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Leaching of silicon from ferronickel (FeNi) smelting slag with sodium hydroxide solution at atmospheric pressure

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Abstract. The present paper reports the leaching behavior of silicon from ferronickel slag under atmospheric pressure using sodium hydroxide solution. The effect of several experimental variables, namely concentration of leaching agent, operating temperature, stirring speed, and slurry density was investigated. The leaching kinetic was also investigated by using shrinking core model. It was determined that leaching of silicon from the slag was controlled by diffusion through product layer, although the activation energy was found to be 85.84 kJ/mol, which was unusually high for such a diffusion-controlled process.

1. Introduction

The production of each ton of ferronickel generates about 8 tons of slags. In contrast to the slag produced by copper, iron or steel smelters that are widely consumed in the cement industry, most of ferronickel smelting slag are only disposed at landfills. This may lead to undesirable environmental impacts considering the immense quantity of its production. It is therefore important to valorize these slags to improve the sustainability of the ferronickel industry and to optimize the value of natural resources utilization.

There have been several attempts to provide such alternative usages of ferronickel slags such as for the production of construction materials [1, 2], cements [3, 4], or geopolymers [5, 6], but there has been no attempt to recover the remaining valuable metals within the slags as pure products to date. This is probably because of the fact that the contained valuable metals such as silicon, magnesium, iron, and aluminum are existing primarily as silicate compounds making them difficult to be dissolved. Theoretically, however, the recovery of these metals would be possible by dissolving the silicates with a strong alkaline solution such as NaOH to expose the metals within the slag for the further recovery process.

This approach has been investigated for leaching of steel slags, which also contain significant amounts of silicates, both at elevated and atmospheric pressure. Xiao, et al. (2010) studied the dissolution of silica using either concentrated NaOH or KOH solutions in a Teflon-lined stainless-steel autoclave at 140□240 °C, and reported that 71% of silica can be dissolved in 2 hours at 240 °C [7]. Nikoli□, et al. (2016) reported that leaching of steel slag using concentrated NaOH solutions at 25□60 °C resulted in low silica dissolution with the highest dissolution of only 26% in 2 hours at 60 °C [8]. Despite its higher leaching rate, however, operating at elevated pressure is deemed to be unattractive for the processing of such secondary resources due to the need of an expensive autoclave.

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The present study focused to investigate the leaching behavior of silicon from the ferronickel slag with concentrated NaOH solution under atmospheric conditions particularly at near boiling temperatures of the solution and longer leaching duration. The dissolution kinetics of silicon from the slag is also investigated to provide theoretical guidance to elucidate the leaching process.

2. Materials and Methods

2.1. Materials

The slag used in this study was obtained from the ferronickel plant of PT ANTAM (Persero) Tbk in Pomalaa, Indonesia. Molten FeNi slag was immediately granulated by water atomization method by introducing high-pressure water to the molten slag in a water pond and hence resulting in the glassy characteristic of the slag. The slag sample taken from the plant was ground using a rotary ball mill to reduce the particle sizes to between 44 and 74 μm for maximizing the exposure of the minerals within the slag to the leaching agent. Its chemical composition was analyzed using a sequential X-ray fluorescence spectrometer (XRF, ADVANT XP Thermo ARL9900) and the results are presented in table 1. The phase analysis of the slag was performed using X-ray diffraction (XRD, PANalytical X'Pert PRO PW3040/x0) and the results show that the slag comprises of enstatite ($MgSiO_3$, 69.3%), forsterite (Mg_2SiO_4, 27.6%) and magnesium-iron-silicate (3.1%). The used leaching agent was prepared from an analytical grade of sodium hydroxide pellets (Merck) dissolved in deionized water.

