

The effect of sulfur, temperature, holding time and reductant on the selective reduction of limonite ore

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Abstract

Laterite ore is used as the manufacture of ferronickel. One method that can increase the levels of nickel in limonite ore is selective reduction. Selective reduction is a process to reduce the metal oxide to the metal with additives. The selective reduction of limonite ore by using the reductant 5%, 10%, and 15% and the sulfur 10 % as additive. The process of selective reduction is performed at the temperature of 950, 1050, and 1150°C with a holding time of 60, 90, and 120 minutes and followed by magnetic separation to separate between the concentrate and tailings. AAS characterization indicates the optimum value at the temperature of 1150°C with 5% reductant and the reduction of the holding time for 60 minutes which give the effect on the grade and recovery of nickel those are 3.72wt% and 95.67%, respectively. The decreasing of grain size of ferronickel in the sample form an average grain size of 38.07 μ m and the forming of FeS phase which is caused the addition of sulfur.

Introduction

Approximately 70% of the world reserves are laterite nickel ore and 30% is sulphide. Increased demand for nickel and the rapid depletion of sulfide rocks forced the industry to begin to consider a backup source of laterite rocks as one of the sources of nickel in the future. Recently, the processing of laterite nickel ore in Indonesia more done in high-grade ore that is done through pyrometallurgy is to produce ferronickel and nickel matte [1].

Laterite ore is used as the manufacture of ferronickel. Levels of nickel in ferronickel ranging from 20-40%. Ferronickel is commonly used to manufacture stainless steel [2]. Another literature, by using the high-temperature 1400°C [3] which could degrade the lining in the process. One method that can increase the levels of nickel in limonite ore is by way of selective reduction with a lower temperature than 1400°C. Selective reduction is a process that aims to reduce the metal oxide to metal using a reducing agent at a given temperature is accompanied by the addition of additives to increase the selectivity of the metal. Selective reduction carried out at a temperature of 800-1200°C. to form nickel which can then be separated from the mineral bully with magnetic separation [4]. Increased levels of Fe and Ni in concentrates can be increased by increasing the amount of reductant, temperature and time reduction [5]. The addition of a sulfur-based material led to the acquisition of the acquisition Ni Fe is low but increases due to formation of the non-magnetic FeS [3]. In this research, the process of selective reduction of low-grade laterite ore using an elemental sulfur additive with the addition of anthracite coal reductant as much as 5%, 10%, and 15% by weight will be investigated.

Experimental

Laterite ore comes from Konawe, Southeast Sulawesi. Atomic Absorption Spectroscopy (AAS) was conducted to determine the chemical composition of laterite ore, as shown in TABLE 1. The elemental analysis is 1.4wt% nickel and 50.5wt% iron which has an indication the laterite ore is the limonite ore. An

also the impurities contained in the limonite ore are 16.5wt% Si, 1.81wt% Mg, 0.177wt% Ca, 4.86wt% Al, 2.68wt% Cr, 0.847wt% Mn, and 0,0662wt% Co.

TABLE 1. The chemical composition of limonite ore.

Element	Ni	Fe	Si	Mg	Al	Ca	Cr	Mn	Co
Amount (wt%)	1.4	50.5	16.5	1.81	4.86	0.177	2,68	0.847	.0662

TABLE 2. Rietveld refinement calculation of limonite ore.

Name	Chemical structure	Total (%)
Goethite	FeHO ₂	49.7
Olivine	MgNiO ₄ Si	37.5
Lizardite	H ₄ Mg ₃ O ₉ Si ₂	7.6
Quartz	SiO ₂	5.3

XRD results of limonite ore can be seen in Fig. 1, limonite ore is dominated by goethite (FeO.OH), olivine (MgNiSiO₄), lizardite (Mg₃(Si₂O₅)(OH)₄), and quartz (SiO₂). Nickel is associated with oxide and the iron in the goethite structure which shows the highest intensity. In this study, the coal as reductant is anthracite with a variation percentage of 5%, 10%, and 15%. The anthracite was analyzed proximate to determine the content of moisture, volatile, ash and fixed carbon, as shown in TABLE 3. The fixed carbon would be used to determine how much of the amount of coal to be used as a reductant for the reduction of limonite ore.

TABLE 3. Results of the proximate analysis of anthracite.

