INDONESIAN MINING JOURNAL Vol.27, No.1, April 2024 : 53 - 62

EFFECT OF THERMAL UPGRADING WITH VARIOUS REDUCTANTS ON SAPROLITIC NICKEL ORE: A PRELIMINARY STUDY

DAMPAK PENINGKATAN PANAS DAN JENIS REDUKTAN TERHADAP SAPROLIT: STUDI PENDAHULUAN

FATHAN BAHFIE[1,2], AZWAR MANAF[2*], WIDI ASTUTI[1], FAJAR NURJAMAN[1], ERIK PRASETYO[1,3], DIAH SUSANTI[4], WAHYU S. SIPAHUTAR[5]
[1] Research Center of Mining Technology, National Research and Innovation Agency of Indonesia
[2] Physic Departement, Faculty of Mathematics and Science, University of Indonesia
[3] Department of Chemical Engineering, Norwegian University of Science and Technology
[4] Metallurgical and Material Engineering Department, Faculty of Industrial Technology and Systems Engineering, Institut Teknologi Sepuluh Nopember
[5] Material Department, Institut Teknologi Sumatra
*Corresponding author: azwar@ui.ac.id/fath007@brin.go.id

ABSTRACT

Indonesia significantly contributes to the global electric vehicle battery market due to its substantial medium- and low-grade nickel reserves. This study utilized saprolitic nickel ore from Halmahera, Maluku, Indonesia. However, the research on saprolite needs some improvements due to its complex mineral composition, which affected on the roasting process significantly. Therefore, a thorough understanding of the properties of laterite ores is critically important, particularly concerning laterite pre-reduction processes. The ore was finely sieved to a particle size of less than 100 mesh and then heated at temperatures of 250, 900, and 1150°C with the variation of reductant (anthracite and palm kernel charcoal). Extensive mineralogical analysis was conducted using X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). The analysis of saprolite showed that it contains about 1.82% nickel, 30.47% iron, 10-20% magnesium, 4.86% aluminum, and 8.1% silicon by weight. Its mineral composition is mainly 53.1% goethite, 38.3% lizardite, and 8.7% quartz. The study found that goethite in saprolite was transformed into hematite around 250°C. At 900°C, the forsterite was crystallized, and at 1150°C, the ferronickel was formed. The transformation of lizardite is important as it affected on nickel diffusion within the iron matrix, which impacted on the material's properties. A thermal upgrading method with reductants like anthracite and palm kernel charcoal was used at lower temperatures to enhance the properties of saprolite. These findings provided valuable insights into saprolite's mineralogical composition and behavior, potentially offering improvements in various industrial processes and applications.

Keywords: microstructure, phase transformation, reductant variation type, saprolite, thermal upgrading.

ABSTRAK

Indonesia memberikan kontribusi signifikan terhadap pasar baterai kendaraan listrik global karena cadangan nikel kadar menengah dan rendah yang besar. Penelitian ini memanfaatkan bijih saprolit dari Halmahera, Maluku, Indonesia. Namun, penelitian mengenai saprolit memerlukan beberapa perbaikan karena komposisi mineral bijih saprolit yang kompleks sehingga berdampak signifikan pada proses pemanggangan. Oleh karena itu, pemahaman menyeluruh tentang sifat-sifat bijih laterit sangatlah penting, khususnya mengenai proses pra-reduksi laterit. Bijih diayak halus hingga mencapai ukuran partikel 100 mesh, ukuran optimal yang diketahui untuk bijih laterit, dan kemudian dilakukan pemanasan terkontrol pada suhu 250, 900, dan 1150°C dengan variasi reduktan (antrasit dan arang cangkang sawit). Analisis mineralogi ekstensif dilakukan dengan menggunakan difraksi sinar-X (XRD), fluoresens sinar-X (XRF), dan pemindaian mikroskop electron dengan spektroskopi dispersive energi (SEM-EDS). Analisis

Received: 16-09-2023, first revision: 28-11-2023, second revision: 29-03-2024, accepted: 24-04-2024.
DOI: 10.30556/imj.Vol27.No1.2024.1533

saprolit menunjukkan mengandung sekitar 1,82% nikel, 30,47% besi, 10-20% magnesium, 4,86% aluminium, dan 8,1% silicon menurut beratnya. Komposisi mineralnya terutama 53,1% goetit, 38,3% lizadit, dan 8,7% kuarsa. Studi ini menemukan bahwa goetit dalam saprolit berubah menjadi hematit pada suhu sekitar 250°C. Pada suhu 900°C, forsterit mengkristal, dan pada suhu 1150°C, feronikel terbentuk. Transformasi lizardit penting karena mempengaruhi difusi nikel dalam matriks besi, sehingga berdampak pada sifat material. Penggunaan metode peningkatan termal pada suhu yang lebih rendah dengan reduktor seperti antrasit dan arang cangkang sawit dimaksudkan untuk meningkatkan sifat saprolit. Temuan ini memberikan wawasan berharga mengenai komposisi dan perilaku mineralogi saprolit, yang berpotensi menawarkan perbaikan dalam berbagai proses dan aplikasi industri.

Kata kunci: strukturmikro, transformasi fasa, jenis variasi reduktor, saprolit, peningkatan secara termal.

