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Effect of Binary Basicity (CaO/SiO_2) on Selective Reduction of Lateritic Nickel Ore

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ABSTRACT

A selective reduction method is being developed in processing lateritic nickel ore to produce high nickel grade's ferronickel using low temperature or energy consumption. This research was carried out to study the effect of binary basicity (CaO/SiO_2) in the selective reduction process. The lateritic nickel ore containing 1.38% Ni and 38.2% Fe was used in this study. The reduction was performed at 1150°C for 60 minutes in a muffle furnace with the addition of sodium sulfate (additives), bituminous coal (reductant), and calcium oxide (basicity modifier). The optimum nickel grade in the selective reduction of lateritic nickel ore was obtained from the 0.1 of binary basicity, which was 6.14 %Ni, due to the breakage of iron and nickel in magnesium silicate bond into metallic iron and nickel. Further increasing of binary basicity decreased the nickel grade of ferronickel due to the formation of a high melting point phase.

Keywords: lateritic nickel ore; selective reduction; binary basicity; reductant; additive.

INTRODUCTION

Nickel ores, which are about 89 million tons of nickel deposits globally are commonly present as sulfidic and lateritic ores (Mineral Commodity Summaries, 2019). Although 70% of nickel resources are in lateritic ore, only 40% of nickel world production comes from laterite. Lateritic nickel ore processing is more complicated than sulfidic due to its low nickel content and chemically complex compounds (Norgate and Jahanshahi, 2010, 2011). The processing of nickel laterite with pyrometallurgy and hydrometallurgy is not sufficient and costly due to it requires high energy consumption and many chemical reagents, respectively, which are not environmentally friendly (Dalvi et al., 2004; Lee et al., 2005).

The selective reduction of lateritic nickel ore with additives and less reductant has been carried out at relatively low temperatures to obtain high-grade ferronickel (Rao et al., 2013; Zhu et al., 2012; Dong et al., 2018). Additives with sulfur-bearing materials have shown exemplary performance in the selective reduction process (Harjanto and Rhamdhani, 2019). Zhu et al. (2019) reported that ferronickel with 5% Ni was generated from the reduction process of nickel ore containing 0.97 Ni at 1250 °C for 60 minutes by adding 3 wt% of calcium sulfate. Jiang et al. (2013) also revealed that 10 wt% of sodium sulfate in the selective reduction process of lateritic ores (1.42 wt% Ni and 23.16 wt% Fe) produced ferronickel contains 9.87% Ni with its recovery of 90.9%. The increase of nickel grade in sulfate addition was caused by the inhibition of iron metallization due to the formation of the non-magnetic and low-temperature melting point of troilite (FeS) (Li et al., 2012). The nickel grade will increase with the increase of sulfate addition. Nevertheless, the addition of more sulfur additives will increase the sulfur content in ferronickel, which could be lowering the mechanical properties of the end product of ferronickel, such as stainless steel, ni-hard, and other steel or cast iron alloys (Elliot et al., 2017). Thus, the use of sulfur-bearing materials as additives should be considered and evaluated.

The liquidus phase plays an important role in selective reduction due to its advantages in the agglomeration of ferronickel particles and suppresses the diffusion rate of gas reductant in the metallization of iron (Zhu et al., 2019). In the smelting process of lateritic nickel ore, basicity is a very important parameter to determine the melting point of slag/impurities (Xueming et al., 2015). Basicity also affects the nickel grade and ferronickel recovery (Pan et al., 2013; Tian et al., 2020). The lower melting point of slag can be obtained by modifying the basicity of slag. Zhu et al. (2016) reported that the optimal binary basicity (CaO/SiO_2) in the smelting of reduced nickel ore is 1.0 with the formation of melilite ($2CaO.MgO.2SiO_2$) structure. The effect of binary basicity (MgO/SiO_2) was also investigated by Park et al. (2014), in which the optimum basicity was 0.8-1.0. The modification of basicity by adding MgO could break the iron and nickel in the silicate bond, thus lowering the melting temperature and slag's viscosity (Xueming et al., 2015; Rehackova et al., 2015).