Element	Content (wt%)
Moisture	3.14
Volatile	18.25
Ash	18.25
Fixed carbon	60.35

The first step, mixing of limonite ore, anthracite, and elemental sulfur additive and then it was homogenized and pelleted by manually. The pellets were dried in an oven at a temperature of 120°C for 4 hours. Then the pellet is heated in the furnace to do selective reduction process with the holding time

variation of 60, 90, and 120 minutes as well as variations of temperature of 950°C, 1050°C, and 1150°C and was quenched, frequently. The pellets were crushed by using a mortar and then milled with a shaker mill to get a size of 200 mesh. Those were separated by magnetic separation with 500 Gauss magnets in the wet method to produce a concentrate and tailings. Concentrates and tailings were analyzed by AAS (Atomic Absorption Spectroscopy) and X-Ray Diffraction (XRD) to influence the weight per cent and recovery of nickel and iron after selective reduction process.

Results And Discussion

3.1 The effect of temperature reduction on levels and recovery in nickel concentrate

The variable fix in the 5% of anthracite, 10% sulfur and the holding time for 60 minutes at that temperature variation 950°C, 1050°C and 1150°C. Results AAS analysis in Fig. 2 shows the increase of temperature could decrease the weight per cent of nickel due to the temperature could produce more gas in the reduction process and it reacts with metal oxides in the ore [5]. The recovery of iron and nickel increases with the increasing temperature reduction due to the selective reduction process is using the additive which could give the effect of the recovery of nickel and iron along with the increasing reduction temperature of 800-1200°C [6]. Sulfur could react with iron to form iron-sulfur (FeS) cause of the sulfur could easily dissolve in the iron and could drop the weight per cent of nickel [7].

XRD analysis performed on samples to find compounds that are formed after reduced to the variation of temperature reduction is 950°C, 1050°C, and 1150°C with a holding time of 60 minutes and 5% reductant. Based on Fig. 3, the phases are fayalite (Fe_2SiO_4), quartz (SiO_2), magnesioferrite (Fe_2MgO_4), wustite (FeO), iron-nickel (FeNi) and pyrrhotite (FeS) which appears in the XRD results. At the temperatures of 950°C, the phases are not formed pyrrhotite (FeS) while at the temperature of 1050°C and 1150°C, it appears. FeS formed temperatures are most numerous in 1050°C and it could explain the FeS is diminishing iron metallization so that the weight per cent of nickel in concentrate is increasing [6]. At the temperatures of 950°C, the iron-nickel (FeNi) phase begins to form but the intensity is low. The reason for the intensity of iron-nickel is low at the temperatures of 950°C that is the element of iron and nickel are stuck in the compound with impurities because the reduction process is not optimal. With the increase of the temperature could obtain the higher of FeNi content in TABLE 4. So it could cause the optimum reduction process to increase the weight per cent of nickel [8]. Wustite phase is only found at a temperature of 950°C while at the temperature of 1050°C and 1150°C, there is no wustite phase, indicating that the FeO has reduced optimally. It could affect the higher of ferronickel content.

TABLE 4. Rietveld refinement of calculation of the reduction with the additive compounds 10% sulfur and variation of temperature.

Compound	The percentage of reduction products (%)		
	950°C	1050°C	1150°C
Fayalite (Fe ₂ SiO ₄)	62.4	47.3	52.7
Quartz (SiO ₂)	3.5	9.0	3.2
Magnesioferrite (Fe ₂ MgO ₄)	28.4	24.0	25.8
Iron oxide (FeO)	4.9	-	-
Iron-nickel (FeNi)	0.9	3.2	7.2
Pyrrhotite (FeS)	-	16.4	11.1

3.2 Effect of holding time reduction on levels and recovery in nickel concentrate

The variables are 5% reductant, 10% sulfur and the temperature of 1050°C with the variation of holding time for 60 minutes, 90 minutes, and 120 minutes. In Fig. 4, AAS analysis of the results shows that the levels of nickel and iron obtained decreases with increasing holding time reduction because the length of the holding time could produce more the amount of CO and cause more the iron which reduces the weight per cent of nickel [4]. Recovery of iron and nickel present the highest value at the optimum holding time of 60 minutes which are 74.95% and 37.01%.