INTRODUCTION

Nickel, recognized for its malleability, corrosion resistance, and magnetic properties, serves diverse industries, including iron and steel manufacturing, electroplating, and battery production, leading to a significant increase in recent nickel production (Butt and Cluzel, 2013; Bloomberg, 2022). Indonesia notably has 44 nickel smelters, contributing an output of 1,468,596 tons of nickel annually (Spence and Listiyorini, 2024). With substantial reserves of medium and low-grade nickel, Indonesia emerges as a key player in the global electric vehicle battery market. Nickel plays a vital role in manufacturing lithium batteries for electric vehicles. Leveraging competitive pricing and cost-efficient production, Indonesia has become a primary exporter of nickel intermediate goods to major nickel-consuming nations such as China, Japan, and South Korea (Bloomberg, 2022).The nickel market has witnessed substantial price fluctuations, with prices hitting US$45,000 per ton in March 2022. Subsequently, prices experienced a decline in July 2019, followed by a resurgence, stabilizing at an average price of US$140,000 per ton in March 2024 (Spence, 2024). According to the nickel prize, nickel in laterite has an important role as a critical element for future, such as the raw material for batteries in electric vehicles.

Nickel ore exists primarily in two forms: sulfide and oxide (laterite). While laterite constitutes 72% of global nickel resources, it only accounts for 42% of the total nickel metal supply. In contrast, nickel sulfide ore yields a higher nickel output, with a nickel content of 58% (Haryadi *et al.*, 2024). As the availability of sulfide nickel ores diminishes, exploration and exploitation of laterite nickel ores have expanded remarkably. The attractiveness of laterite nickel deposits lies in their abundant supply, cost-effective mining, convenient transportation access, and potential into various products like ferro-nickel, nickel matte, and nickel oxide (Butt and Cluzel, 2013). It is essential to categorize nickel laterite ores' chemical and physical configurations: saprolite and limonite (Kyle, 2010). Saprolite comprises minerals like goethite, lizardite, and quartz. Limonite includes minerals such as goethite, gibbsite, chromite, as well as cristobalite and protoenstatite within their substrata (Rao *et al.*, 2013; Yuwang, 2015; Rodrigues *et al.*, 2017).

The mechanical properties of nickel laterites present challenges due to their inherently poor crystalline structure and microporous nature. Physical treatment methods to improve ore quality often present formidable challenges. Consequently, pyrometallurgical extraction processes take the lead, offering potential processing for significant nickel recovery rates (Bahfie, Manaf, Astuti, Nurjaman, *et al.*, 2021; Nurjaman *et al.*, 2021; Bahfie, Manaf, Astuti, Nurjaman and Prasetyo, 2022; Bahfie, Manaf, Astuti, Nurjaman, Prasetyo, *et al.*, 2022; Bahfie, Murti, *et al.*, 2022). The intricate mineral composition of laterite ores significantly influences the roasting process. Thus, understanding the dissolution behavior of laterite ores, especially in the context of laterite pre-reduction, is important (Zhen, Hao and Peng, 2013; Zhou *et al.*, 2015, 2017; Yang *et al.*, 2016; Bahfie, Manaf, Astuti, Nurjaman, *et al.*, 2021). This research aims to investigate the thermal transformation effects on saprolite due to the saprolite already investigated in pyrometallurgy process. Through material characterization, it seeks to provide valuable reductants for the most optimal processes for the extraction and refinement of these valuable resources. The study primarily focused on the thermal sequence and resulting structural changes in saprolite, highlighting significant transformations in goethite and other phases within the material transformation.

MATERIAL AND METHODS

The study investigated saprolite ore from Halmahera, Maluku, Indonesia. The ore and reductants (anthracite and palm kernel shell charcoal) were sieved less than 100 mesh. They were mixed homogenously and pelletized into diameters of 10-15 mm. The composition of each reductant was 2.5 % from saprolite. Furthermore, the pellets were heated at temperatures of 250°C, 900°C, and 1150°C to investigate their mineral properties. The elemental analysis was performed with a Benchtop PANalytical Epsilon 3XLE X-ray fluorescence (XRF) instrument. The raw materials, ball-milled samples, and concentrates were evaluated using 200 mesh samples. The X-ray diffraction (XRD) analysis was conducted with a PANalytical X'Pert3 Powder instrument, and the data were processed with High Score Plus software. The microstructure was examined using a Thermo-scientific Quatro 6 scanning electron microscope and Energy-Dispersive X-ray Spectroscopy (SEM-EDS) at magnifications of 2000x and 5000x. All processes can be seen in Figure 1.

