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Double acting liberation of Ni and Co in the pre-treatment process to increase recovery of nickel from low-grade nickel laterite

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Keywords

limonite, sulfation roasting, sodium fluoride, recovery

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Abstract

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Keywords: limonite, sulfation roasting, sodium fluoride, recovery

1. Introduction

The main deposits of nickel laterite are found in equatorial areas where rock weathering is more likely to occur in hotter and rainy areas [1]. Indonesia, which is located in the tropics, has the highest amount of laterite nickel reserves in the world, 21 million tonnes and mining production of 760,000 tonnes in 2020 [2]. One of the laterite nickel ore deposits in Indonesia comes from Halmahera Island, North Maluku. Investigations carried out by PT Weda Bay revealed that laterite ore originating from Halmahera Island is a type of limonite ore. Generally, limonitic-type ore has low Ni content

(< 1.50 wt.%) and high Fe content (> 40 wt.%) [3]. Halmahera laterite nickel reserves have an average Ni content of 1.50 wt.% [4]. Laterite with nickel content above 1.50 wt.% is usually processed pyrometallurgically to produce ferronickel, while ore with a nickel content of less than 1.50 wt.% has not undergone further processing.

The general method for processing low-grade nickel ore is through hydrometallurgical processes such as acid leaching at high temperature and pressure (HPAL) [5], atmospheric leaching [6–11], combined pyrometallurgy/hydrometallurgy with the Caron process [12] or process with calcination as leaching pre-treatment [13]. The HPAL process is

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quite effective for recovering nickel and cobalt due to high-pressure process conditions and low requirement of acid. However, it has low selectivity because of the dissolution of contaminants as well. Moreover, the costs of procuring an autoclave and maintaining it are extremely high. In addition, the Caron process results in low nickel and cobalt extraction even though the energy and reagent demand are large [12]. Furthermore, atmospheric leaching is an easier method to control and needs lower costs, but its selectivity is also low because many elements, such as iron and aluminum are dissolved as well during the leaching process [8,14,15]. A following process, such as solvent extraction, employing chelating agents and ionic liquids, needs to be applied to separate nickel and cobalt. Specific solvents or chelating agents, however, are difficult to access and costly.

The sulfation roasting process is an alternative method that can increase the selectivity of nickel extraction against iron [16–18] from either laterite material [19] or other materials such as spent lithium-ion batteries [20,21]. This process of sulfurization can be carried out with the addition of substances containing sulfates such as H_2SO_4 [22,23], ammonium sulfate and iron sulfate [20]. Basically, the sulfation roasting process consists of sulfating the ore using concentrated sulfuric acid at room temperature, which causes minerals in the ore, such as goethite, changing into sulfate compounds spontaneously. Then, the ore is roasted at a temperature range of 200–700°C. During the roasting stage, nickel and cobalt form sulfate compounds, which are easily soluble in water, while iron sulfate will form oxide compounds so that at the leaching stage, the iron could remain in the residue while nickel and cobalt dissolve in water to form a solution of nickel and cobalt sulfate [1,16–18,24–30]. Therefore, lower energy consumption could be employed for sulfation roasting since the process is conducted at atmospheric pressure and lower temperatures. Moreover, the high selectivity of Ni and Co could be achieved since the main element, iron, could be separated in the residue, that further can be used to generate hematite as a side product. The potential environmental hazard from sulfation roasting is acid-liquid waste from the leaching process. It, however, can be recycled through a simple process. This process can increase the selectivity of nickel extraction by roasting at temperatures up to 700°C.

Research on limonite ore originating from the Philippines through an activation pretreatment process has been conducted by Ma et al. [23]. The ore sample was added with sodium fluoride (NaF) with a range of 0–7 wt.%, then sulfuric acid was

added at 15–60 wt.%. The mixture of sodium fluoride and sulfuric acid was then activated at a temperature and time range of 200–450°C and 5–150 min, respectively. The activation results were leached using water with a solid/liquid ratio of 20 wt.%, stirring speed of 300 rpm, temperature of 90°C and leaching time of 3 h. The research results showed that nickel and cobalt recoveries of 85.3% and 93.9% were obtained under the conditions of adding 50 wt.% sulfuric acid, activation temperature of 400°C, activation duration of 60 min and adding 3 wt.% NaF. The addition of NaF could reduce the surface tension of the mineral interface, thus facilitating the liberation of Ni and Co from the complex phase during pre-treatment. Furthermore, NaF could react with Fe-sulfate, forming sodium jarosite, which reduces the Fe content in leach liquor [23]. Ribeiro et al. [31] have also conducted similar research on nickel laterite ore originating from Brazil through a sulfation roasting process. This research was carried out by adding sulfuric acid to ore samples with variations of 34–68 wt.%, pre-roasting at a temperature of 256°C for 60 min, followed by roasting at a temperature of 680–830°C and a time of 5–60 min. The roasting results were then leached using water at a temperature of 80°C and a stirring speed of 400 rpm with variations in leaching time and solid/liquid ratio, namely 15–360 min and 2.5–12.5 wt.%. Optimum nickel and cobalt recoveries of 83.3% and 90 wt.%, respectively, were obtained under the conditions of adding 50 wt.% sulfuric acid, pre-roasting at 256°C for 60 min, roasting at 740°C for 20 min and leaching with a solid/liquid ratio of 12.5 wt.% at 80°C for 30 min.

In this research, process modification to improve the condition of the sulfation roasting to the limonite ore from Halmahera, Indonesia was conducted. It aims to increase the recovery of nickel and cobalt from low-grade nickel laterite. The combination of NaF addition and sulfation-pre-roasting processes is the novel process of this research. It could allow double-acting liberation for Ni and Co by reducing the surface tension of the interface of the phases and reducing specific surface area through heat treatment along with the formation of SO_3 gas that subsequently initiates partial decomposition to form NiSO_4 , CoSO_4 and Fe_2O_3 . CaF addition could effectively destroy silicate minerals [32]. Utilization of NaF which is Na is more reactive than Ca is expected to provide more penetration in devastating silicate minerals. Moreover, the dehydroxylation temperature of lizardite at about 594°C [33] could be decreased and occurred at the pre-roasting conditions. Furthermore, the formation of water-soluble

Ni and Co as well as undissolved iron in the roasting process is essential to recover Ni and Co in the leachate optimally and separate iron in the residue. Besides energy effectiveness, this research will provide a significant contribution to the optimization of Ni and Co extraction by strictly suppressing Fe dissolution of low-grade lateritic nickel ore. The factors that influence the extraction of nickel, cobalt and iron that will be studied include temperature, roasting time and the addition of NaF. Temperature and time are estimated to be the dominant factors that will influence the formation of SO_3 gas. The addition of NaF was observed to determine its effect on the sulfation roasting process which was previously proven to be able to increase the percent extraction of Ni and Co in the activation pretreatment process.