According to on Fig. 5, the compounds are fayalite (Fe₂SiO₄), quartz low (SiO₂), magnesioferrite (Fe₂MgO₄), wustite (FeO), iron-nickel (FeNi) and pyrrhotite (FeS) which is characterized by the emergence of the peak (peak) in the diffractogram XRD. From TABLE 5, the percentage is more details for the phases. The longer of holding time at the temperature of 1050°C could get the peak of iron-nickel (FeNi) is low. It could be caused the longer of holding time and the increasing of amount carbon monoxide which reduce the iron oxides to metal iron so it reduces the weight per cent of nickel in FeNi [4]. Iron could dissolve into FeNi added that the acquisition of Ni content in the concentrate to be reduced [8]. SiO₂ peak decreases with the increasing holding time reduction due to it binds with FeO to form a fayalite phase (Fe₂SiO₄). The addition of sulfur could reduce the amount of magnetite to form FeS. In general, it has been proved the addition of sulfur could increase the weight per cent and recovery of nickel [9].

TABLE 5. Rietveld refinement of calculation of the reduction with the additive compounds 10% sulfur and the holding time variation.

Compound	The total percentage of reduction products (%)		
	60 minutes	90 minutes	120 minutes
Fayalite (Fe ₂ SiO ₄)	47.3	50.8	59.4
Quartz (SiO ₂)	9.0	1.5	-
Magnesioferrite (Fe ₂ MgO ₄)	24.0	26.4	24.6
Iron-nickel (FeNi)	3.2	3.1	0.1
Pyrrhotite (FeS)	16.4	16.8	13.3

3.3 Effect of anthracite coal reductant variations on levels and recovery in nickel concentrate

The fixed variables are 10% sulfur, holding time for 60 minutes and the temperature of 1150°C with a variation of the amount of reductant 5%, 10% and 15%. The AAS results in Fig. 6 present the increasing of the percentage of the reductant could decrease the weight per cent and recovery of nickel and iron due to the addition of carbon is greater than the requirement of the process which could obtain the high peak is in recovery but the low peak is in the weight per cent of nickel due to the increase of the reduction of iron oxide into metallic iron [10]. The increasing percentage of reductant to the optimum amount of carbon might be contributing to the reduction of iron and nickel so the metal increases and the excessive carbon decrease [11].

In Fig. 7, the phases are fayalite (Fe₂SiO₄), quartz low (SiO₂), magnesioferrite (Fe₂MgO₄), wustite (FeO), iron-nickel (FeNi) and pyrrhotite (FeS) which is characterized by the emergence of the peak in the diffractogram XRD. From TABLE 6, the percentage is more details for the phases. More reductant has been added the peak of FeNi gain cause of more the number of carbon could reduce optimally to get iron-nickel (FeNi). There is no metal iron phase in the XRD results due to it combines with sulfur to form FeS. FeS phase increased with the addition of the reducing agent and diminish the fayalite phase. It could be formed from the reaction between FeO and SiO₂.

TABLE 6. Rietveld refinement of calculation results of the reduction with the additive compounds 10% sulfur and the variation addition of reductant.

Compound	The total percentage of reduction products (%)		
	5%	10%	15%
Fayalite (Fe ₂ SiO ₄)	52.7	29.3	-
Quartz (SiO ₂)	3.2	7.3	22.1
Magnesioferrite (Fe ₂ MgO ₄)	25.8	29.0	22.3
Iron-nickel (FeNi)	7.2	12.0	25.4
Pyrrhotite (FeS)	11.1	20.7	27.4

3.4 SEM-EDS analysis

The fixed variables are the variations of the reductant amount, additives of 10% at the temperature of 1150°C with the holding time of 60 minutes. Figure 8 shows the high concentration of reductant caused the decreasing of grain size on FeNi (white). In reductant 5% gained an average grain size of 24.69 μm, the reductant 10% gained an average grain size of 20.86 μm and the reductant 15% gained an average grain size of 17.35 μm. This is because the high amount of reducing agent will react the CO gas in addition to iron and nickel compounds that can decrease the growth of ferronickel grains [4].