Unfortunately, there is still less information about the effect of binary basicity in the selective reduction process. Therefore, this study was carried out to investigate the effect of CaO addition to modifying the binary basicity (CaO/SiO_2) in the selective reduction process of lateritic nickel ore.

MATERIAL AND METHODS

The lateritic nickel ore, which was used in this experiment, is from Southeast Sulawesi, Indonesia. The composition of nickel ore was analyzed using XRF, as listed in Table 1. The binary basicity (CaO/SiO_2) of this lateritic nickel ore is 0.01.

From XRD analysis, as shown in Figure 1, the nickel ore is dominated by goethite (FeO.OH). Thus, this lateritic nickel ore is classified as limonite. A small amount of olivine ($FeMgSiO_4$), lizardite ($Mg_3(Si_2O_5)(OH)_4$), and quartz low (SiO_2) are also found.

In this work, the limonitic lateritic nickel ore, bituminous coal as reductant, and sodium sulfate (Na_2SO_4) as additive are crushed into less than 147 μm. They were mixed and pelletized into 10-15 mm of diameter. The binary basicity was modified from 0.1 to 1.0 by the addition of calcium oxide (CaO). Sodium sulfate and calcium oxide are chemical grades. As well as from the previous study, the reduction process of pellets was carried out at 1150 °C for 60 minutes in a muffle furnace (Nurjaman et al., 2019). The low temperature reduction (below 1200 °C) was carried out to avoid the sticky-agglomerated reduced ore which could result in the formation of "kiln-ring" in industrial kiln, such as rotary kiln.

The reduced ore was crushed until passed 90% of 74 μm prior to wet magnetic separation. It was performed using 500 gausses of the magnetic field to separate the concentrate/ferronickel (magnetic) and tailing/impurities (non-magnetic).

RESULT AND DISCUSSION

Effect of Reductant Dosage

In this work, the reduction process was carried out at 1150 °C for 60 minutes with the addition of 10 wt% of sodium sulfate. The effect of the reductant dosage on this selective reduction process is shown in Figure 2. It is observed that the nickel grade decreased from 5.88% to 2.719% with the increases of reductant dosage from 0.1 to 0.5 stoichiometry. The recovery of nickel seems relatively constant. Nevertheless, the recovery of iron increases with the increase of reductant dosage.

$$Mg_3Si_2O_5(OH)_4 \rightarrow (Mg,Fe,Ni)SiO_3+(Mg,Fe,Ni)SiO_4+2H_2O \quad (1)$$
$$2FeOOH \rightarrow Fe_2O_3+H_2O \quad (2)$$
$$C+CO_2 \rightarrow 2CO \quad (3)$$
$$3Fe_2O_3+CO \rightarrow 2Fe_3O_4+CO_2 \quad (4)$$
$$Fe_3O_4+CO \rightarrow 3FeO+CO_2 \quad (5)$$
$$FeO+CO \rightarrow Fe+CO_2 \quad (6)$$
$$NiO+CO \rightarrow Ni+CO_2 \quad (7)$$
$$Fe+Ni \rightarrow FeNi \quad (8)$$

Table 1. Chemical composition of lateritic nickel ore.

Element	Ni	Fe	SiO_2	Al_2O_3	CaO	MgO
wt%	1.38	38.2	10.12	5.3	0.13	1.46

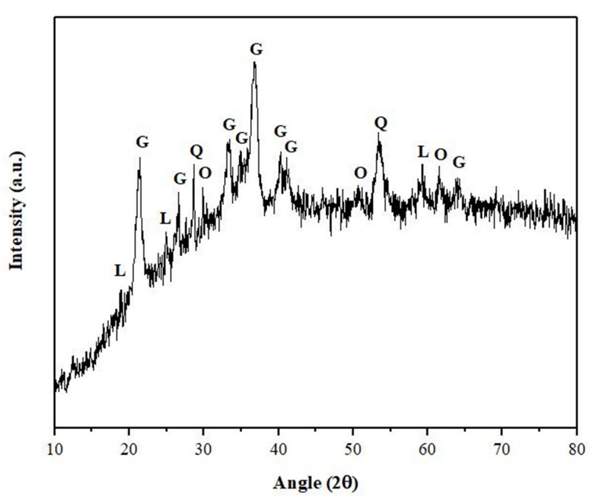

Figure 1. XRD pattern of nickel laterite ore (L: lizardite; G: goethite; O: olivine; Q: quartz).