Table 1. Chemical composition of ferronickel slag

Element	Weight (%)	Component	Weight (%)
Si	23.06	SiO_2	52.10
Mg	16.90	MgO	27.06
Fe	7.88	Fe_2O_3	11.26
Al	3.43	Al_2O_3	6.49
Cr	0.84	Cr_2O_3	1.22
Ca	0.56	CaO	0.79
Mn	0.48	MnO	0.61
Ni	0.07	NiO	0.09
Na	0.00	Na_2O	0.00
LOI	0.00	0.00	0.00

2.2. Methods

The experiments were performed in batch mode. The leaching tests were carried out in a 5-neck 1000 ml cylindrical Teflon reactor. In order to avoid contamination, polypropylene tubes were used for sampling. The slurry was heated and stirred using a hot plate equipped with temperature control system and magnetic stirrer. Evaporation loss was minimized by installing a condenser that circulates vaporized water back to the reactor. The slag was added into the reactor only after the sodium hydroxide solution has reached the desired temperature. Samples were taken at selected intervals (i.e. after 0.25, 0.5, 1, 2, 4, 8, and 12 hours) and filtered. The filtrate was analyzed using atomic absorption spectrophotometer (AAS, Shimadzu AA-6300), while the residue was washed with deionized water and analyzed using scanning electron microscopy (SEM, JEOL-6510A)) equipped with energy dispersive spectroscopy (EDS). The variations made in leaching experiment are shown in table 2.

Table 2. Variations of experimental variables of FeNi slag leaching

Parameter	**Values**
NaOH concentration (M*)	6, 8, 10, 12, 14

Agitation speed (rpm)	200, 300, 400, 500, 600
Solid percentage (%)	5, 10, 15, 20, 25
Reaction temperature (±2 °C)	25, 50, 70, 90, 110

*) M= molarity unit (mol/l)

3. Results and discussions

3.1. Leaching chemistry

Figure 1 shows the stability fields for silicon-containing species in sodium hydroxide solutions at temperature of 90 °C and pressure of 1 bar. The figure shows that the dissolution of silica may occur through the formation of soluble sodium silicates (Na_2SiO_3) at pH about 10.5–13.5 at relatively oxidizing environment that is slightly above the water stability region. Based on the XRD result that showed that the ferronickel slag was comprised of forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$), and iron magnesium silicate ($FeMgSiO_4$), the leaching reaction may occur through the following reactions:

$$SiO_{2(s)} + 2\,NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \quad (1)$$

$$MgSiO_{3(s)} + 2\,NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + Mg(OH)_{2(aq)} \quad (2)$$

$$Mg_2SiO_{4(s)} + 2\,NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2SiO_{3(aq)} + 2Mg(OH)_{2(aq)} \quad (3)$$

$$Fe_2Mg_{18}Si_{10}O_{40(s)} + 20NaOH_{(aq)} + 10\,H_2O_{(l)} \rightarrow 10Na_2SiO_{3(aq)} + 18\,Mg(OH)_{2(aq)} + 2\,Fe(OH)_{2(aq)} \quad (4)$$

Clearly, these reactions are oversimplified but they show that divalent metals such as magnesium and iron would be dissolved, it given the solution alkalinity, they would be quickly precipitated afterward. The overall process would then result in relatively fine solids that are rich in magnesium and iron for the further recovery process.