2. Materials and methods

The raw material used in this research is laterite ore originating from Halmahera, North Maluku. The ore was dried at a temperature of 110°C for 24 h, crushed using a disk mill and sieved until particles' size $\leq 74\ \mu\text{m}$ were obtained. A total of 10 g of sample was mixed with sodium fluoride (NaF) and moistened using 20 wt.% water. Demineralized water was used for this experiment. The sulfation process was carried out by adding 50 wt.% concentrated sulfuric acid (purity of 98% as described on the package without any dilution) then stirring evenly. The sulfated samples were then roasted using a closed-system horizontal tube furnace connected to a water-trapping system at the outlet. The roasting process was carried out in two stages, pre-roasting and roasting, which were conducted at a temperature of 270°C for 1 h and at a temperature of $500\text{--}750^\circ\text{C}$ for 10–30 min, respectively. Pre-roasting, which was assisted with the addition of NaF and H_2SO_4 , previously aimed to reduce the specific surface area and surface tension of the mineral to liberate Ni and Co trapped in the complex phases. Besides the decomposition process of $\text{Fe}_2(\text{SO}_4)_3$ that formed from the sulfation process, SO_3 was also formed, which initiated partial decomposition of liberated Ni-Co and iron basic sulfate. Further decomposition process occurred in the roasting process to form water-soluble Ni-Co sulfate and undissolved hematite that is easily separated afterwards. The roasting results were crushed using an agate mortar and then leached using water to dissolve the sulfate compounds. The leaching stage was carried out in a reactor with a stirring speed of 400 rpm, temperature of 80°C , solid/liquid ratio of 12.5 wt.% and leaching time of 30 min. The leaching

slurry was filtered to obtain a filtrate containing metal sulfate and leaching residue. The residue was dried in an oven for 6 h at a temperature of 110°C . Characterizations using XRD (X-Ray Diffraction), XRF (X-Ray Fluorescence) and FE-SEM (Field Emission-Scanning Electron Microscopy), respectively, were carried out to determine the phase structure, chemical composition and morphology of the limonite ore samples, roasting products and leaching residues. Quantitative analysis using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) was carried out to determine the metal content in nickel ore samples and leaching filtrate. The scheme of the research process is described through the flow diagram in Fig. 1.

3. Results and discussion

3.1. Characterization of limonite nickel ore

Tables 1 and 2 reveal that the results of chemical composition analysis of limonite ore samples using XRF are not much different compared to ICP-OES. Based on XRF analysis, limonite ore contains 1.70 wt.% Ni and 51.3 wt.% Fe, while based on ICP-OES analysis, it contains 1.74 wt.% Ni and 49.4 wt.% Fe. The Co element was not detected in XRF analysis because its content was relatively small. This can be seen in the ICP-OES analysis, the Co content is 0.069 wt.%. The Si element was not detected in the ICP OES test solution, because the sample (limonite) was dissolved using aquaregia ($\text{HCl} + \text{HNO}_3$) so that the silica did not dissolve in the solution and was still in the residue. The sample preparation technique between solids (for XRF) and solutions resulting from the digestion of laterite samples (for ICP) affects the difference in elemental contents from analytical results using XRF and ICP. However, by pointing out that there is no statistically significant difference in the measurement findings between the two, the analysis results can both be accepted.

The results of XRD analysis of laterite nickel ore sample from Halmahera Island in Fig. 2 shows that the dominant minerals in the ore sample are goethite ($\text{FeO}(\text{OH})$), quartz (SiO_2) and lizardite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). By looking at the chemical compositions, the laterite nickel ore sample mostly consists of iron hydroxide, especially in the goethite ($\text{FeO}(\text{OH})$) phase. However, the presence of Ni or Co elements was associated with Fe in the goethite structure despite the nearly identical atomic weights of Ni, Co and Fe. Due to the highest concentration of Fe in the ore, the XRD analysis identifies the phase of goethite as the dominant nickel-bearing mineral

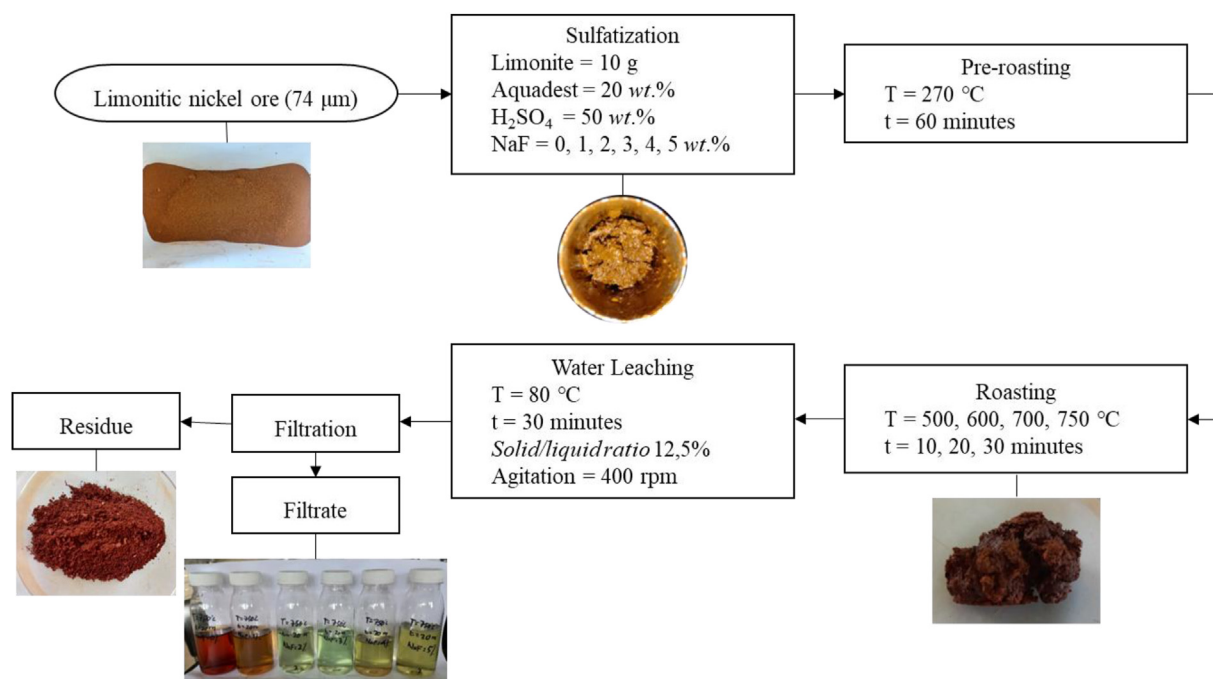


Fig. 1. Experimental design.

Table 1. XRF analysis of raw limonite ore.