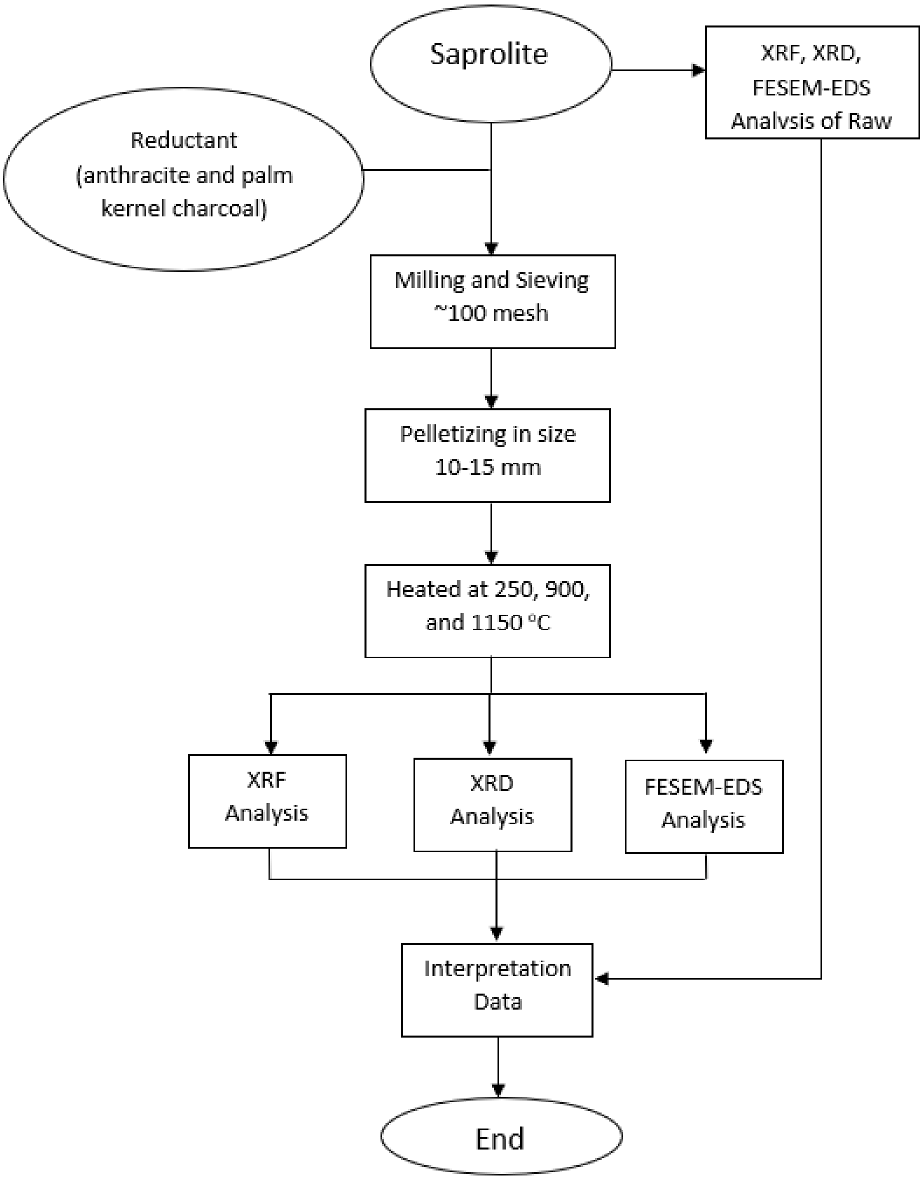

Figure 1. Flow chart of this research.

RESULTS AND DISCUSSION

Characteristics of Saprolitic Nickel Ore

Based on the data presented in Table 1, the saprolite's composition is mostly iron, and the other elements are nickel, magnesium, and silica. These percentages represent critical elements constituting the chemical structure of saprolite. However, the saprolite is not merely a simple amalgamation of these elements.

The production of nickel oxide in the saprolite occurred due to complex chemical reactions. Notably, nickel oxide interacts significantly with the iron content present in goethite and lizardite structures. It is crucial to emphasize that nickel oxide primarily forms and associates with the iron found in goethite, which underscores the dynamic nature of these chemical transformations (Bahfie, Manaf, Astuti and Nurjaman, 2021). To further validate these compelling results, it was referred to the outcomes obtained from Rietveld refinement, which are detailed in Table 2. The saprolite is mainly composed of goethite ($Fe(OH)_2$), lizardite ($H_4Mg_3O_9Si_2$), and quartz (SiO_2), as shown in Figure 2. Furthermore, this investigation highlights the crucial of specific elements within the saprolite, with iron, magnesium, and silicon being the main components that define its composition (Table 1). Notably, nickel, the main element of interest in this study, shows an exceptional association with iron and magnesium within the intricate structure of the saprolite in Figure 3. These findings provide a deeper insight into the nature of saprolite and its composition, which could have significant implications for future research in this field.

Table 1. The chemical composition of saprolite ore

	Composition (wt%)								
Ore Type	Ni	Fe	Si	Mg	Al	Ca	Cr	Mn	Co
Saprolite	1.82	30.47	16.5	18.1	4.86	0.179	0.952	0.817	-