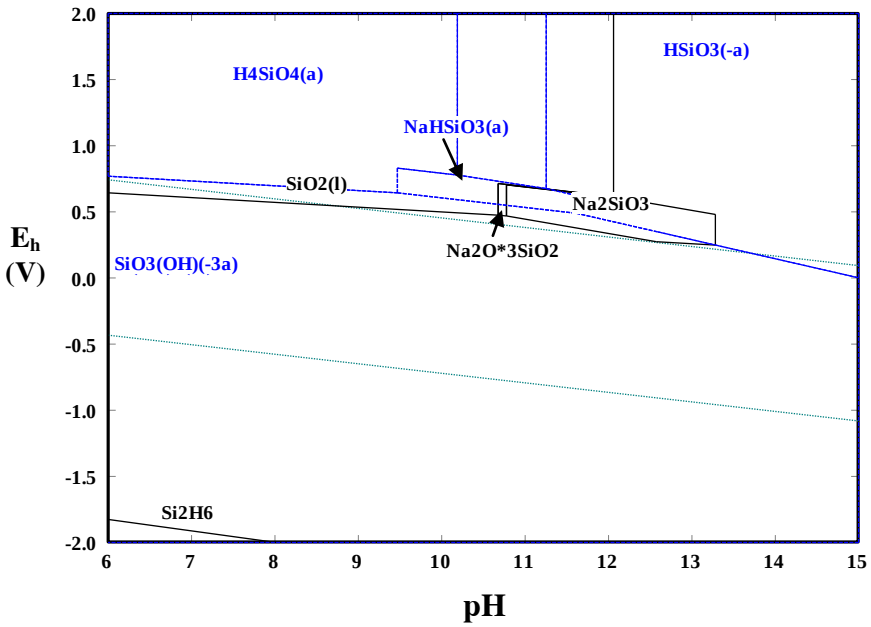


Figure 1. Eh-pH diagram of Si-Na-H_2O system as constructed by HSC software version 5.11 at 90°C, 1 bar, Si (5 M), Na (10 M)

3.2. Effect of sodium hydroxide concentration

The effect of the reagent concentration on the silicon leaching rate was investigated by varying the initial concentration of NaOH solution from 6 to 14 M at operating temperature of 90 °C, solid percentage of 5%, agitation speed of 300 rpm, and leaching duration of 12 hours. The results, as summarized in figure 2, show that the leaching rates are relatively constant at the studied NaOH

concentrations except at 10 M in which significant increase in silicon dissolution was observed. A similar trend, wherein silicon dissolution from a ferronickel slag was significantly increased with the increase NaOH concentration up to a certain concentration and decreased significantly afterward, was also observed by Maragkos et al. (2009) [6]. They attributed this behavior to the formation of secondary aluminosilicate precipitates that hinders further dissolution of the silicon at higher NaOH concentrations. This is also seemed to be the case for the present results but in addition to the secondary aluminosilicates, there may also be some significant amounts of Na_2SiO_3 that are precipitated at the surface of the reacted particles due to the lack of water at the higher concentrations of leaching agent.

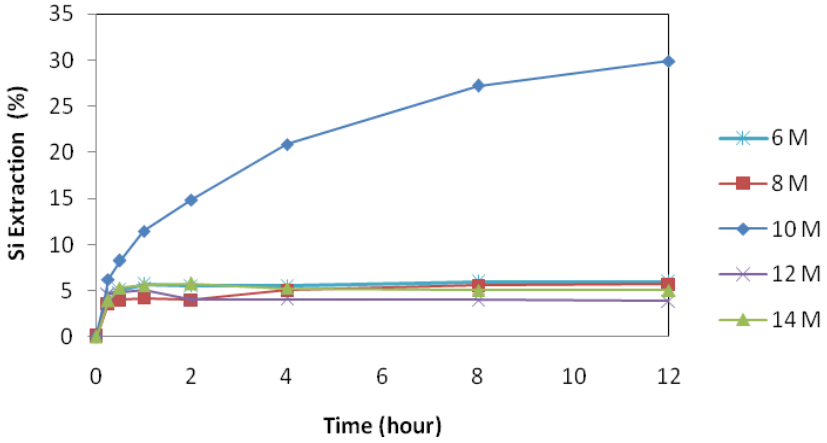


Figure 2. Effect of the NaOH concentration on the leaching rate of silicon from ferronickel slag

3.3. Effect of stirring speed

The effect of stirring speed on the leaching rate was studied to examine the effect of diffusion through liquid film surrounding the solid particles on Si extraction by varying the speed of the magnetic stirrer from 200 to 600 rpm at temperature of 110 °C, NaOH concentration of 10 M, solid percentage of 5%, and leaching duration of 12 hours. The results, as shown in figure 3, show that stirring speed has a notable effect on the leaching rate. Interestingly, the leaching rate of silicon is decreased with the increase in stirring speed suggesting that the reaction is not likely to be controlled by diffusion through the liquid film surrounding the particle. In all the succeeding leaching experiment, therefore, 200 rpm was selected to ensure effective suspension of the particles while minimizing the effect of liquid film diffusion.