Elements	Fe	Si	Al	Ni	Cr	Mg	Ca	Mn	Cl	K	P	S	Ti
wt.%	51.30	4.60	3.70	1.70	1.60	1.10	1.00	0.70	0.10	0.10	0.10	0.10	0.10

(mineral host) [23,34–37] and it is common to be able to write it as a phase with the formula (Fe,Ni)OOH as in the previous research by Nurjaman et al. [38]. Therefore, this laterite nickel ore is included in the limonitic type ore [33].

Mg is also found in the laterite ore in trace amounts, but it is linked to silicates that form the lizardite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) phase in which its crystal lattice is separated from the iron-oxide phase, but due to the differences in atomic weight that separate it from interactions with Fe, Ni and Co, it can be identified as a distinct phase.

3.2. Mechanism of reaction upon the sulfation-roasting-water leaching process

The sulfation and roasting stages in the sulfation roasting process aim to change the properties of the ore so that it will be easily dissolved in the leaching process using water as the solvent. Laterite nickel

ore is difficult to beneficiate because of its complex mineralogy [31,39]. Therefore, sulfation and roasting stages are carried out to convert nickel and cobalt oxide compounds into sulfate compounds that are easily soluble in the water.

Based on the XRD data, the phases involved during the sulfation process are $\text{FeO} \cdot \text{OH}$ and $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, while SiO_2 does not undergo a reaction with sulfuric acid. The reactions that may take place in the sulfation roasting process are as follows:

1. Sulfation and pre-roasting

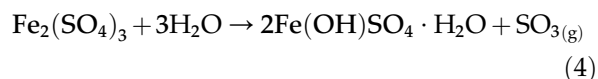
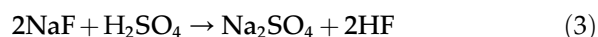
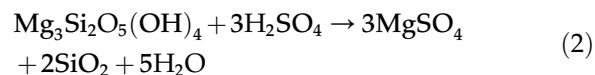
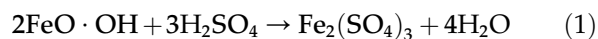


Table 2. ICP-OES analysis of raw limonite ore.

Elements	Fe	Al	Ni	Ca	Cr	Mn	Mg	Na	Co
wt.%	49.4	3.70	1.74	1.37	1.14	0.86	0.76	0.71	0.069

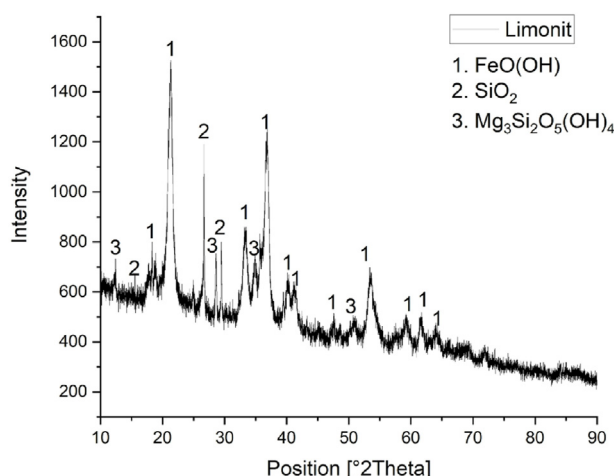
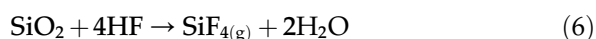
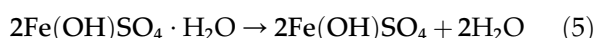
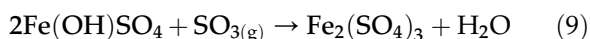
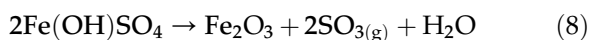
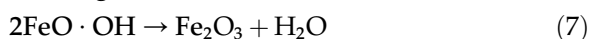


Fig. 2. XRD pattern of sample.



2. Roasting Process



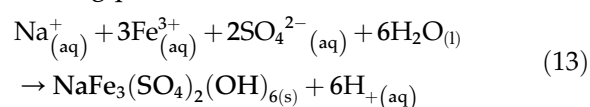
3. The untrapped Ni and Co during sulfation reacting with SO_3 gas formed during roasting



4. Dissociation of the sulfates formed during sulfation in the roasting process



5. The formation of sodium jarosite in water leaching process



3.3. Effect of roasting parameters to the leaching percentage of elements

The leaching percentage of Ni, Co and Fe with respect to the NaF addition in the pre-roasting process, roasting temperature and time were studied to determine the effectivity of the process in the

escalating Ni and Co recovery from low-grade nickel laterite. Likewise, the leaching percentages of other elements are also studied subsequently.

3.3.1. Effect of NaF addition, roasting temperature and time to the leaching percentage of Ni, Co and Fe

The optimal temperature of sulfation roasting without NaF addition was studied by Ribeiro et al. [31,33]. The effect of sodium fluoride (NaF) addition, along with pre-roasting and sulfation roasting at 270°C for 60 min and 750°C for 10 min, respectively, was studied. The NaF addition was varied from 0 to 5 wt.% to the ore mass used.

The graph in Fig. 3 forms a parabola for the percent recovery of Ni and Co. The highest percent recovery of nickel reached at 71.3% with the addition of 3 wt.% NaF, while cobalt gained the highest recovery at 98.8% with the NaF addition of 2 wt.%. In contrast to Ni and Co, the percent recovery for Fe attained its lowest value of 3.27% with the addition of 3 wt.% NaF. Rising the NaF addition further escalated the Fe recovery significantly, which is hindered. It is in good agreement with the results of research conducted by Ma et al. [23]: the peak of the parabolic curve for Ni is steeper than for Co. The percent extraction of Ni and Co reached the maximum value with the addition of 2–3 wt.% NaF with an increase in percent recovery of 50% and 25% for Co and Ni, respectively.

The addition of sulfuric acid and NaF along with heat treatment could destroy the goethite and lizardite structure, thereby releasing trapped Ni and Co. Accordingly, extraction of Ni and Co experienced an upward trend, while the dissolution of Fe

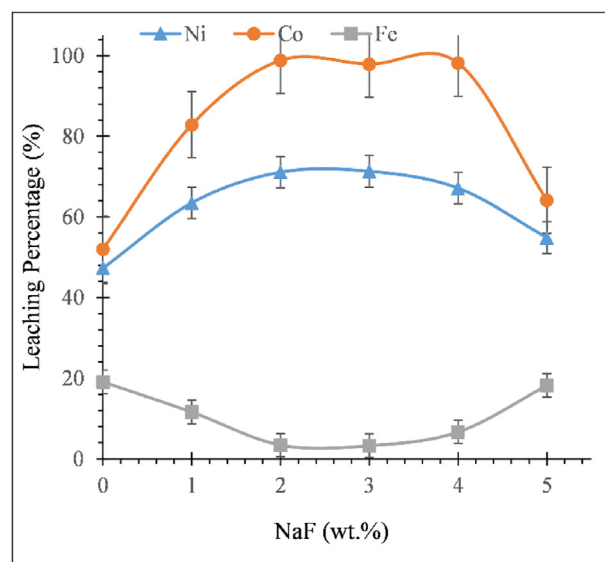


Fig. 3. Effect of NaF addition to the recovery of Ni, Co, and Fe.

plummeted due to the formation of the undissolved hematite in the roasting process.