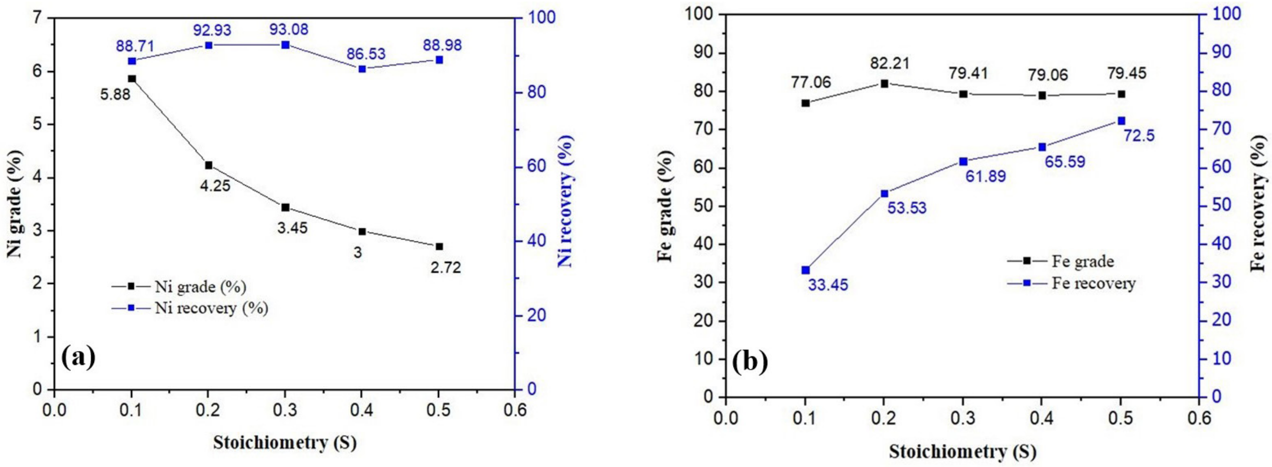

Figure 2. Effect of reductant dosage stoichiometry 0.1-0.5 with addition 10 wt% Na_2SO_4 (a) nickel grade and recovery; (b) iron grade and recovery.

The chemical reaction of the reduction process of nickel and iron oxide in lateritic nickel ore is expressed in equation (1-7). From the Ellingham diagram (Figure 3), the reduction of nickel and iron oxide occurred when the CO crossed the nickel and iron oxide line. It is showed that the reduction temperature of nickel oxide (440 ºC) is lower than iron oxide (690 ºC). Ilyas et al. (2020) reported that ferronickel could be obtained at a reduction temperature of 800 ºC with the addition of 9 wt% of sodium sulfate. However, more coal will generate more CO gas, as expressed in equation 3, to reduce more iron oxide into metallic iron at a higher temperature. Thus, it will be lowering the nickel grade in concentrate.

The XRD analysis was performed on the reduced ore, as shown in Figure 4. The result shows that magnesioferrite ($MgFe_2O_4$), quartz low (SiO_2), troilite (FeS), wustite (FeO), ferronickel (FeNi), and fayalite (Fe_2SiO_4) are found in reduced ore. The formation of troilite could