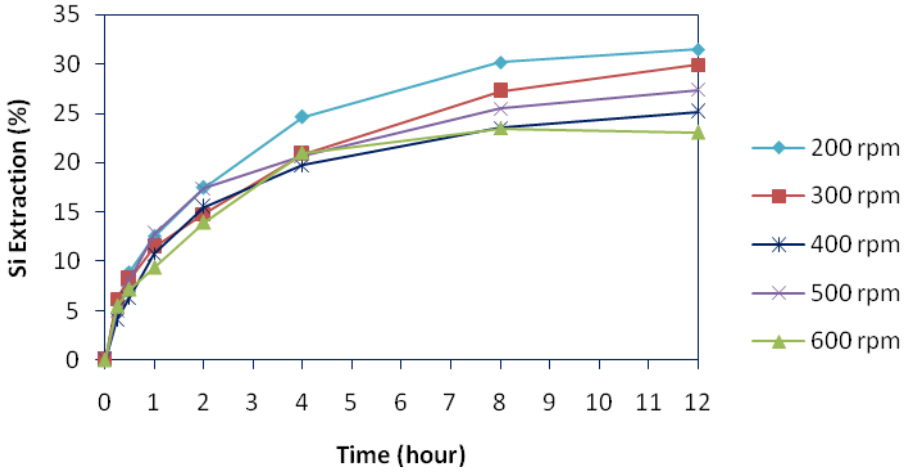


Figure 3. Effect of agitation speed on the leaching rate of silicon from ferronickel slag.

3.4. Effect of reaction temperature

The effect of temperature on the leaching rate of silicon from ferronickel slag was carried out by varying the operating temperature in the range of 25 to 110 °C using NaOH concentration of 10M, agitation speed of 200 rpm, solid percentage of 5%, and leaching duration of 12 hours. The results, as summarized in Figure 4, show that the leaching rate of silicon was highly dependent on temperature. This can be attributed to the higher solubility of sodium silicate coupled with the wider stability of its formation at higher temperature. In addition, this may also be the result of the decrease in the slurry viscosity at the higher temperature improving the mass transfer associated with the acceleration of the leaching reactions [9].

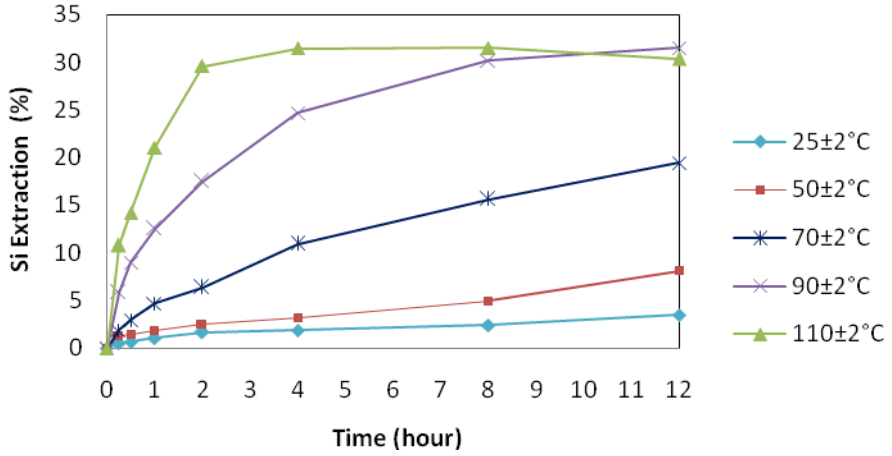


Figure 4. Effect of temperature on the leaching rate of silicon from ferronickel slag.

It is worth to be noted that the experimental result at 110 °C suggests the formation of a product layer on the surface of the leached particles that inhibit further dissolution of silicon. It can be seen that silicon dissolution was relatively fast within the first 4 hours, which was up to 31.48%, but no further dissolution was seemed to occur afterward.