The optimum variables are 10% elemental sulfur additive at a temperature of 1150°C with a holding time of 60 minutes and 10% reductant which is used in the SEM-EDS analysis. Point 1 could imply the highest element is oxygen and another element such as iron, silicon, and magnesium and the possibility phases formed are Fe₂SiO₄ and Fe₂MgO₄. Point 2 indicates the highest element is iron with another element nickel and should be formed iron-nickel (FeNi). The last point presents the highest element is iron and other element sulfur which form FeS. The indication of sulfur can press the forming of iron and decreased the grain size of ferronickel.

Conclusion

The addition of sulfur suppresses the formation of Fe metallization by forming FeS so it raises the grade of nickel in concentrate FeNi. The test results of XRD with the variables 10% sulfur is dominated by compounds such as fayalite (Fe₂SiO₄), quartz low (SiO₂), magnesioferrite (Fe₂MgO₄), wustite (FeO), iron-nickel (FeNi), pyrrhotite (FeS) and nickel oxide (NiO). The results of the grade and recovery of nickel show an optimal temperature of 1150 °C with a holding time of 60 minutes and 5% reductant which obtain 3.72wt% and 95.67% which sulfur has the important rules when the selective reduction has been done on the increasing nickel content, the forming of FeS, and decreasing the grain size of ferronickel.

Declarations

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Declaration

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Figures

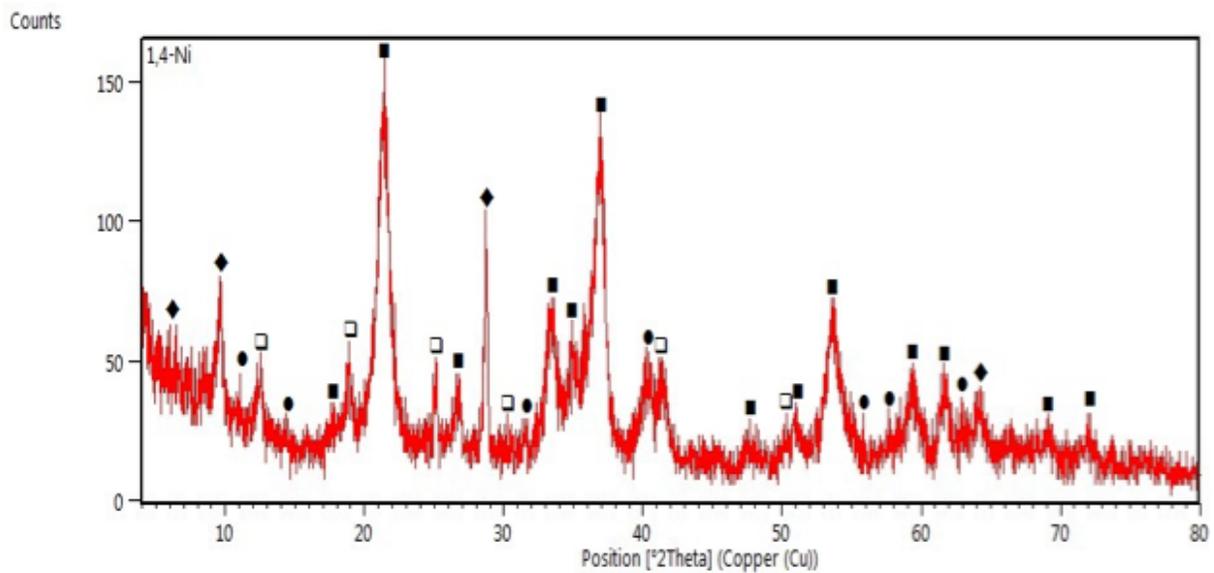


Figure 1

XRD of limonite ore (symbol: ■ = goethite, ● = olivine, ◻ = lizardite, and ◆ = Quartz).