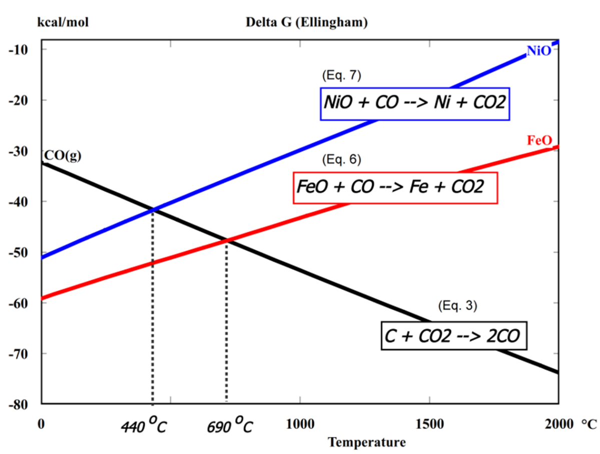

Figure 3. The Ellingham diagram of iron and nickel oxide.

accelerate the mass transfer of metal ions to facilitate the agglomeration of the ferronickel particle during the reduction of laterite ore due to its low melting point of Fe-FeS eutectic temperature (985 °C) (Rao et al., 2013). The intensity of wustite declines as the reductant addition increases, which means more iron oxide is reduced into the metallic iron. Nevertheless, the fayalite is found at 0.2-0.5 stoichiometry of coal, which might be formed by the reaction of FeO with SiO_2. Fayalite is more difficult to reduce than metal oxide (Zhu et al., 2019). It covers the iron and nickel oxide, thus suppress the reduction of the metallic oxide (Li et al., 2012). Nickel also could be entrapped in a silicate matrix of fayalite to promote the olivine phase or $(Fe, Ni)_2SiO_4$, due to its close atomic radii with iron. Therefore, it will be lowering the nickel recovery. At stoichiometry 0.3 (Figure 4), it shows no-quartz peak intensity because the SiO_2 has completely reacted with wustite to form fayalite (Ma et al., 2013).

From microstructure analysis by SEM EDS, as shown in Figure 5, the white grains, which are identified as ferronickel, look scattered in a small size at 0.1 stoichiometry of reductant. The ferronickel grain size is getting larger at 0.5 stoichiometry of reductant. It shows that it increase with the increase of metallic iron. The large particle of ferronickel improves the liberation degree of the metallic particle from impurities at the magnetic separation process to obtain high recovery of iron and nickel. Nevertheless, the more metallic iron in the concentrate, the lower the nickel grade will be generated.

Effect of Binary Basicity (CaO/SiO_2)

The effect of binary basicity in this selective reduction was carried out with optimal stoichiometry reductant. The binary basicity of 0.1-1.0 was modified by CaO addition. Figure 6 shows that nickel grade in concentrate increases with the increase of basicity from 0.01 (as-nickel ore) to 0.1, then it decreases until basicity 1.0. Nevertheless, the iron grade increases with the increase of basicity. The recovery of iron increases with the increasing of basicity, while the nickel recovery is relatively constant. Highest nickel grade in concentrate was obtained from binary basicity 0.1, which was 6.14 %Ni with nickel recovery 89.94%.

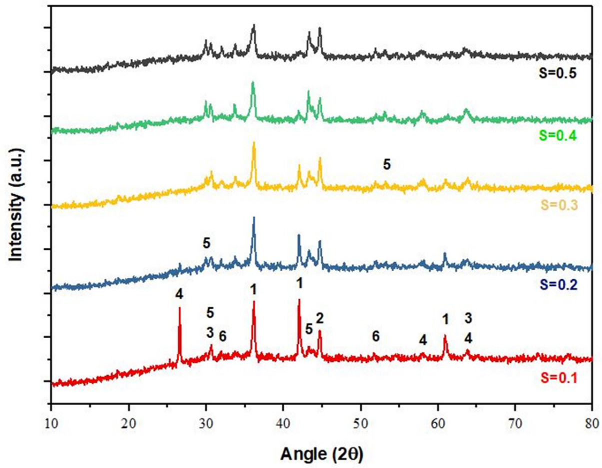

Figure 4. The XRD pattern of 0.1 to 0.5 stoichiometry of reductant dosage (1-wustite; 2-ferronickel; 3-magnesioferrite; 4-quartz; 5-troilite; 6-forsterite).