The presence of dissolved Na was reacted with Fe from remaining $\text{Fe}_2(\text{SO}_4)_3$ forming sodium jarosite [23]. However, the addition of NaF in more than 3% led to the escalation of Fe dissolution. It might be caused by the destruction of goethite and lizardite, the destruction has widely occurred as NaF addition accelerated, initiating more liberation of Ni and Co, including Fe from lizardite. As a result, more Fe reacted forming excess $\text{Fe}_2(\text{SO}_4)_3$ and shifting the equilibrium to the left; thus, hematite cannot be formed in the roasting process as a reaction (12) that triggered an ascending trend for the leaching percentage of Fe. Meanwhile, the existence of Na^+ ion from NaF addition might not be sufficient to form sodium jarosite completely. Consequently, Fe dissolved in the leachate and soared the leaching percentage of Fe considerably, while the leaching percentage of Ni and Co declined.

Roasting temperature is one of the factors that greatly influence the sulfation roasting process. Using an inappropriate temperature can result in the decomposition reaction of iron(III) sulfate that is less than optimal so that the levels of iron oxide and SO_3 gas are not high enough. This will reduce iron oxide residue and reduce the level of formation of nickel and cobalt sulfate.

Fig. 4 shows the effect of roasting temperature in the sulfation roasting process on percent recovery with process parameters in the form of NaF addition of 3 wt.% and roasting time of 30 min. Based on this graph, there was an increase in the percent recovery

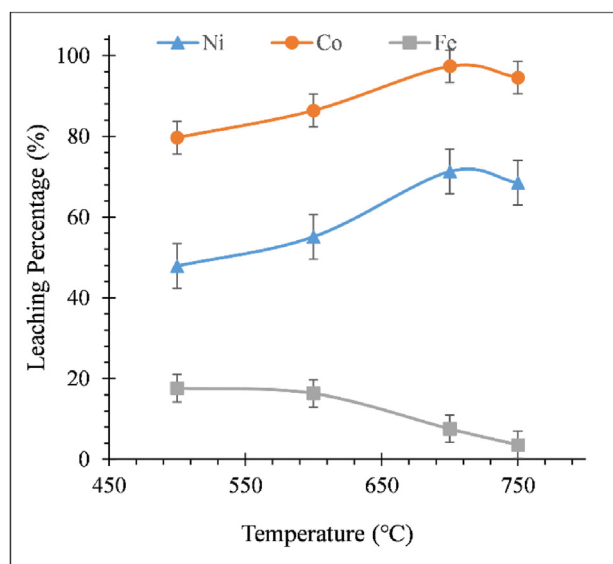


Fig. 4. Effect of roasting temperature on percent recovery of Ni, Co, and Fe.

for nickel up to 71.3% and cobalt 97.3% at a temperature of 700°C, then decreased to 61.6% for nickel and 94.5% for cobalt at a temperature of 750°C. The percent iron recovery experienced a significant decrease from 17.6% at a temperature of 500°C to 3.58% at a temperature of 750°C.

The decrease in percent recovery that occurred for nickel and cobalt at a temperature of 750°C was due to the decomposition of sulfate compounds at high temperatures. Based on calculations carried out by Ribeiro et al. [31], the higher the temperature causes the Gibbs free energy of sulfate compounds to decrease. At temperatures higher than 685°C, iron sulfate has a lower Gibbs free energy than other sulfate compounds, so it is less stable. Iron sulfate begins to decompose at temperatures above 570°C, followed by nickel, cobalt and magnesium sulfate at temperatures of 675°C, 800°C and 850°C.

The appropriate roasting time or duration is needed so that the formation of sulfate compounds can be maximized. Research conducted by Guo et al. [18] showed that the maximum percent extraction of Ni and Co was obtained at a roasting time of 30 min. Roasting for more than 30 min has a negative influence on the percent extraction of nickel and cobalt due to the decomposition of sulfate into oxides that are insoluble in water. However, there was a decrease in the percent extraction of iron and aluminum at a roasting time of 60 min, which would increase Ni and Co levels. By referring to the research of Guo et al., in this study the roasting time was limited to 10, 20 and 30 min. Experimental data is presented in Fig. 5 with process parameters including a roasting temperature of 700°C and the addition of 3 wt.% NaF. Based on that graph, there was an increase in the nickel recovery percentage from 67.9% to 71.3% with a change in roasting time from 10 to 30 min. The same thing also happened to the percentage recovery of cobalt from 89.3% to 97.3% with the same change in time. The percent iron recovery experienced a slight increase from 6.9% to 7.7% with a roasting time of up to 20 min, then decreased at a roasting time of 30 min to 7.55%.

The longer the roasting process, the more nickel and cobalt sulfate compounds will be produced so that more nickel and cobalt can be dissolved. The percent iron recovery value did not experience a significant change in value. The change in value that occurred was only 0.8% between a roasting time of 10 and 20 min and 0.15% between a roasting time of 20 min and 30 min. A similar thing also happened in the research conducted by Ribeiro et al., where the iron recovery percentage obtained were 27.2% and 28.9% at roasting times of 20 and 40 min,

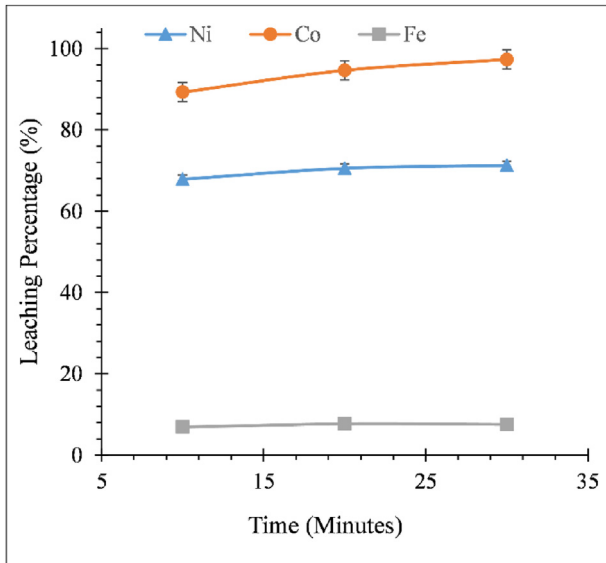


Fig. 5. Effect of roasting time on percent recovery of Ni, Co, and Fe.

respectively [31]. Thus, roasting time can increase the percent recovery of nickel and cobalt but does not significantly affect the percent recovery of iron, so the optimum roasting time is 30 min.