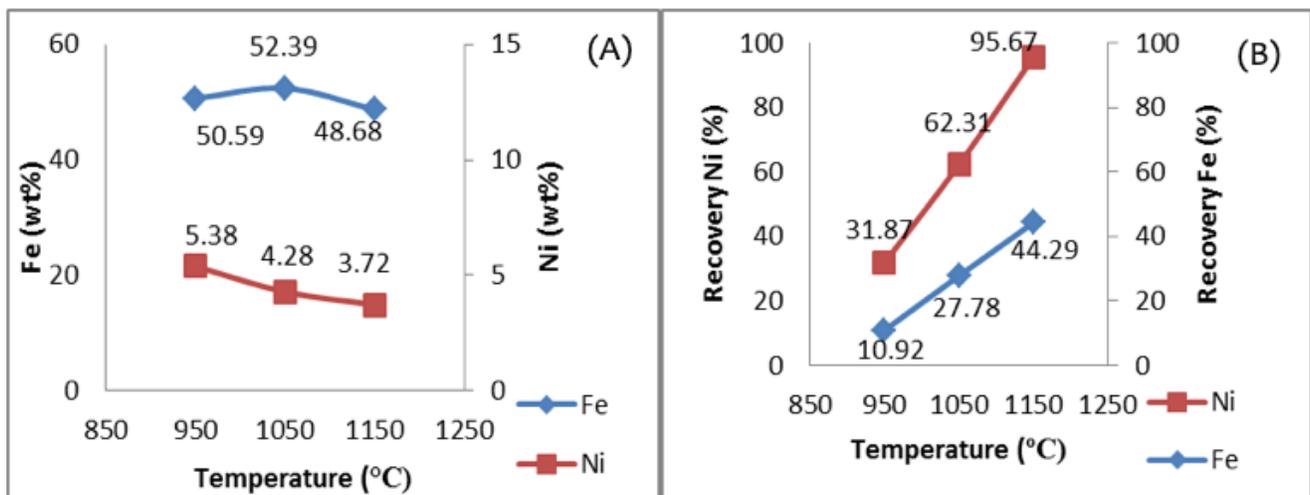


Figure 2

The effect of temperature reduction to (a) the weight per cent of nickel and iron, and (b) the recovery of nickel and iron.

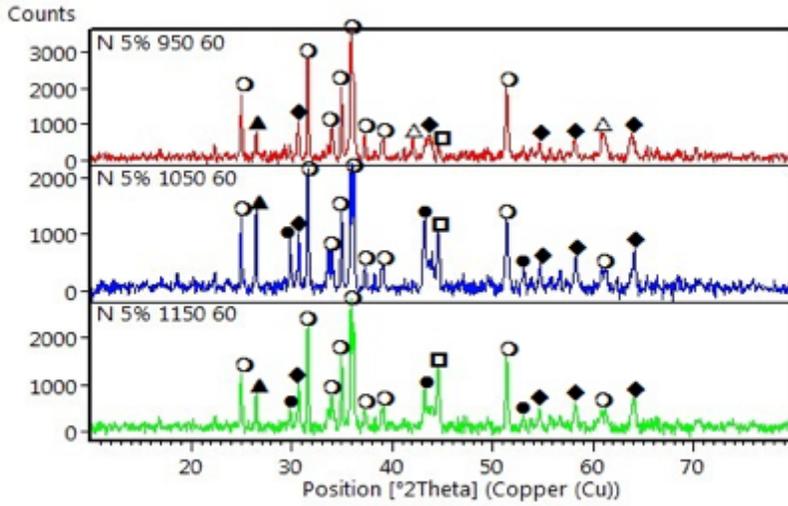


Figure 3

XRD pattern of the effect of temperature of (a) 950°C (red line), (b) 1050°C (blue line), (c) 1150°C (green line) and the changing phase with the holding time for 60 minutes (symbol: ● = Fe₂SiO₄, ▲ = SiO₂, ◻ = Fe₂MgO₄, ◻ = FeO, ◻ = FeNi, ● = FeS).