3.5. Effect of slurry density

The effect of slurry density on the leaching rate of silicon from ferronickel slag was conducted by varying the solid percentage from 2 to 25% at temperature of 110 °C, NaOH concentrations of 10 M, stirring speed of 200 rpm, and leaching duration of 12 hours. The results, as shown in figure 5**,** show that the increase in the slurry density, decrease the leaching rate of silicon to a point where the change is no longer apparent. This is because of the lower the ratio of solid to liquid, the higher the amounts of the free NaOH for the reaction and the lower the viscosity of the slurry.

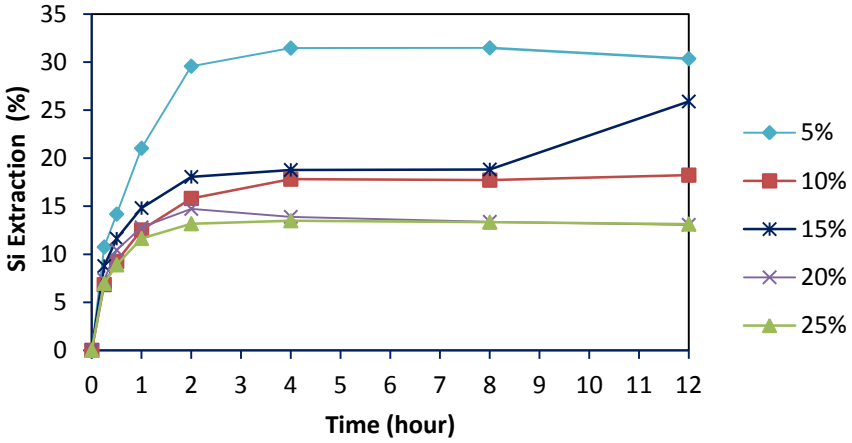


Figure 5. Effect of solid percentage on the leaching rate of silicon from ferronickel slag

3.6. Analysis of leaching kinetics

Visual observations from the experiments suggest that the leaching process of the slag follows the shrinking core model. The leaching process, therefore, can generally be controlled whether by chemical reaction at the surface of the core of un-reacted particle, diffusion of the reactant through liquid film surrounding the particle, or diffusion of reactants through the product layer [10]. Assuming that the geometry of the slag particle is spherical, the following conversion-time equations represent the dissolution kinetics of the system when surface chemical reaction (Eq. (5)), diffusion through liquid film (Eq. (6)), or diffusion through the solid product layer (Eq. (7)) is the rate-controlling step:

$$t/\tau = 1-(1-X_B)^{1/3},\ \tau = \frac{\rho_\beta R_0}{bk"C_A} \quad (5)$$

$$t/\tau = X_B\ ,\ \tau = \frac{\rho_\beta R}{3bk_f C_{Af}} \quad (6)$$

$$t/\tau = 1-3(1-X_B)^{2/3}+2(1-X_B),\ \tau = \frac{\rho_\beta R^2}{6b\mathcal{D}_e C_{Af}} \quad (7)$$

where X_B is the fraction of B in solid that is converted to product at time t, τ is the time for complete conversion of B by reactant A, $k"$ is chemical reaction rate constant, k_f is mass transfer coefficient of the fluid film, b is number of moles of B consumed per mole of reacted A, C_{Af} is the concentration of reactant A in the bulk of solution, ρ_β is the density of the solid, R_0 is the initial radius of the solid, and D_e is the diffusion coefficient through the product layer. By plotting the values of Eq. (5), (6), and (7) using the fractions of the dissolved silicon that were obtained in the previous experiments at various temperatures, it was found that Eq. (7) exhibited the best fit among the three equations based on it corresponding values of R^2 (0.9868-0.9996) as shown in figure 6. The results thus suggest that the leaching process is controlled by diffusion through the product layer.

