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Performance of Kulon Progo low grade manganese ore leaching using acetic acid and its selectivity

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Abstract. The need of manganese to support human life has led to the exploitation of low-grade manganese ore. However, the appropriate technique has not been established and still under development. Having total amount of 120 thousand metric tons, Indonesia has huge potential of low grade manganese ore deposited in several areas such as Kulon Progo, Yogyakarta. In this study, leaching of low grade manganese ore was conducted using acetic acid which is environmentally friendly due to its ease to decompose naturally. Ore characterization was performed by X-Ray Diffraction (XRD), X-Ray fluorescence (XRF), and Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS) showing that 7.16 % is manganese while 32 % of the ore is dominated with calcite. Effects of leaching temperature and particle size on Kulon Progo low grade manganese ore were investigated. Particle sizes under study were less than 200 mesh and between 70 mesh and 100 mesh. The pH and temperature of experiment were varied on 0.7, 1.7, and 3; and 30 °C, 60 °C and 80 °C, subsequently. It was obtained that the ore particle size has no significant effect on Mn recovery. The manganese recovery of 76.08 % was obtained, containing lower recovery of calcium and iron which were 10%. The findings showed acetic acid is more selective towards manganese than to calcium and iron.

1. Introduction

Among other metals, manganese has important role for human life other than iron, copper, and nickel. According to Hegelstain (2009) almost 90% of world's manganese is used for iron and steel industry [1]. Manganese increase the ductility in steel, so that it is not easily broken. In addition to metallurgical purposes, manganese metal is also used for the production of chemical compounds such as KMnO_4 used for disinfectants, MnSO_4 for animal feed, manufacturing materials, addictive substances in gasoline, and manganese dioxide used as dry components that work for depolarizers [2]. Those varieties of applications lead to the rapid increase of manganese metals consumption every year. Although there are big amount of manganese metal, the deposit of high grade manganese become more limited. Therefore, it is necessary to explore and develop some techniques for processing deposits with low grade manganese. Manganese in Indonesia especially in Kulon Progo, can be a potential low grade manganese ore resources for full filling the industries needs. The acidity of a lot of inorganic acid used as leaching reagent was generally high, so it is expected that their selectivity is not much, the probability of corrosion effect to occur is high, and the controlling pH is



more difficult [3]. Extraction of heavy metals by inorganic acids and complexing agent has severe drawbacks. Otherwise, for inorganic acid, fast dissolution abilities may be an advantage. Organic acids have high selectivity although the dissolving abilities of them are weak. They could be an attractive extracting agent because the extraction can be performed under mildly acidic conditions (pH=3-5), and they are biologically degradable [4]. Additionally, in industrial processes, organic acids can cause a lesser corrosion effect. Even, the corrosion effect can be controlled by adding chemical substances called inhibitors such as benzoic acid and salicylic acid [5].

Wang et al. (2017) investigated the hydrometallurgical process and kinetics of leaching manganese from semi-oxidized manganese ore with sucrose. He found the optimum ratio of sulphuric acid with sucrose about 5 mol/L of sulphuric acid concentration with 0.035 mol/L of sucrose concentration on 60 minutes and 363.2 K of leaching temperature can reach leaching efficiencies about 91.4-96.9 % Mn [6]. However, this experiment still used an inorganic acid for the leachant.

As indicated above, in the previous studies, inorganic leachant was generally used in manganese leaching. But in this study, the extraction of manganese from Kulon Progo low grade manganese ore was investigated using organic acid under atmospheric pressure to reduce the risk of environmental damage caused by the leaching process. The effects of temperature, particle size, and acetic acid pH on leaching of Kulon Progo low grade manganese ore were determined.

2. Materials and Method

The low grade manganese ore used in present study was supplied from the source in Kulon Progo, Yogyakarta. First of all the ore were crushed and sieved with various sizes of -200 mesh and -70 until + 100 mesh. The elemental contents in ores were analyzed using x-ray fluorescence (XRF). Table 1 showed that the element that dominates the Kulon Progo manganese rock is calcium (Ca), whereas the manganese contained in the sample is 7.16%. In addition to XRF testing, an x-ray diffraction (XRD) analysis was also performed to identify the mineral crystal structure contained in the sample. Figure 1 shows that the main constituent mineral phase of manganese Kulon Progo is Calcite (CaCO_3). The XRD test results further strengthen XRF test results where iron is the component that dominates the sample.