Table 2. Rietveld refinement calculations of saprolite ore

Ore Type	Composition (%)		
	Goethite	Lizardite	Quartz
Saprolite	53.1	38.3	8.7

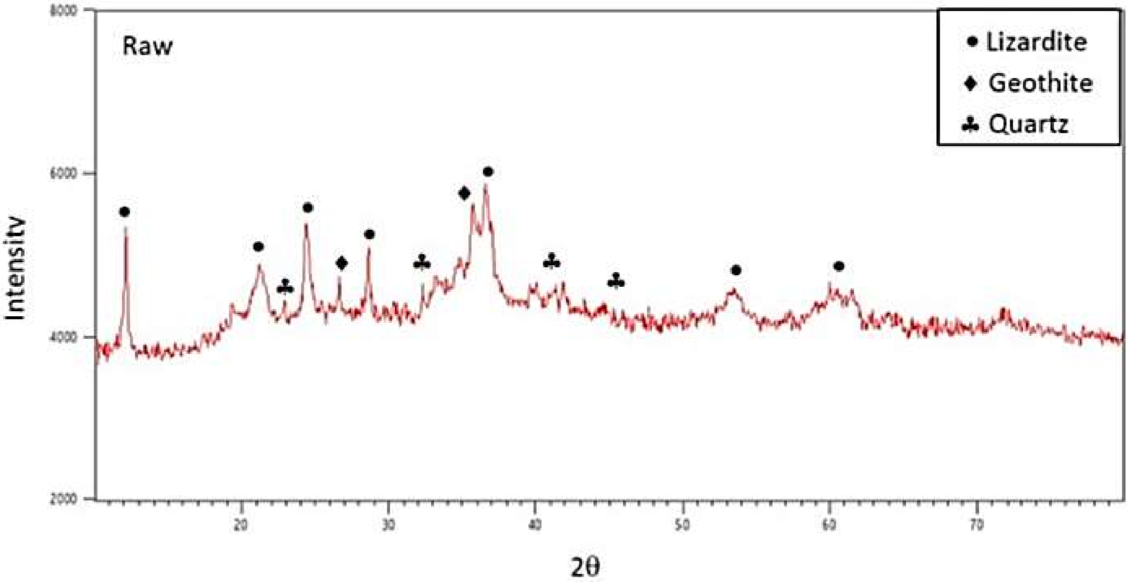

Figure 2. XRD analysis of saprolite(● = lizardite, ◆ = goethite, and ♣ = quartz).

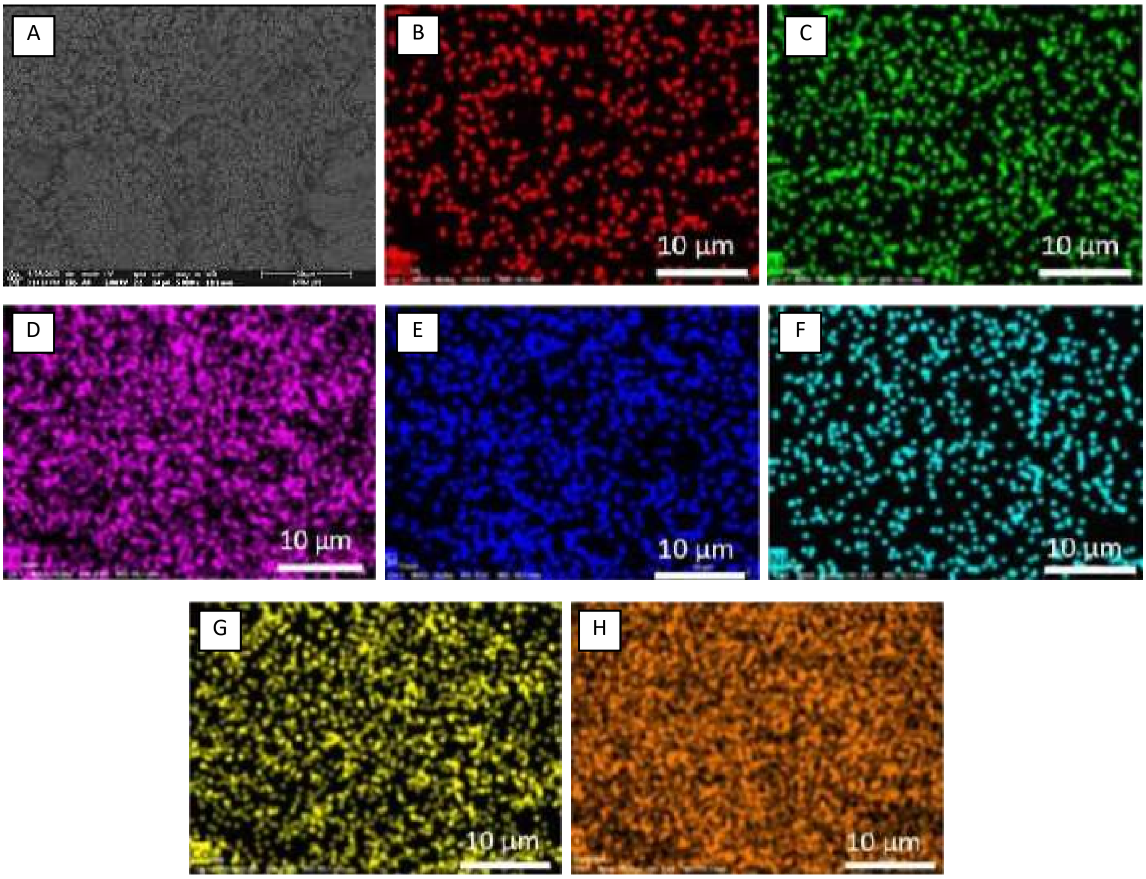

Figure 3. SEM analysis of: (A) morphology with magnification 5000x; and the mapping elements analysis of: (B) magnesium; (C) aluminum; (D) iron; (E) silica; (F) nickel; (G) cobalt; and (H) oxygen.