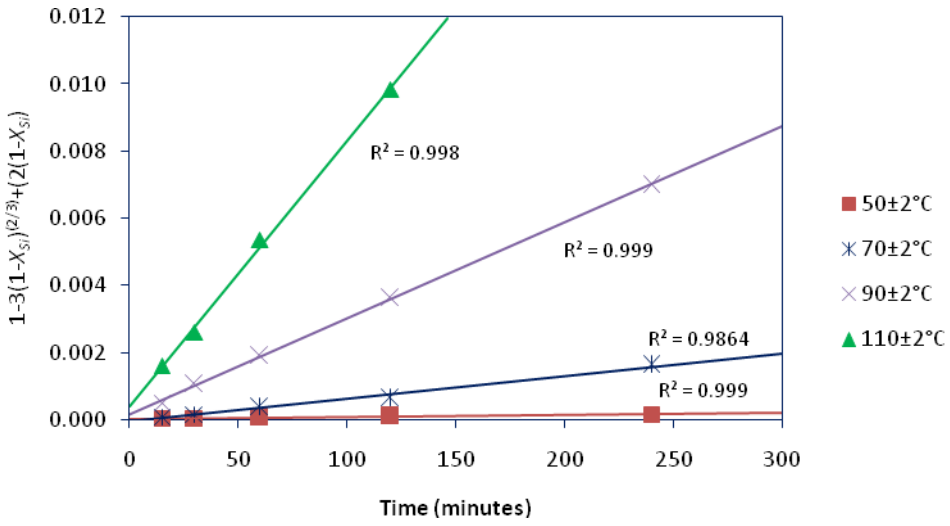


Figure 6. The plot of $1-3(1-X_B)^{2/3}+2(1-X_B)$ versus time at various leaching temperature

The activation energy can then be determined by plotting the dependence of the apparent rate constant that was obtained from Eq. (7) versus 1/T based on Arrhenius equation:

$$k = k_o e^{-Ea/RT} \quad (8)$$

where k is the overall rate/kinetic constant, k_o is the frequency factor, E_a is the apparent activation energy, R is the ideal gas constant (8.314 J/(K.mol), and T is the leaching temperature. The slope of Arrhenius plot in figure 7 reveals that the activation energy for the leaching process is 85.84 kJ/mol. This is unusual because such high value of activation energy usually refers to a chemical reaction controlled process, but previous investigators have reported that some diffusion controlled reactions can also have unusually high activation energy [11, 12, 13, 8].