Table 1. Composition of low grade manganese ore with XRF and XRD instrument

<i>Element</i>	<i>% Mass</i>	<i>Mineral</i>	<i>Mineral Name</i>	<i>% Mass of mineral</i>
<i>Ca</i>	32	<i>CaCO₃</i>	<i>Calcite</i>	66.14
<i>Mn</i>	7.16	<i>MnO₂</i>	<i>Pyrolusite</i>	7.03
<i>Si</i>	0.72	<i>SiO₂</i>	<i>Quartz</i>	1.29
<i>Zn</i>	0.53	<i>ZnS</i>	<i>Sphalerite</i>	0.46
<i>Fe</i>	0.14	<i>FeS</i>	<i>Sphalerite</i>	0.13
<i>Al</i>	0.3	<i>Al₂O₃</i>	<i>Alumina</i>	1.67
<i>Ti</i>	0.05	<i>TiO₂</i>	<i>Rutile</i>	0.05
<i>Cr</i>	0.00114	<i>Cr₂O₃</i>	<i>Chromite</i>	0.0038
<i>O</i>	59			

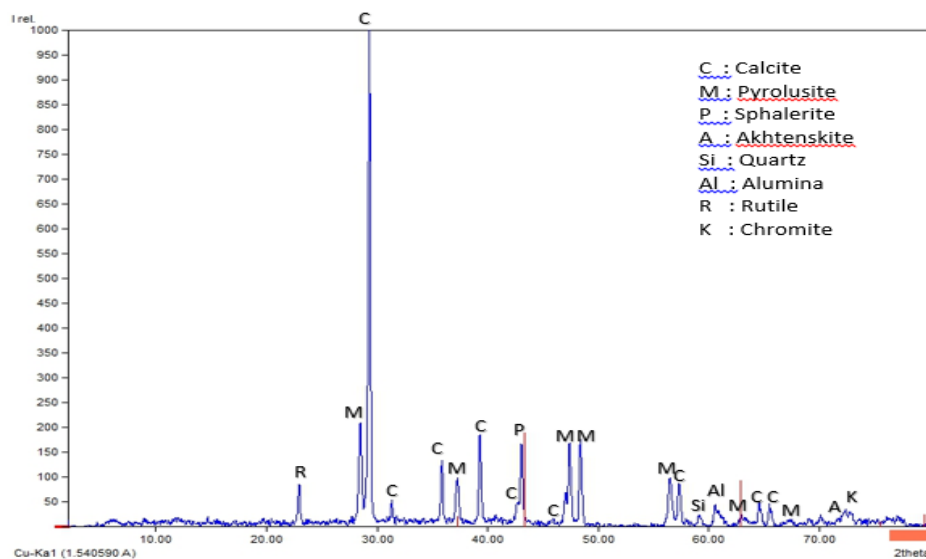


Figure 1. XRD pattern of raw manganese ore

The leaching process was carried out in 500 mL three-necked round-bottomed glass reactor at atmospheric pressure. A mechanical stirrer was used to stir the reactor contents, and a water heater batch was employed to maintain the reaction medium at a given temperature. To prevent loss of the reactants and products by evaporation, a cooler was attached to the reactor. The particle characteristics and the experimental conditions are summarized here. In the leaching experiments 300 ml of CH_3COOH solution was first put into the reactor, and after it reached the desired temperature, a given 60 gram of the ore sample was added to the solution while 400 rpm stirring started. Samples were taken at 5 mL with intervals of 5, 15, 30, 60, 120 and 240 min. The sample which taken was a suspension solution and was separated by aqueous phase and solid phase by syringe with millipore. At the end of the time reaction of 240 minutes the stirring was stopped, and all of the reactor contents were filtered off. The amount of Mn, Ca, and Fe recovery content of the filtrate was determined by AAS methods. The parameters and ranges used in the experiments are given in Table 2.

Table 2. Parameters and range employed in experiments

Parameters	Selected Parameter Values
Acetic Acid pH	0.7; 1.7; 3
Reaction Temperature ($^{\circ}\text{C}$)	30; 60; 90
Particle Size (mesh)	-70+100; -200

3. Result and Discussion

3.1. Characterization Kulon Progo Low Grade Manganese Ore after Leaching

Low grade manganese ore used in the present work was obtained from Kulon Progo. Comparison of both before leaching samples and after leaching samples were characterized by powder X-Ray Diffraction (XRD) to define the differences between the mineralogical composition before and after leaching. Figure 2 shows that there were decreased intensity of pyrolusite peaks after leaching. It was a proof that manganese have recovered in fluid phase.