These revelations contribute to the dynamic interplay of elements and phase transformations occurring within saprolite under the influence of thermal processes. Understanding these mechanisms enables the potential utilization of its unique properties for a wide range of industrial applications and processes.

Phase Transformation of Saprolite During Thermal Upgrading Process

Based on the data presented in Figure 4, a comprehensive analysis of the raw material characteristics reveals a phase transformation occurring at three different temperatures: 250°C, 900°C, and 1150°C. At initial temperature of 250°C, there is a transformation from the presence of goethite to hematite, while the transformation of quartz remains unchanged. As the temperature increases to 900°C, an even more significant and fundamental transformation is observed. Once again, the goethite phase deep metamorphosis, transformed to hematite. Notably, and in agreement with previous observations, quartz stands up firmly to the effects of high temperatures, retaining its original features.

Table 3 presents the quantitative data that provide a numerical perspective, clearly illustrating the sharp decline in the proportion of goethite, as shown in Table 2. The reduction is so significant that goethite is effectively reduced to zero. This shift in material composition indicates a significant structural change, showing a transformation from a configuration characterized by hydroxide (OH) groups representing goethite to an oxide configuration. These findings reveal the dynamic nature of the material's response to different temperature conditions. The material can undergo structural metamorphosis, shedding its original composition and assuming a new configuration when exposed to thermal influences. These insights have broad implications and can inform the design and optimization of processes that rely on controlled thermal treatment of materials.

Table 3. Rietveld refinement of saprolite with carbon type (i) anthracite and (ii) palm kernel charcoal in the condition 250 °C (A), 900 °C (B), and 1150 °C (C)

Phase	Total percentage(%)					
	i			ii		
	A	B	C	A	B	C
Forsterite	-	34.8	80.2	-	46.5	87.2
Magnetite	-	54.6	-	-	44.1	-
Iron nickel	-	-	13.1	-	-	4.3
Hematite	45.5	-	-	41.3	-	-
Lizardite	21.1	-	-	27.5	-	-
Periclase	-	-	6.7	-	-	6.1
Quartz	13.8	10.6	-	11.6	9.4	2.4

The X-ray diffraction (XRD) data shows a clear transformation of goethite to hematite. These changes are consistent with the observed thermal changes, which result the mass loss at 250°C using anthracite as the reductant. When the temperature increases to 900°C and then to 1150°C, an interesting crystallization process occurs, leading to the development of forsterite and iron-nickel compounds. This transformation is well illustrated in Figure 4i B. This report provides data on the potential impacts of thermal enhancement, which could potentially increase nickel percentages. These possibilities are shown in Table 4.

Table 4. The chemical composition of iron and nickel after thermal upgrading at 1150 °C on saprolite with a variation of reductant.

Composition (wt%)		
Reductant	Fe	Ni
Anthracite	36.734	7.029
Palm Kernell Charcoal	29.718	3.043

These findings demonstrate the material's adaptability to controlled heat treatment, leading to significant structural changes, including the conversion of goethite to hematite and the formation of forsterite and iron-nickel compounds. Data in Table 4 indicates the potential to increase nickel content, which could influence various applications and processes.

From Figure 4, the thermal upgrading process with various reductants shows a similar transformation phase, both for anthracite and palm kernel charcoal. Nevertheless, ferronickel, which resulted from thermal upgrading process using anthracite as a reductant, has higher nickel content than palm kernel charcoal.

Morphology of Saprolite after Thermal Upgrading

The effect of heating the pellets at 250 °C on their phase transformation is clearly visible by using SEM-EDS analysis, as shown in Figure 4. This transformation, known as the goethite transformation, occurs when goethite evolves into the hematite phase. At the same time, a redistribution of iron occurs while nickel begins to dissociate from its structure. This initial phase causes structural changes that are reflected in the XRD analysis. This marks the transformation from lizardite to hematite, which led to the separation of magnesium from iron and nickel. As a result, the magnesium-aluminum-silica dispersion becomes clearer as the phase shift from lizardite to hematite progresses. These structural changes are supported by the XRD results. At 900 °C, the appearance of forsterite crystallization became obvious. The on going agglomeration process can be seen before reaching the next temperature phase, as depicted in Figure 4. It also confirms the appearance of iron-nickel at 1150 °C, marking the start of iron-nickel crystallization.

According to Figure 5, a similar structure of reduced pellet with various types of reductant was observed. However, the amount of ferronickel resulted from the use of anthracite as a reductant more than palm kernel shell charcoal. The different characteristics, such as fixed carbon content and reactivity of these two types of reductant, influenced the result of this thermal upgrading process.