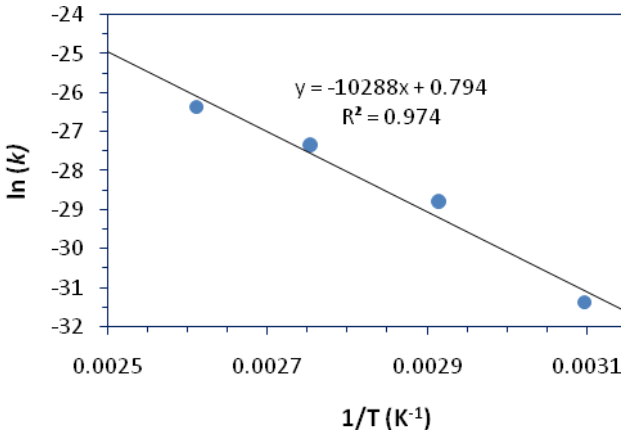


Figure 7. Arrhenius plot for the dissolution of silicon from ferronickel slag

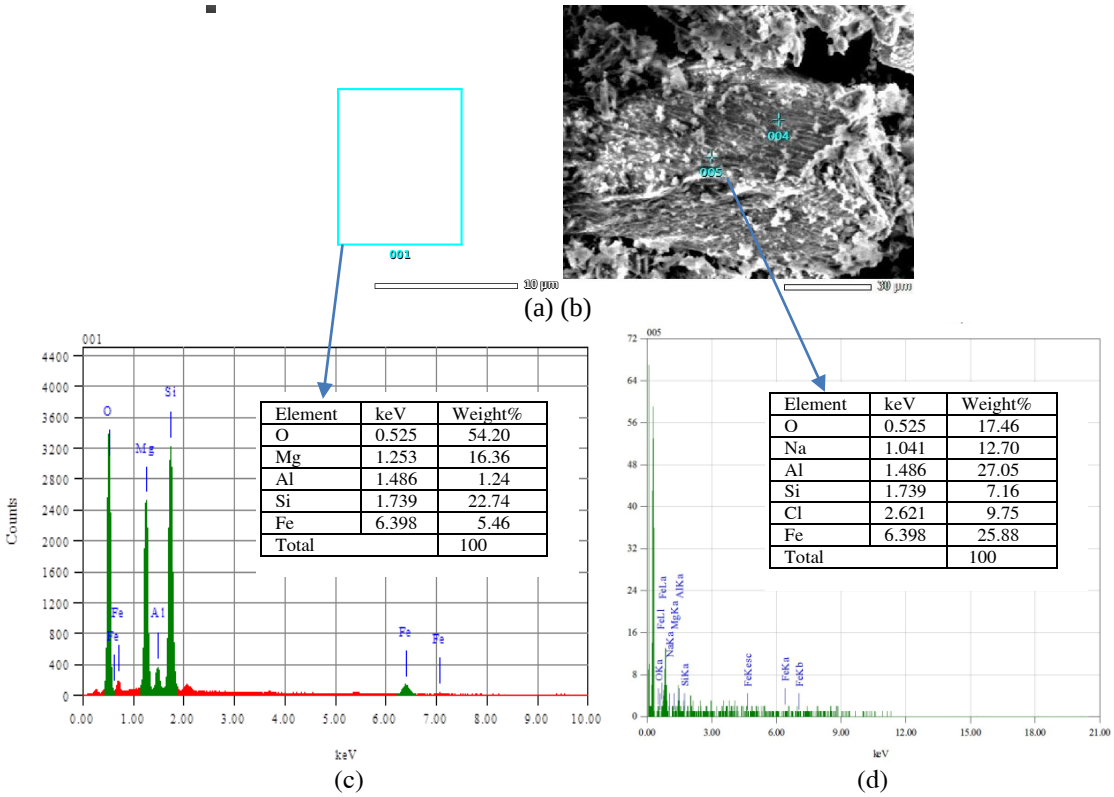


Figure 8. SEM images and EDS analyses of the original ferronickel slag (a and c) and residue (b and d).

The analysis of the leaching residue that was obtained under the optimum leaching conditions (i.e. at NaOH concentration of 10 M, temperature of 110 °C, solid percentage of 5%, and leaching duration of 12 hours) supports that the leaching process is controlled by diffusion through the product layer (figure 8). The morphology of the slag before (figure 8 (a)) and after leaching (figure 8 (b)) shows progressive oxidation on the surface of the particles which is reflected by their rough and porous appearance. The formation of the product layer as aluminosilicates and sodium silicates was indicated by the EDS analyses that show a significant increase of aluminum and sodium concentrations on the surface of the leached particles (figure 8 (c), and (d)).

4. Conclusions

The present study investigated the effect of several operating parameters on silicon dissolution from ferronickel slag under atmospheric pressure and the kinetics of the dissolution process. It was found that concentration of the leaching agent, stirring speed, temperature, and slurry density have the significant effect on the leaching rate of silicon from ferronickel slag under atmospheric pressure. It was determined that the dissolution of silica from the slag was controlled by diffusion through solid product layer, although the apparent activation energy, which was 85.84 kJ/mol, was unusually high for a diffusion-controlled process. The formation of the product layer was apparent from the result of the leaching test at the most optimum conditions found in the present study, namely at NaOH concentration of 10 M, temperature of 110 °C, stirring speed of 200 rpm, and solid percentage of 5%, that showed relatively fast dissolution of silicon up to 31.48% during the first 4 hours, but no further dissolution was observed afterward. This was then supported by dissolution kinetics that was found to fit well to the shrinking core model with diffusion through product layer as the rate-controlling step, and the analysis of the solid residue that indicated the formation of aluminosilicates and sodium silicates precipitates on the surface of the leached particle.

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