The XRD results are shown in Figure 7. Magnesioferrite, quartz (SiO_2), troilite (FeS), wustite (FeO), and ferronickel (FeNi) are formed at basicity 0.1. It shows that the intensity of wustite decreased as the basicity increased. The peaks intensity of forsterite, which is an iron-nickel-magnesium silicate, are not found at basicity 0.1, which indicates that CaO addition can break the silicate structure of magnesium, iron, and nickel, thus increasing the metallic grade and recovery (Ma et al., 2018). However, with the addition of more CaO, the calcium silicate of melilite is formed.

In the selective reduction of nickel laterites, the presence of a low melting point temperature phase could promote the reduction rate and mass transfer. Nepheline with a low eutectic melting point, which is around 1150 °C (Wang et al., 2016) was started to found at basicity 0.6, where the nepheline's peaks seem to increase with

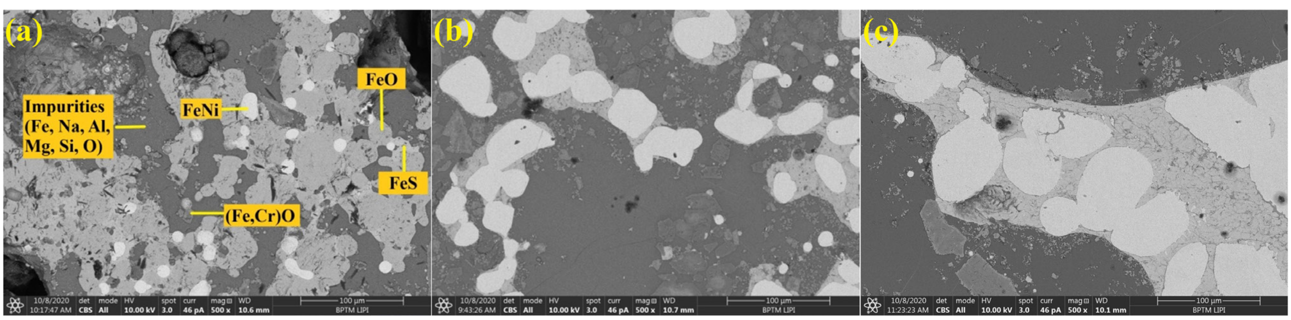

Figure 5. Microstructure of reduced ore with various reductant dosage at stoichiometry (a) 0.1; (b) 0.3; (c) 0.5.