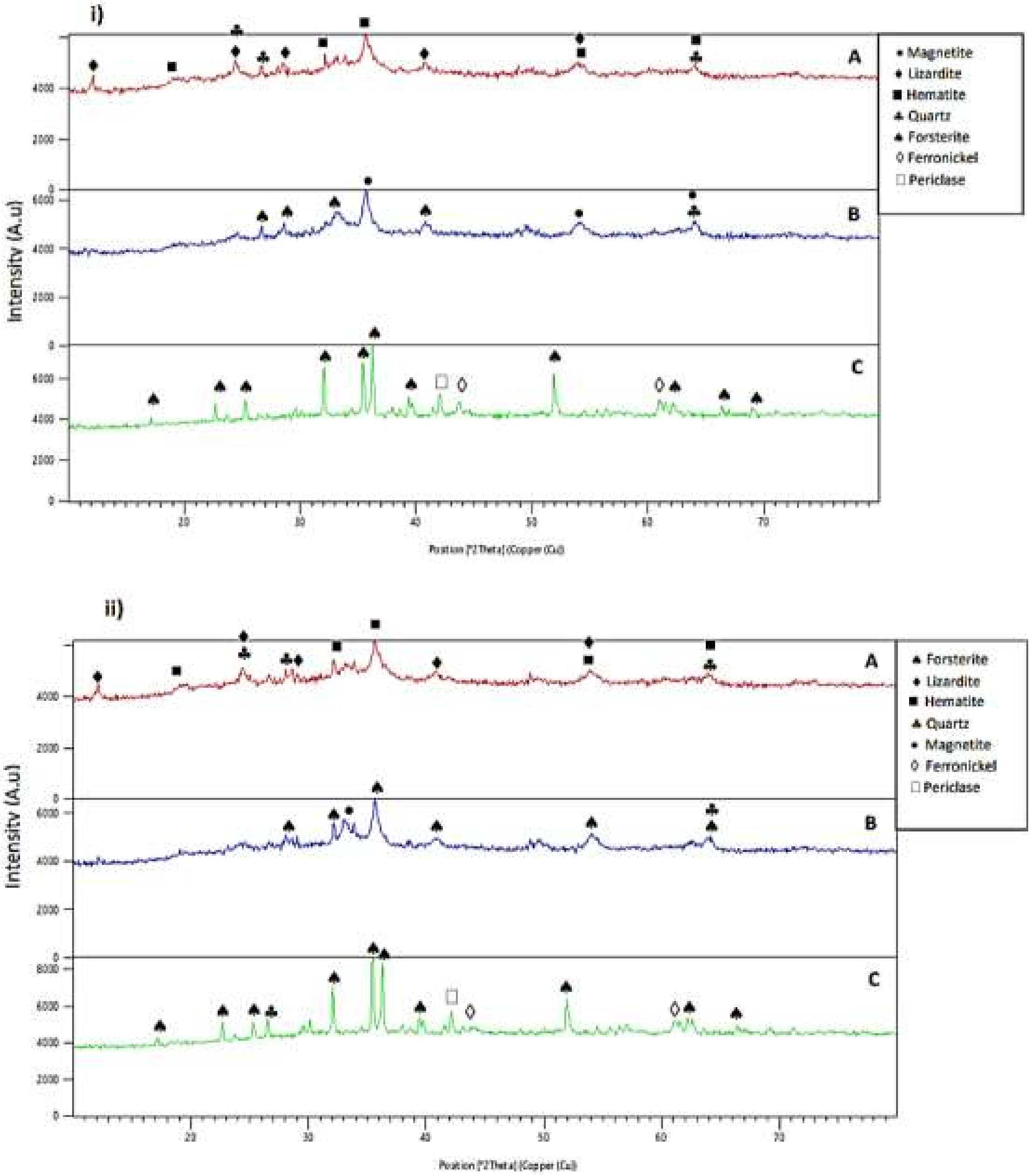

Figure 4. XRD pattern of saprolite with carbon type (i) anthracite and (ii) palm kernel charcoal in the condition 250 °C (A), 900 °C (B), and 1150 °C (C).