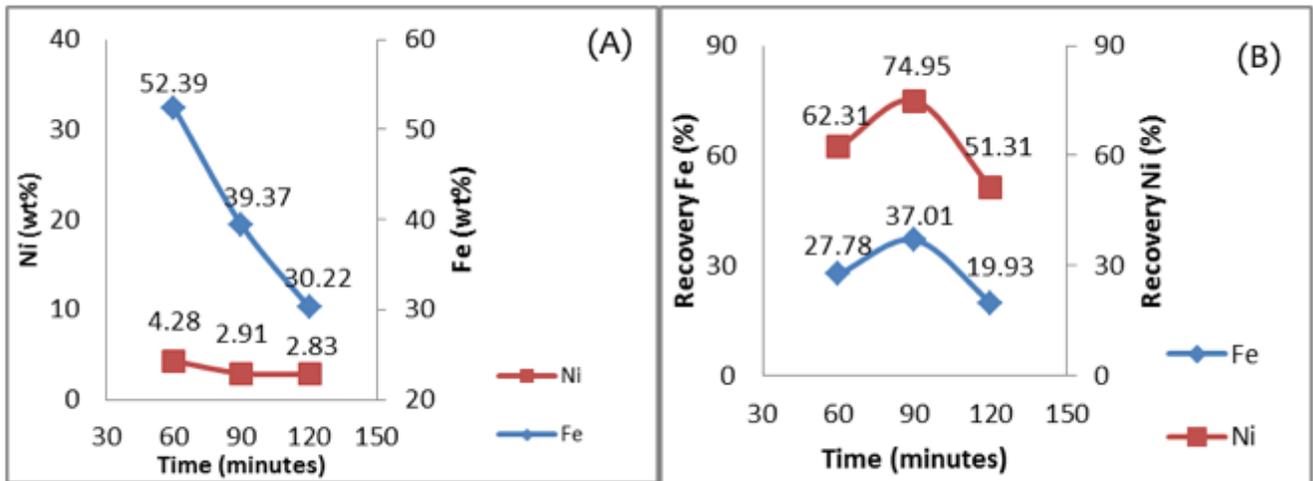


Figure 4

The effect of holding time variation to (a) the weight per cent of nickel and iron, and (b) the recovery of nickel and iron.

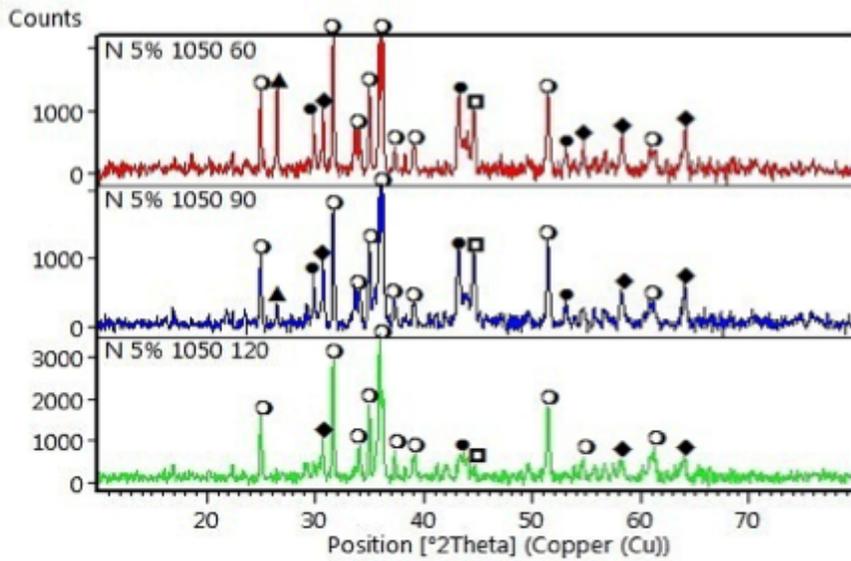


Figure 5

XRD pattern of the effect of holding time 60 minutes (green), 90 minutes (blue), and 120 minutes (red) on the changing phase with the 10% sulfur and temperature of 1050°C (symbol: ● = Fe₂SiO₄, ▲ = SiO₂, ◻ = Fe₂MgO₄, ◻ = FeNi, ● = FeS).