3.3.2. Effect of NaF addition, roasting temperature and time to the leaching percentage of other minor elements

For all process parameters examined, as shown in Figs. 6–8, the leaching behavior of the elements Mg, Mn and Al follows the same pattern as Ni and Co, whereas Cr follows the same pattern as Fe. For Mg, the extraction pattern is similar to Co, while Mn

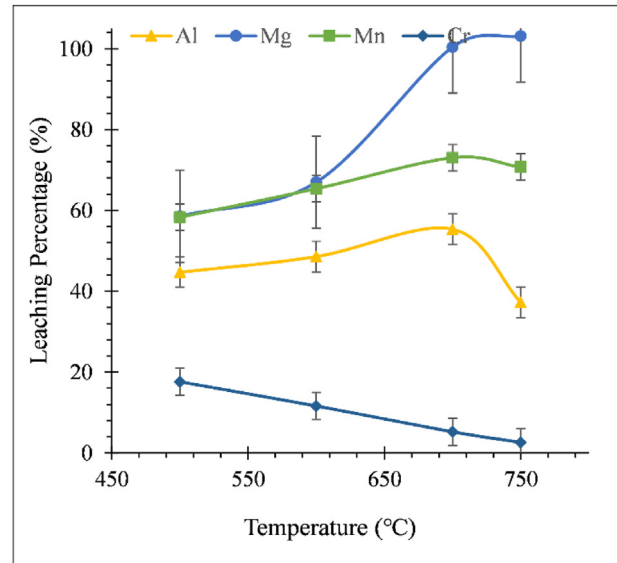


Fig. 7. Effect of roasting temperature to the recovery of other minor elements.

pattern, is similar to Ni. The third graph shows that magnesium has the highest reactivity of all the elements, particularly when the temperature rises, which sharply increases the leaching percentage. In all process parameters, the Al element has a lower leaching percentage than Mg and Mn. This might be due to Al is linked to the phase that contains Mg, meaning that the sulfation process is dominated by the host element.

From the discussion above, the optimum leaching percentages of nickel, cobalt and iron are 71.3%, 98.8% and 3.43%, respectively. Table 3 compares Ni,

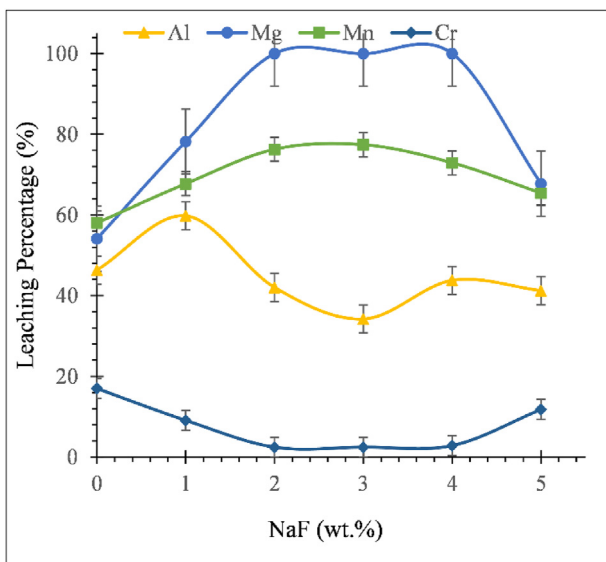


Fig. 6. Effect of NaF addition to the recovery of other minor elements.

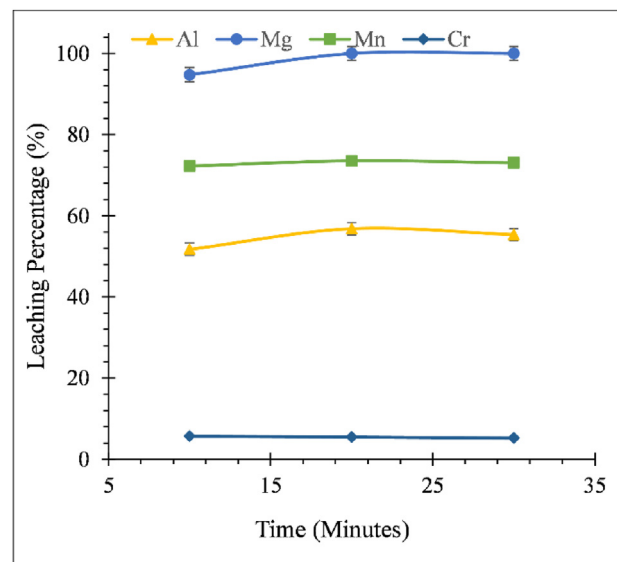


Fig. 8. Effect of roasting time to the recovery of other minor elements.

Table 3. Comparison of Ni, Co, and Fe recovery from various processes.

Process	Recovery (%)			
	Ni	Co	Fe	Reference
Atmospheric leaching	<60	n.d	< 60	[9]
HPAL	78.92	79.07	21.66	[40]
Sulfation roasting with NaF addition + water leaching	93.9	85.3	7.7	[23]
Sulfation + pre-roasting + roasting + leaching	83	90	5.5	[41]
Double acting pre-treatment + roasting + leaching	71.26	98.80	3.4	this study

n.d. = not defined.

Co and Fe recovery from various of processes. The finding shows that the Fe dissolution can be suppressed significantly and the highest Co leaching percentage can be gained. The Ni leaching percentage can be increased by maximizing hematite formation in the roasting process. Therefore, sodium jarosite formation that caused the absorption of Ni through physical adsorption [26] can be hindered.

In contrast to limonite ore, saprolite ore has a much higher magnesium percentage. Since sulfuric acid is more reactive towards magnesium oxide than it is towards iron and nickel, magnesium oxide will consume more sulfuric acid than it does with those metals. The residual sulfuric acid will react with iron and nickel oxide after the magnesium oxide reacted, rendering the method ineffective. The addition of NaF to HPAL or AL processes can potentially improve leaching efficiency, selectivity and operational performance while also offering benefits such as reduced energy consumption and corrosion mitigation of equipment. However, it is essential to carefully optimize the NaF concentration and process conditions to maximize these benefits while minimizing potential drawbacks such as increasing complexity or safety concerns.

Considering the possibility of corrosion due to the discharge of corrosive gas released from the reaction, the inner tube of the furnace needs to be replaced periodically.

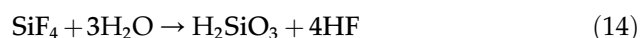
3.4. Analysis of roasting results and leaching residues

3.4.1. XRD analysis

XRD analysis of the roasted products and the leaching residue were carried out to determine the phase transformation that occurred after the pre-roasting, roasting and leaching processes. Fig. 9 shows a graph of XRD analysis carried out on samples roasted at various temperatures with the addition of 3 wt.% NaF and a roasting time of 30 min. In accordance with the results of the XRD analysis of the initial sample in Fig. 2, initially,

limonite was composed of compounds with the phase structures of goethite ($\text{FeO} \cdot \text{OH}$), quartz (SiO_2) and lizardite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})$).