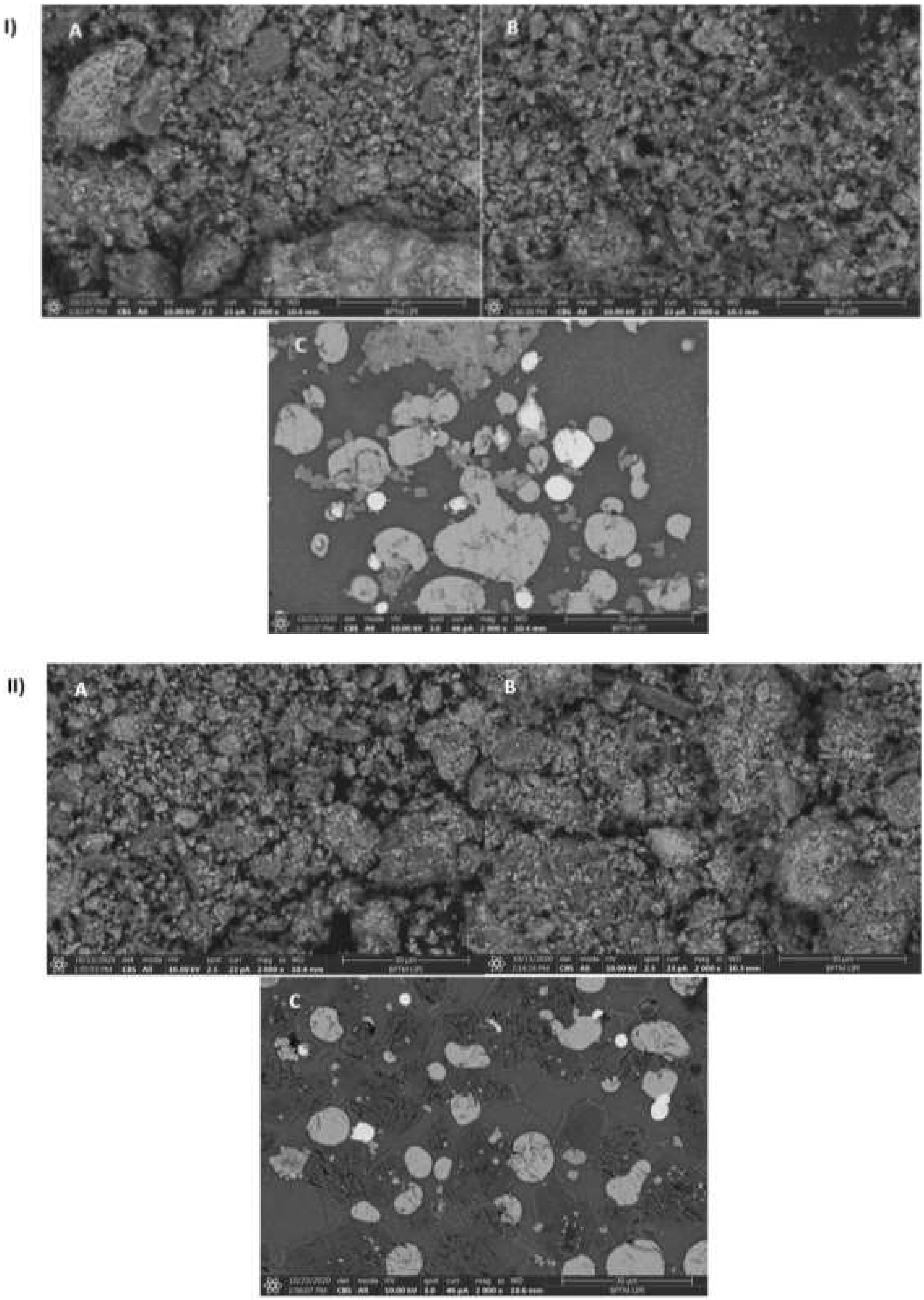

Figure 5. SEM of saprolite with carbon type (I) anthracite and (II) palm kernel charcoal at 250 °C (A), 900 °C (B), and 1150 °C (C) with magnification 2000x.

CONCLUSION

The research findings show that the most favorable phase transformation, from goethite to hematite, occurred at 250°C. At 900°C, interesting crystallization of forsterite and magnetite in saprolite was observed. Additionally, at 1050°C, iron-nickel crystallization became apparent, supported by various analytical techniques, including XRD and SEM. These results have broad implications and provide a valuable reference point for future research. In particular, this could guide future investigations, such as selective reduction experiments, in which the material is temperature of 250°C as an initial step before continuing the reduction process. Moreover, the potential use of anthracite, a type of carbon-rich coal, can be explored to achieve optimal nickel percentage and recovery. This discovery is not just interesting scientifically; it could help improve how to use saprolite resources in the future.

DECLARATION

There are no conflicts of interest associated with this publication, and there has been no significant financial support for this work that could have influenced its outcome. As the Corresponding Author, I confirm that the manuscript has been read and approved for submission by all the named authors.

ACKNOWLEDGMENT

We are thankful for the financial support provided by the Ministry of Education, Culture, Research, and Technology-Directorate of Higher Education, Research, and Technology under research project KDN 2023 and contract no NKB-1129/UN2.RST/HKP.05.00/2023. The authors gratefully acknowledge the support of Materials Science Universitas Indonesia and the Research Center of Mining Technology-National Research and Innovation Agency of Indonesia for the research facilities.

REFERENCE

Bahfie, F., Manaf, A., Astuti, W. and Nurjaman, F. (2021) 'Studies on reduction characteristics of limonite and effect of sodium sulphate on the selective reduction to nickel', *Journal of The Institution of Engineers (India): Series D*, 102(1), pp. 149–157. Available at: https://doi.org/10.1007/s40033-020-00240-3.

Bahfie, F., Manaf, A., Astuti, W., Nurjaman, F. and Herlina, U. (2021) 'Tinjauan teknologi proses ekstraksi bijih nikel laterit', *Jurnal Teknologi Mineral dan Batubara*, 17(3), pp. 135–152. Available at: https://doi.org/10.30556/jtmb.Vol17.No3.2021.1156.

Bahfie, F., Manaf, A., Astuti, W., Nurjaman, F. and Prasetyo, E. (2022) 'Studies of carbon percentage variation and mixing Saprolite-Limonite in selective reduction', *Materials Today: Proceedings*, 62, pp. 4156–4160. Available at: https://doi.org/10.1016/j.matpr.2022.04.679.