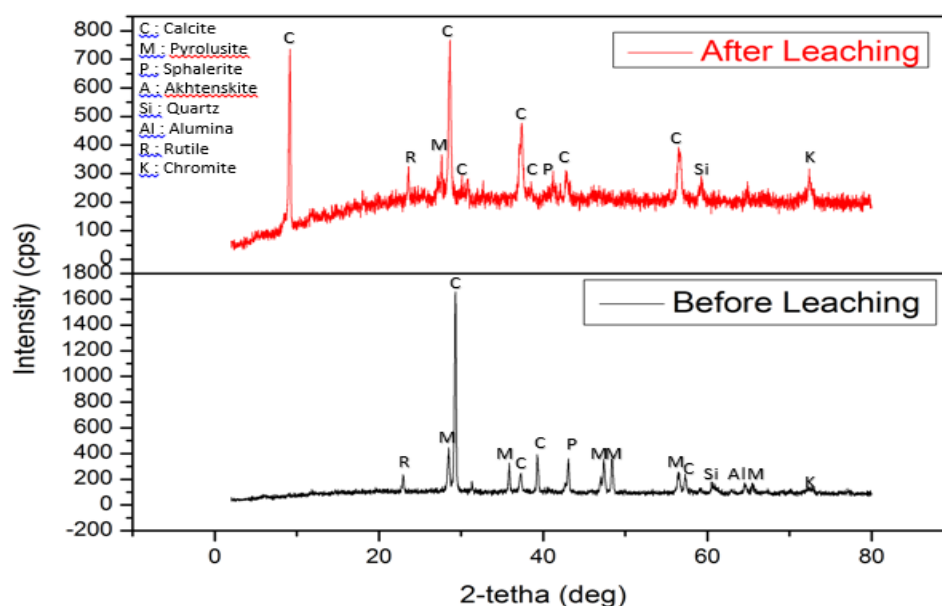
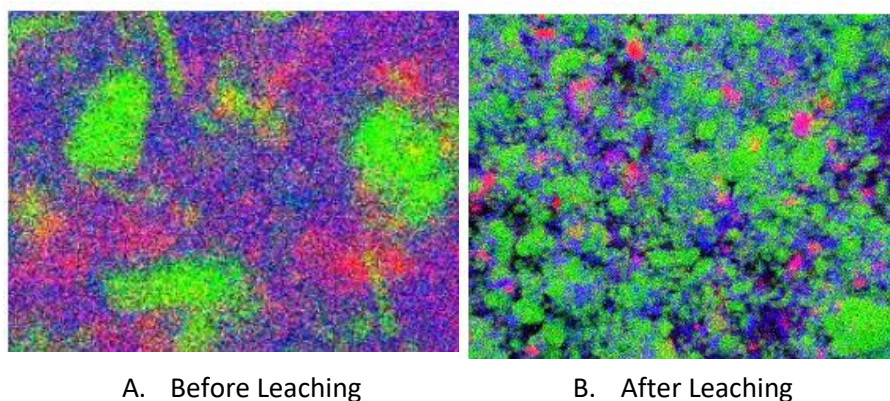


Figure 2. XRD pattern of before and after leaching of Kulon Progo manganese ore using acetic acid (temperature of 80 °C, pH of 0.7, particle size of -200 mesh, stirring speed at 400 rpm, and solid-to-liquid ratio at 20 % (w/v))

Both of before and after leaching samples were characterized by powder Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) mapping to define the difference of the element composition mapping before and after leaching. From Figure 3, it is observed that manganese element was decreased after leaching. It also could be seen that the large amount of manganese element were positioned on the surface of the ore.

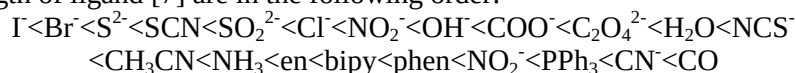


Note:



Figure 3. SEM-EDS analysis of Kulon Progo Low Grade Manganese Ore (temperature of 80 °C, pH of 0.7, particle size of -200 mesh, stirring speed at 400 rpm and solid-to-liquid ratio at 20 % (w/v))