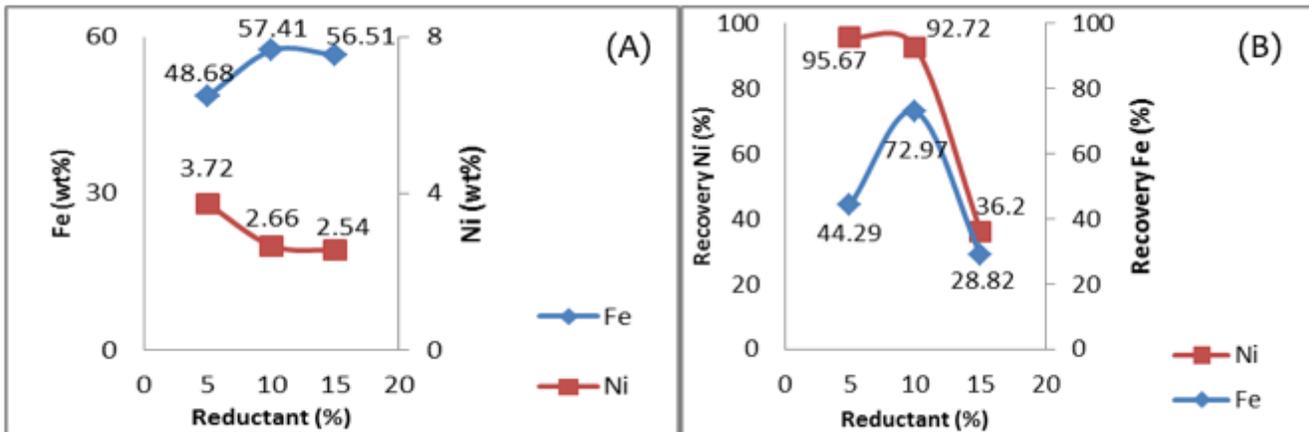


Figure 6

The effect of percentage variation of reductant to (a) the weight per cent of nickel and iron, and (b) the recovery of nickel and iron.

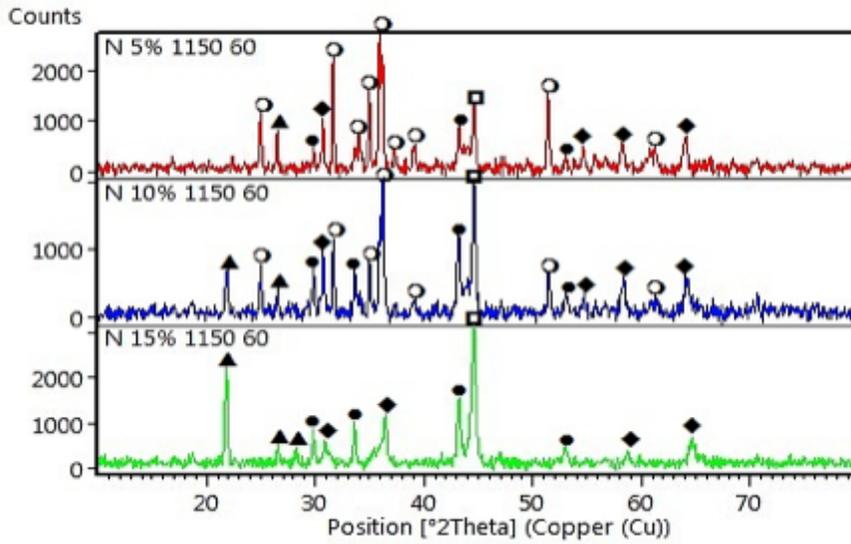


Figure 7

XRD pattern of the effect of percentage reductant 5% (green), 10% (blue), and 15% (red) on the changing phase with temperature reduction of 1150°C and a holding time of 60 minutes (symbol: ● = Fe₂SiO₄, ▲ = SiO₂, ◻ = Fe₂MgO₄, ◻ = FeNi, ● = FeS).