During the pugging of the sample using water and concentrated sulfuric acid, goethite was reacted spontaneously at room temperature with sulfuric acid to become iron(III) sulfate according to reaction equation (1). This reaction was exothermically and characterized by the occurrence of a slight increase in the temperature of the mixture. Lizardite reacted with sulfuric acid to form magnesium sulfate and silica according to the reaction (2). In addition, NaF also reacted with H_2SO_4 , forming Na_2SO_4 and HF according to the reaction (3). Na_2SO_4 can then re-role in the water-leaching process to form sodium jarosite, while HF reacted with silica, forming SiF_4 according to the reaction (6). This corresponds to the XRD analysis chart in Fig. 9, showing a decrease in the SiO_2 intensity. Since SiF_4 is a volatile gas, the heating system for pre-roasting and roasting were conducted in a tube furnace, which had a closed system. The outlet of the furnace was connected to a water trap, allowing the evaporated SiF_4 was reacted with water to form silicic acid and HF in accordance with the reaction (14) as follows:



When the pre-roasting process at a temperature of 270°C , the water remaining in the mixture evaporated and reacted with iron(III) sulfate, forming SO_3 gas and iron hydroxide sulfate according to the reaction (4), which was then be dehydrated again releasing all the water bound in the compound according to the reaction (5) as in the previous research [33]. This is similar to the other research, which states that the pre-roasting process causes the change of ferric sulfate to basic iron sulfate, which is also influenced by the addition of water before sulfation [31]. The goethite phase is still detected after thermal treatment at this temperature, but the intensity was weaker. In the XRD graph analysis for the pre-roasting product, the peak phase of hematite (Fe_2O_3) was not detected, indicating that the process of decomposition of goethite into hematite

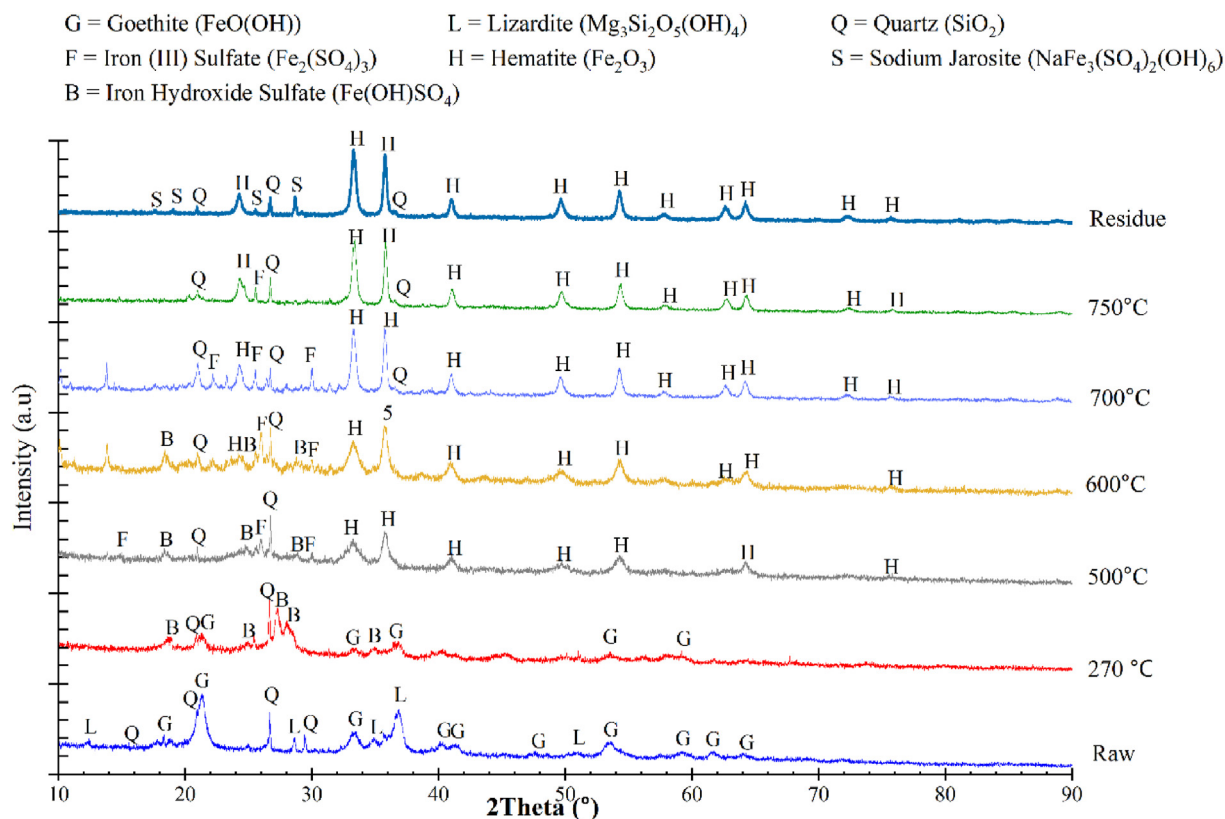


Fig. 9. XRD pattern of roasting product at various temperatures and residue of water leaching.

according to equation (7) was not occurred. This decomposition reaction can take place at a higher temperature, depending on the high crystallinity of goethite [42].

The roasting process at a temperature of 500°C causes an increase in the intensity of iron(III) sulfate formed during the sulfation process. Thermal treatment up to this temperature also causes the formation of hematites as a result of the decomposition process of goethite that takes place at temperatures > 270°C. The iron hydroxide sulfate phase resulted from phase transformation during pre-roasting decomposed again to form iron oxide and SO_3 gas according to the reaction equation (8). When the roasting temperature was increased to 600°C, the peak intensity of the hematite phase increased, while the iron hydroxide sulfate gradually disappeared. The formed SO_3 gas will react with iron hydroxide sulfate to form iron(III) sulfate according to the reaction (9) so that the $\text{Fe}_2(\text{SO}_4)_3$ phase appeared to experience a slight increase. Apart from that, there is a possibility of the release of elements Ni and Co from the structure of goethite during the decomposition process of goethite into hematite. In this case, it is assumed that Ni and Co is presented as NiO and CoO which

was then reacted with the SO_3 gas produced during the roasting process to form NiSO_4 and CoSO_4 according to the reaction (10–11). Both of these compounds are stable as sulfate up to a temperature of 780°C [33].