Figure 4 showed that the recovery of manganese in acetic acid leaching was higher than other element such as calcium and iron. It was represented that acetic acid was more selective to manganese element. This condition operation experiment are temperature of 80 °C, pH of 0.7, particle size of -200 mesh, stirring speed at 400 rpm and solid-to-liquid ratio at 20 % (w/v). In Figure 4, it also can be seen the comparison between ore leaching with organic acid such as acetic acid and ore leaching with sulphuric acid. It was represented that acetic acid was more selective to recover manganese than sulfuric acid. The ore leaching with sulfuric acid could recover all of element in the ore. So that sulfuric acid could not selective with one elements especially manganese. The selective leaching agent was necessary to decrease load consumption of H^+ concentration which would attack to recover element because the leaching agent can be selective with one specific desired element. Decreasing load consumption of H^+ concentration made the process become more effective and efficient. It also was represented that manganese ore leaching using acetic acid could recover manganese of 76.08 %, higher than manganese ore leaching using sulfuric acid which recover of 72.07 %. It was because ligands in organic acid are stronger than ligand in inorganic acid. In order to recover an element to body of fluid, the reaction always produce complex compound. The complex compound was formed by interaction transition element with strong ligand. According to Fessenden (1982) the strength of ligand [7] are in the following order:



It was represented that ligand COO^- is stronger than SO_3^{2-} in order that COO^- ligand can recover many of desired elements than SO_3^{2-} ligand.

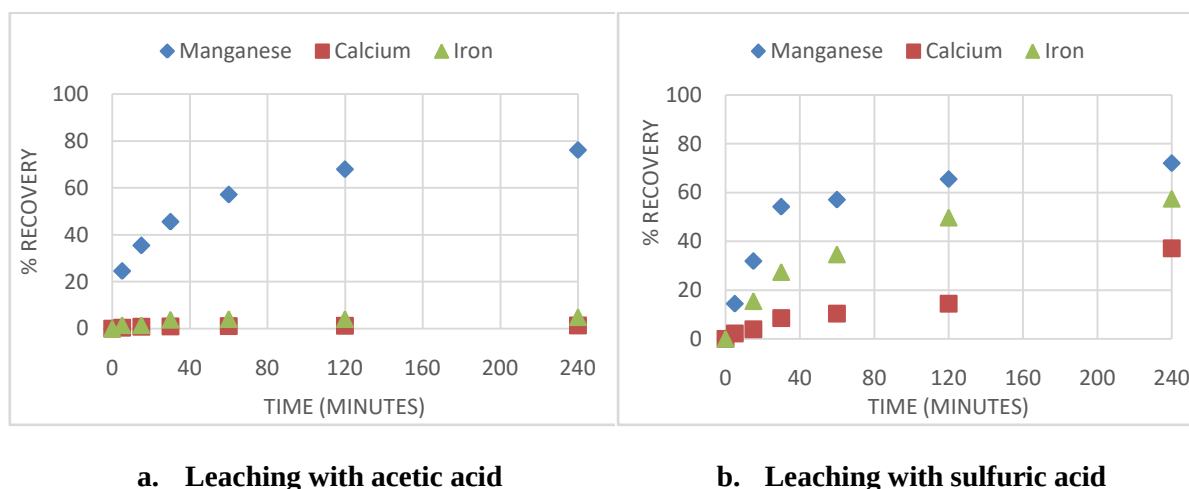


Figure 4. Comparison of Kulon Progo manganese ore leaching with organic acid and inorganic acid (temperature of 80 °C, pH of 0.7, particle size of -200 mesh, stirring speed at 400 rpm, and solid-to-liquid ratio at 20 % (w/v))

3.2. The effects of leaching parameters

3.2.1 The effect of reaction temperature

Experiments on the effect of temperature were carried out in the temperature with range of 30-80 °C, maintaining the solid-to-liquid ratio at 20 % (w/v); stirring speed at 400 rpm, the average particle size of -200 mesh, and acid pH at 0.7. As seen from the experimental results given in Figure 5, the leaching rate increases regularly as the temperature increases. Figure 5 showed that in different of temperature, recovery of manganese, calcium and iron were increase with the increase of temperature. It showed recovery of manganese in different temperature is higher than recovery of calcium and iron. As observed, the leaching rate of Mn increases from 48.43 % to 76.08 % as

leaching temperature increases from 30 °C to 80 °C. The results obtained are illustrated in Figure 5. As observed, the leaching rate of Ca increases from 1.08 % to 1.38 % as leaching temperature increases from 30 °C to 80 °C. The leaching rate of Fe increases from 3.14 % to 4.83 % as leaching temperature increases from 30 °C to 80 °C. It was adjusted that acetic acid is selective with manganese ion. This behavior can be explained by the fact that high leaching temperature can accelerate reaction rate between Kulon Progo manganese ore and acetic acid. Therefore, the leaching temperature of 80 °C was chosen as the optimum condition in the next experiment. The same results was obtained by Yuksel Abali et al. (2007) which showed that the leaching rate increases gradually as the temperature increases [7].