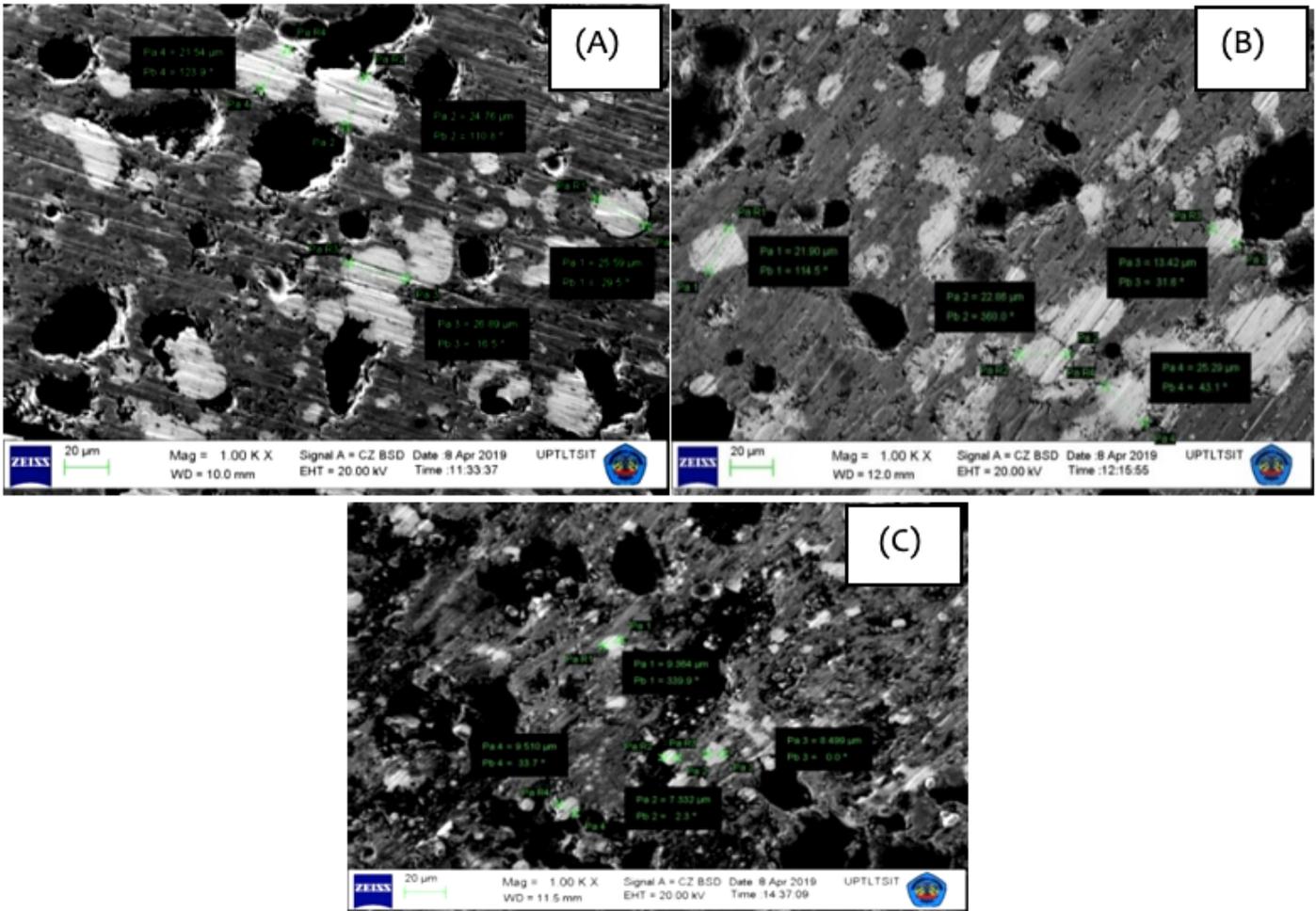
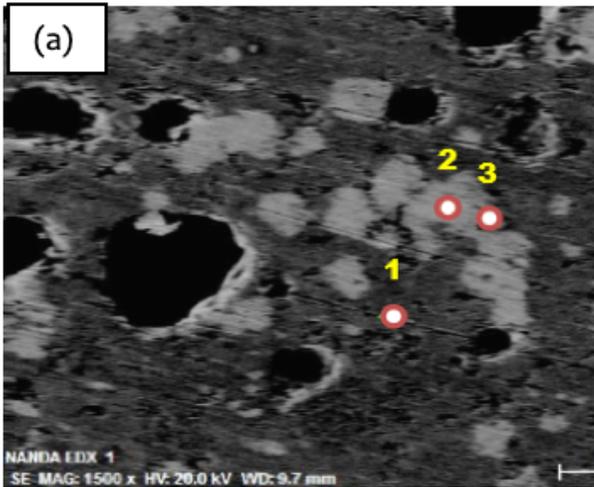


Figure 8

The results of the grain size reduction of the sample with additives of 10% sulfur at the temperature of 1150°C with the holding time of 60 minutes and the variation of reductant (a) 5%, (b) 10% and (c) 15%.



(b)	Element	Point 1 (wt%)	Point 2 (wt%)	Point 3 (wt%)
	O	98.03	-	-
	Fe	1.92	98.26	75.31
	Si	0.03	-	-
	Mg	0.02	-	-
	Ni	-	1.74	-
	S	-	-	24.69

□

Figure 9

a) The SEM images of 10% elemental sulfur additive at the temperature of 1150°C with the holding time of 60 minutes and 10% reductant; b) EDS spectra of point 1, 2, and 3.