At a temperature above 700°C, the peak of Fe_2O_3 increases. The $\text{Fe}_2(\text{SO}_4)_3$ phase slightly increased and the iron hydroxide sulfate peak disappeared. At a temperature of 750°C, $\text{Fe}_2(\text{SO}_4)_3$ is getting weaker while the Fe_2O_3 phase increased, indicating that there is more decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 according to the reaction (12). The occurrence of this reaction is characterized by an increase in the intensity of the Fe_2O_3 phase. Although based on HSC Chemistry 6, the iron (III) sulfate decomposition reaction occurs at a temperature of 780°C, some literature states that the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ begins to occur at a temperature of 400°C [43] or 530–590°C by forming the α phase, β , or γ - Fe_2O_3 [44]. Furthermore, Fe_2O_3 dominates the phase in the residue after water leaching, accompanied by the formation of sodium jarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$) according to reaction (13). This phase is the result of the reaction between Fe^{2+} with Na^+ and SO_4^{2-} (from the dissolution of Na_2SO_4 , NiSO_4 and CoSO_4) in the presence of water according to the reaction (5)

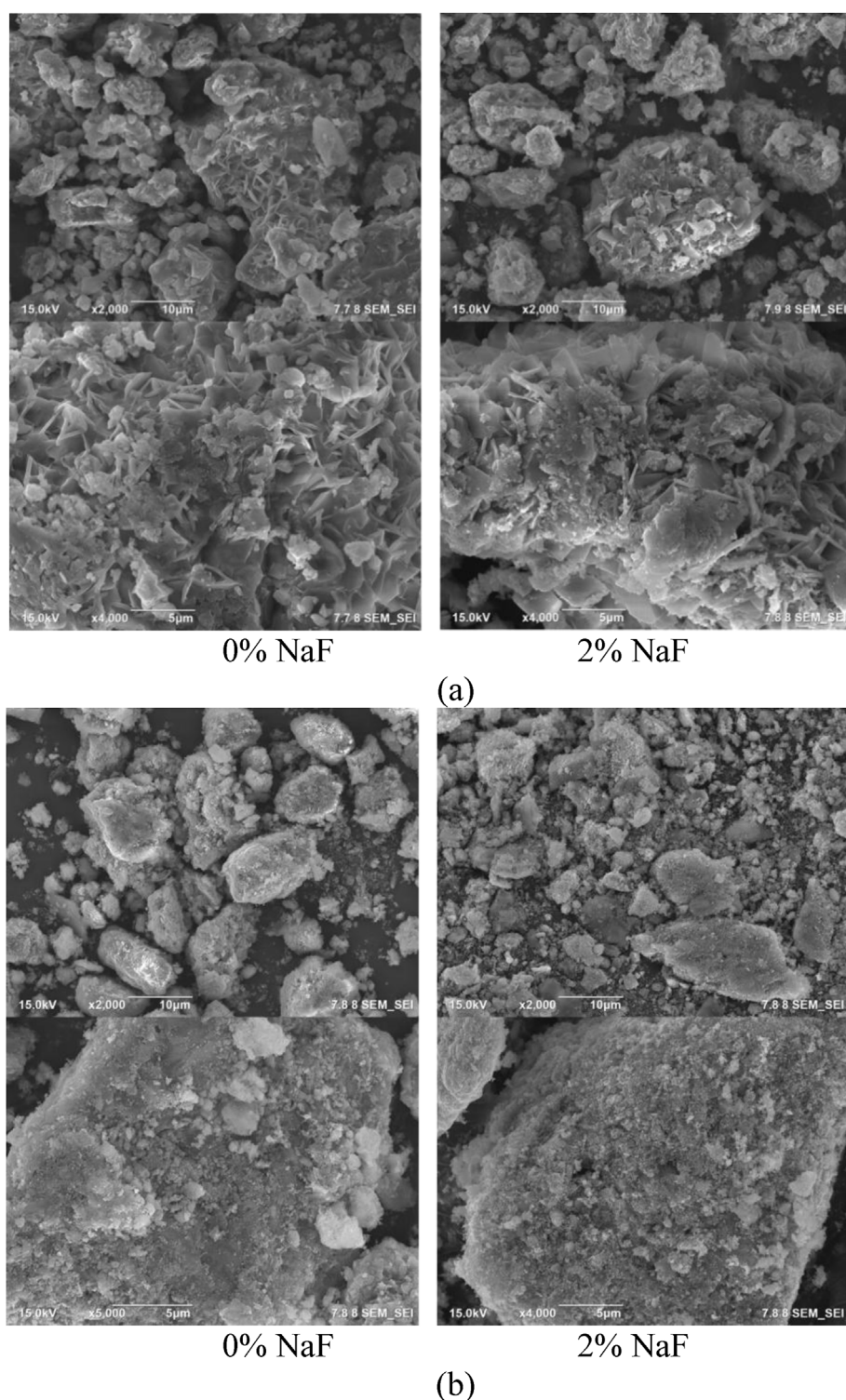


Fig. 10 FE-SEM morphology of roasting results (a), residue after leaching (b), and elemental Ni mapping of roasted sample (c).

stated by Ma et al. [45]. The large number of SO_4^{2-} ions might increase acidity when in the water environment.

In the leaching residue, no sulfate compounds were found due to the dissolution of the sulfate

compounds during the leaching process. Meanwhile, SiO_2 was not experienced significant changes by increasing roasting temperature. Meanwhile, the Ni, Co and Mg-sulfate were not detected from the results of the XRD analysis.

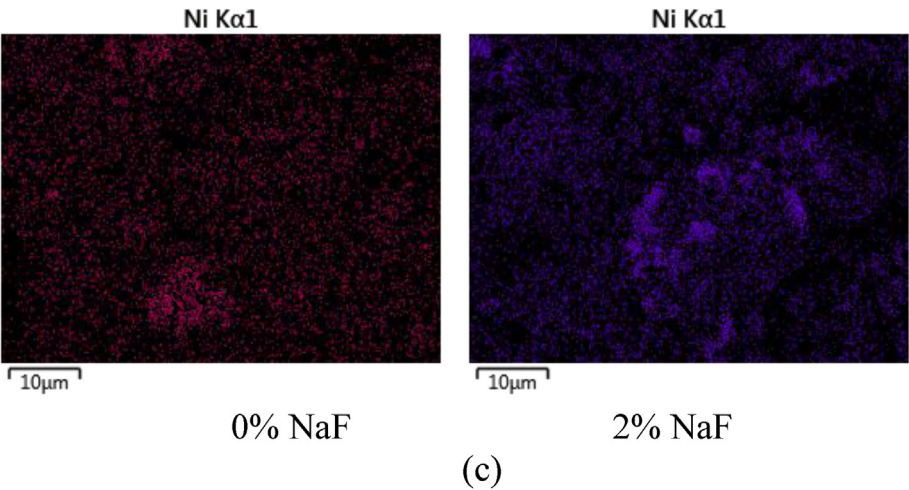


Fig. 10. (continued).