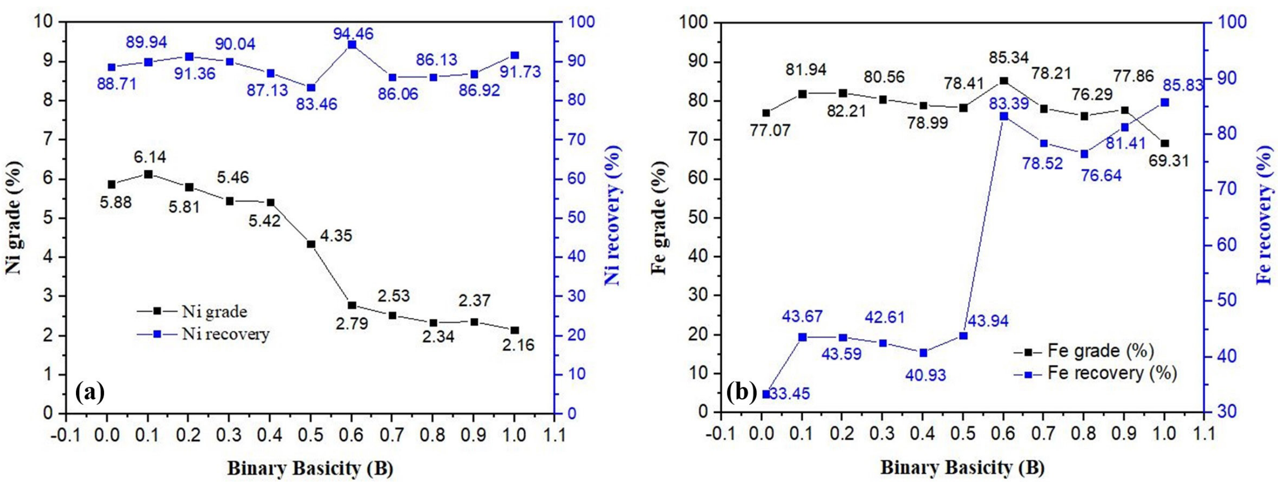

Figure 6. Effect of binary basicity 0.01 to 1.0 (a) nickel grade and recovery; (b) iron grade and recovery.

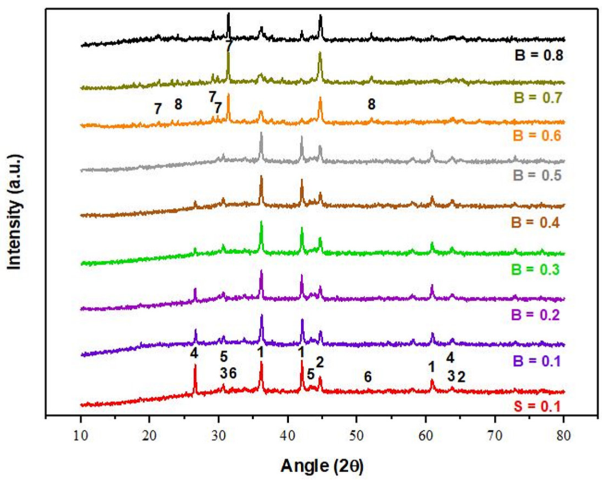

Figure 7. XRD pattern of reduced ore with various binary basicity (1-wustite; 2-ferronickel; 3-magnesioferrite; 4-quartz; 5-troilite; 6-forsterite; 7-nepheline; 8-meililite).

the increase of basicity. Jiang et al. (2013) reported that nepheline (I) was obtained from the reaction of sodium oxide, which resulted from the decomposition of sodium sulfate with iron silicate (Equation 9-11). According to Wang et al. (2016), nepheline (II) can also be generated from sodium oxide's reaction with calcium alumina silicate, as expressed in Equation 12. From this work, the nepheline (I) is generated at basicity 0.1 to 0.5, while the nepheline (II) is formed at basicity 0.6 to 1.0. It is also appropriate with this study due to the presence of 5 wt% aluminum content in lateritic nickel ore.

$$Na_2SO_4+3CO \rightarrow Na_2O+S+3CO_2 \quad (9)$$
$$2FeO+SiO_2 \rightarrow Fe_2SiO_4 \quad (10)$$
$$Na_2O+2Fe_2SiO_4 \rightarrow 4FeO+Na_2Si_2O_{5(nepheline\ I)} \quad (11)$$
$$Na_2O+CaAl_2Si_2O_8 \rightarrow 2NaAlSiO_{4(nepheline\ II)}+CaO \quad (12)$$
$$Fe+S \rightarrow FeS \quad (13)$$

Liquidus phase of nepheline and troilite (Equation 13) will promote the agglomeration of ferronickel particle by lowering its surface tension (Zhu et al., 2019). As shown from microstructure analysis of reduced ore (Figure 8), the ferronickel grains are getting larger as the increase of binary basicity. It also shows that the wustite, which pointed by gray colour, looks decreasing with the increase of binary basicity, which indicates that liquid phase also could promote the reduction rate of metallic oxide.

Melilite, which is a binary solid solution of gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$) (Chuang et al., 2009), is starting to observed at basicity 0.6, as shown in Figure 7. From the ternary diagram of CaO-MgO-SiO_2 with 5 wt% Al_2O_3 (Figure 9) shows that melilite has a high relatively melting point, i.e., 1400 ºC. This high melting point phase could decrease the nickel oxide reduction rate. Thus, as shown in Figure 6(a), the nickel grade is decreased significantly at 0.6 basicity due to melilite formation. At basicity 0.1, the presence of cristobalite (SiO_2) is advantageous to promote the formation of nepheline (I) and iron silicate for agglomerating ferronickel and inhibit the metallization of iron, respectively.