Bahfie, F., Manaf, A., Astuti, W., Nurjaman, F., Prasetyo, E. and Sumardi, S. (2022) 'Thermal upgrading of nickel from limonite by means of selective reduction', *Izvestiya. Ferrous Metallurgy*, 65(7), pp. 471–478. Available at: https://doi.org/10.17073/0368-0797-2022-7-471-478.

Bahfie, F., Murti, D.U., Nuryaman, A., Astuti, W., Nurjaman, F., Prasetyo, E., Sudibyo and Susanti, D. (2022) 'Kinetic properties of nickel leaching by ANOVA method', *Progress in Physics of Metals*, 23(3), pp. 476–488. Available at: https://doi.org/10.15407/ufm.23.03.476.

Bloomberg (2022) *Bnef's 2022 Electric Vehicle Outlook*. Bloomberg Finance L.P.

Butt, C.R.M. and Cluzel, D. (2013) 'Nickel laterite ore deposits: Weathered serpentinites', *Elements*, 9(2), pp. 123–128. Available at: https://doi.org/10.2113/gselements.9.2.123.

Haryadi, H., Suseno, T., Herlina, U., Nurjaman, F., Prasetyo, E., Handoko, A.S., Okfarina, S., Susanti, D. and Bahfie, F. (2024) 'SWOT analysis (strengths, weaknesses, opportunities, threats) of nickel to reach global electric battery market in Indonesia', *Mineral Processing and Extractive Metallurgy: Transactions of the Institutions of Mining and Metallurgy*, 133(1–2), pp. 21–32. Available at: https://doi.org/10.1177/08827508231225025.

Kyle, J. (2010) ‘Nickel laterite processing technologies – where to next?’, in *ALTA 2010 Nickel/Cobalt/Copper Conference*. Melbourne: ALTA Metallurgical Services Publications, pp. 30–66.

Nurjaman, F., Saekhan, K., Bahfie, F., Astuti, W. and Suharno, B. (2021) ‘Effect of binary basicity (CaO/SiO2) on selective reduction of lateritic nickel ore’, *Periodico di Mineralogia*, 239–245(90), p. 2. Available at: https://doi.org/10.13133/2239-1002/17045.

Rao, M., Li, G., Jiang, T., Luo, J., Zhang, Y. and Fan, X. (2013) ‘Carbothermic reduction of nickeliferous laterite ores for nickel pig iron production in China: A review’, *JOM*, 65(11), pp. 1573–1583. Available at: https://doi.org/10.1007/s11837-013-0760-7.

Rodrigues, F., Pickles, C., Peacey, J., Elliott, R. and Forster, J. (2017) ‘Factors Affecting the Upgrading of a Nickeliferous Limonitic Laterite Ore by Reduction Roasting, Thermal Growth and Magnetic Separation’, *Minerals*, 7(9), p. 176. Available at: https://doi.org/10.3390/min7090176.

Spence, E. (2024) *Nickel prices may soon recover from Indonesia-Induced slump*, *Bloomberg*. Available at: https://www.bloomberg.com/news/newsletters/2024-03-07/nickel-prices-may-soon-recover-from-indonesia-induced-slump (Accessed: 7 July 2023).

Spence, E. and Listiyorini, E. (2024) *New Freeport, Amman smelters boost Jokowi’s downstreaming legacy*, *Bloomberg.com*. Available at: https://www.bloomberg.com/news/articles/2024-09-23/new-freeport-amman-smelters-boost-jokowi-s-downstreaming-legacy.

Yang, S., Du, W., Shi, P., Shangguan, J., Liu, S., Zhou, C., Chen, P., Zhang, Q. and Fan, H. (2016) ‘Mechanistic and kinetic analysis of Na2SO4-Modified laterite decomposition by thermogravimetry coupled with mass spectrometry’, *PLOS ONE*. Edited by G. Y, 11(6), p. e0157369. Available at: https://doi.org/10.1371/journal.pone.0157369.

Yuwang, X. (2015) ‘Research on process mineralogy for the reverberatory furnace slag in Yunnan’, *Multipurpose Utilization of Mineral Resources*, 36(1), pp. 51–57. Available at: https://doi.org/https://dx.doi.org/10.3969/j.issn.1000-6532.2015.01.012.

Zhen, S., Hao, J. and Peng, Z. (2013) ‘Practice research of RKEF process on smelting ferronickel for laterite nickle ores’, *Non-Ferr. Min. Metallurgy*, 29, pp. 35–39.

Zhou, S., Li, B., Wei, Y., Wang, H., Wang, C. and Ma, B. (2015) ‘Effect of additives on phase transformation of nickel laterite ore during low-temperature reduction roasting process using carbon monoxide’, in T.P. Battle, J.P. Downey, L.D. May, B. Davis, N.R. Neelameggham, S. Sanchez-Segado, and P.C. Pistorius (eds) *Drying, Roasting, and Calcining of Minerals*. Cham: Springer International Publishing, pp. 177–184. Available at: https://doi.org/10.1007/978-3-319-48245-3_22.

Zhou, Y., Zhang, C., Xie, T., Hong, T., Zhu, H., Yang, Y., Liu, C. and Huang, K. (2017) ‘A microwave thermostatic reactor for processing liquid materials based on a heat-exchanger’, *Materials*, 10(10), p. 1160. Available at: https://doi.org/10.3390/ma10101160.