3.4.2. Morphological analysis

The results of morphological analysis using FE-SEM on limonite particles after going through the roasting process at a temperature of 700°C and

leaching residue are shown in Fig. 10(a) and (b), while the quantitative EDS analysis of both samples are shown in Fig. 11(a) and (b). Those figures reveal that the roasting particles and leaching residue have

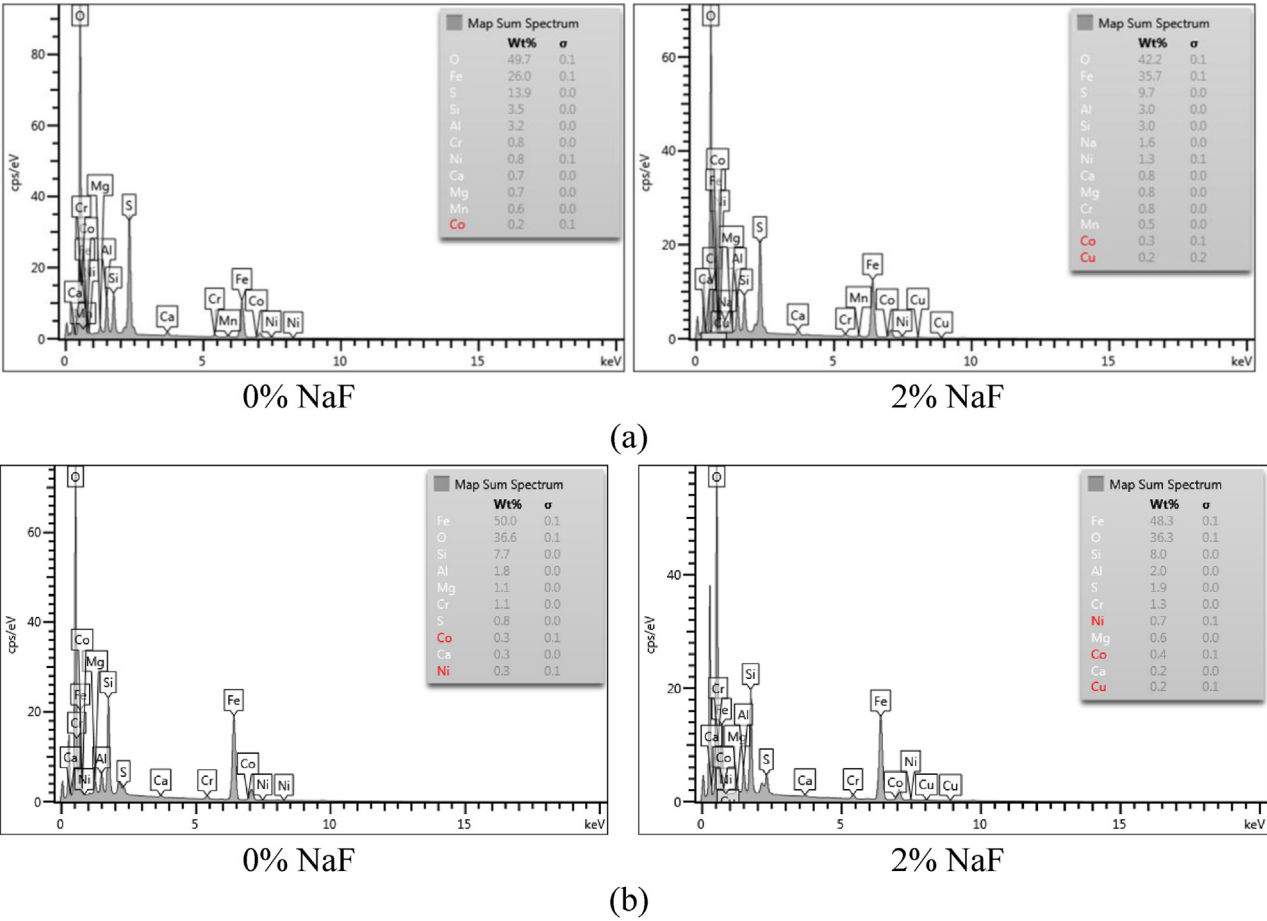


Fig. 11. EDX graph of roasting results (a) and residue after leaching (b).

quite varied sizes. Heating treatment causes crystal water removal, crystal structure collapse and forming an amorphous phase [32]. It can be seen in Fig. 10(a), which presents porous morphology due to the roasting process. At a greater magnification of 4000 \times , the structure forms small round particles between the flakes, like flower petals, which are spread over almost all the surfaces of the particles. Moreover, elemental mapping of roasted results over Ni (Fig. 10(c)) shows that NaF addition is sensitive to Ni decomposition, but the effect on Co decomposition cannot be determined. Mapping to the roasted result without NaF addition illustrates that the Ni mapping distribution is just concentrated in one area, while the roasting result with NaF addition shows the distribution of Ni in some areas. It illustrates that NaF addition is sensitive to Ni extraction [23] and boosts aggregation [46]. In Fig. 10(b), the morphology of the sample after leaching shows that the flower petals full of debris are no longer visible due to being dissolved in water as a leaching medium.

From Fig. 11, EDS results for roasting results (a) and residue after leaching (b) show that roasting results without NaF and with NaF are dominated by iron, oxygen and sulfur. The presence of sulfur content is due to the addition of sulfuric acid in the initial process before roasting. In the roasted samples with the addition of NaF, the presence of sodium elements can be seen along with a higher content of Ni and Co. It depicts that NaF addition is effective in reducing the surface tension of phases in the lateritic nickel; thus, the trapped Ni and Co in the complexed phase can be released. In addition, there appears to be an increase in Fe content in the residue due to an increase in Fe₂O₃ intensity, as seen from the XRD graph in Fig. 9.

4. Conclusions

Based on research that has been carried out regarding the effect of the addition of sodium fluoride, roasting temperature and roasting time on nickel and cobalt recovery in nickel laterite extraction, it can be concluded that increasing the roasting temperature can increase the percent recovery of nickel and cobalt. The highest percent recovery of nickel and cobalt was obtained at a roasting temperature of 700°C, then decreased at a roasting temperature of 750°C due to the decomposition of sulfate compounds. The longer the roasting time can increase the percent recovery of nickel and cobalt. The highest percent recovery of nickel and cobalt was obtained at a roasting time of 30 min. The addition of sodium fluoride (NaF) to the extraction

of nickel laterite through a series of sulfation roasting processes can increase the percent recovery of nickel and cobalt. The highest percent recovery of nickel and cobalt was obtained when NaF addition is 3 wt.%. The addition of NaF more than 3 wt.% decreases the percent recovery of nickel and cobalt. The highest nickel and cobalt recovery percentages are 71.3% and 97.3%, respectively, that were obtained at a roasting temperature of 700°C, a roasting time of 30 min and the addition of 3 wt.% NaF.

Ethical statement

The authors state that the research was conducted according to ethical standards.

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Conflicts of interest

The authors declare no conflict of interest.

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