CONCLUSION

In the selective reduction of lateritic nickel ore, the nickel grade in ferronickel could be improved by limiting the reductant dosage to inhibit iron metallization. More addition of reductant will lower the nickel grade due to the increasing of metallic iron. However, it resulted in larger ferronickel particles, which promote the liberation of ferronickel from its impurities.

Modifying the binary basicity with CaO addition also could increase the nickel grade in ferronickel due to its ability to breakage the nickel and iron in silicate chemical bonds. The low melting point phase, i.e., nepheline, also promotes the increasing recovery of the metallic phase. The optimum binary basicity is 0.1, which resulted in ferronickel with 6.14% and 89.94% for nickel grade and recovery, respectively. Nevertheless, the excess of calcium oxide addition could promote the high melting point temperature phase, i.e., melilite, thus lowering the reduction rate of nickel oxide.

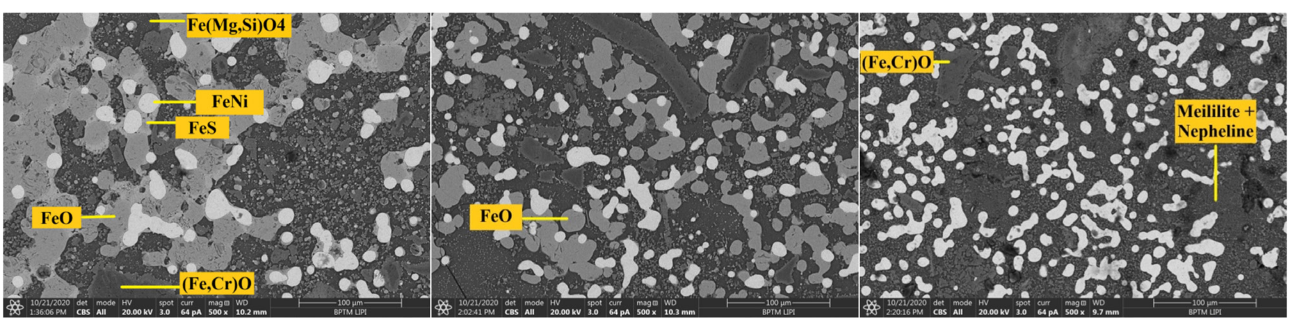

Figure 8. Microstructur analysis of reduced ore with various binary basicity: (a) 0.1; (b) 0.5; and (c) 1.0.

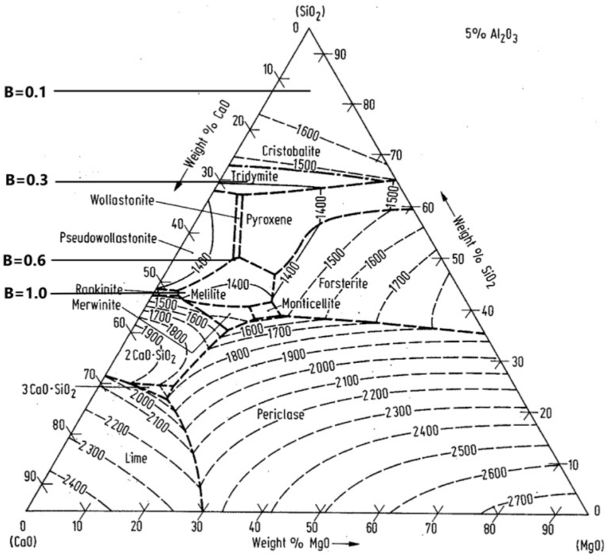

Figure 9. The quarternary diagram of $CaO-MgO-SiO_2$ with 5 wt% Al_2O_3 (Allibert et al., 1995).

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