4$    | 31.02  | 2.9    |

It can be seen from the table, the sample with the addition of Na$_2$SO$_4$ has higher number of Ti compared to those who are not. This is suspected due to the ineffectiveness of the mixed rice husk to give the needed support to reduce the hematite into magnetite. The ineffectiveness is suspected due to the accumulation of high gas of rice husk after being burned.

In the quantitative test, the data shows the increasing of titanium content in the tailing after being separated by magnetic separation. The Ti content in tailing is much higher than in concentrate. Because, mostly, the element that successfully magnetized is the higher Fe content. As the result of the reduction process shows that the sample 2, or the one who proceed with the addition of the Na$_2$SO$_4$, has the higher recovery for the Ti Content, then, the researcher decided to continue the quantitative test of the sample after being separated. The results of the magnetic separation are named as the concentrate and tail. Concentrate usually has the higher Fe content and on the other hand, the tail is the one that consists higher Ti. The numbers of each result show in Table 4.
The contents of Ti and Fe elements in iron sand after magnetic separation that measured by using ICP-MS.

| Sample | Fe (%) | Ti (%) |
|--------|--------|--------|
| Concentrate | 47.97  | 0.221  |
| Tail    | 34.22  | 0.692  |

It clearly can be seen from the result, the number of the Ti content in tail product is higher than the concentrate. This result can be the approval of the hypothesis that the Fe and Ti can be separated through the magnetic separation process and tail product should has the higher number of Ti compared to concentrate. The same result, where the content of Ti in the tail is greater than the content of Ti in concentrate, was also obtained by Jin-Fang L et al in his study to get Ti and Cr from raw ilmenite [8]. But some of the miscalculation error can be seen in this case, the Ti content that recorded before the magnetic separation has been done, the number of the reduction result has the higher number of Ti. At the first place, sample 2 underwent same procedure as sample 2, with the same amount of rice husk, reduction time differs them. With more time added to the process, more carbon monoxide gas would be observed for the reduction process. The sufficient amount of gas produced for the reduction reaction to occur. So, the miscalculated number or unexpected low number that quantitative test result may be caused by the error of the magnetic separations.

4. Conclusion
The reduction process done have been able to recover Ti content from iron sand while The weight of the added rice husk and the time have an optimum point that has to be reached but cannot be surpassed in order to get the best Ti concentration. The addition of Na$_2$SO$_4$ will increase the content of Ti, therefore, can be known as the result of transformation of hematite into magnetite phase during roasting reduction process and accelerated by rice husk as reducing gas agent.

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