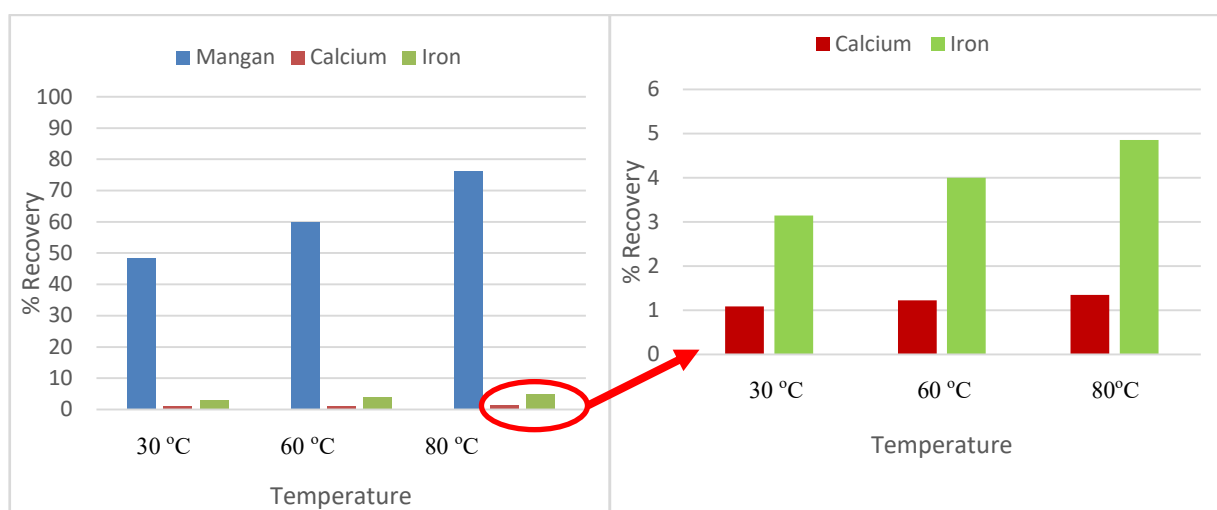
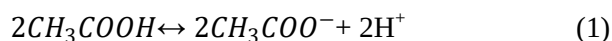


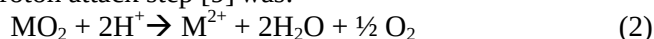
Figure 5. Effect of temperature on the leaching in the range of 30-80 °C in some elements (solid-to-liquid ratio at 20 % (w/v); stirring speed at 400 rpm, the average particle size at -200 mesh, and acid pH at 0.7)

3.2.2 The effect of pH

The effect of acidity level on the leaching was studied using the values of pH in the range of 0.7-3. For these experiments the value of the other parameters maintained constant during the reaction were: leaching temperature of 80°C, stirring speed at 400 rpm, the average particle size of -200 mesh, and solid-to-liquid ratio of 20 % (w/v). The results obtained by these experiments are shown in Figure 6. Leaching rate was increased by decreasing the acid pH. Smaller of acid pH then H^+ concentration was increased or amount of hydrogen ion which from dissociation step of acetic acid was increased. According to Yuksel Abali et al. (2007), the reaction occurred in dissociation step [8] was:



Increased of the hydrogen ion amount would involve the increased activity in proton attack step. The reaction of proton attack step [9] was:



Hydrogen Ion (H^+) which formed attacks pyrolusite mineral on the ore. Increased of the hydrogen (H^+) ion amount which reacted with pyrolusite mineral make manganese ion detached from the ore and increase the amount of proton attack step. Because of that, the recoveries of manganese on leaching were increased. The results are summarized in Figure 6. The leaching rates of Mn, Ca, and Fe in Figure 6 are enhanced with the increase of the pH of acetic acid from 3 to 0.7. However, the leaching rate of Mn is almost unchanged when the pH is over 0.7, indicating that leaching reaction nearly reaches equilibrium. A pH of acetic acid of 0.7 corresponds to the maximal leaching rate of Mn being 76.08 %, leaching rate of Ca being only 1.38 % and leaching rate of Fe being only 4.83 %.

It was represented that acetic acid in same of pH is selective with manganese ion. Thus, the most favorable pH of acetic acid is 0.7 in this work.

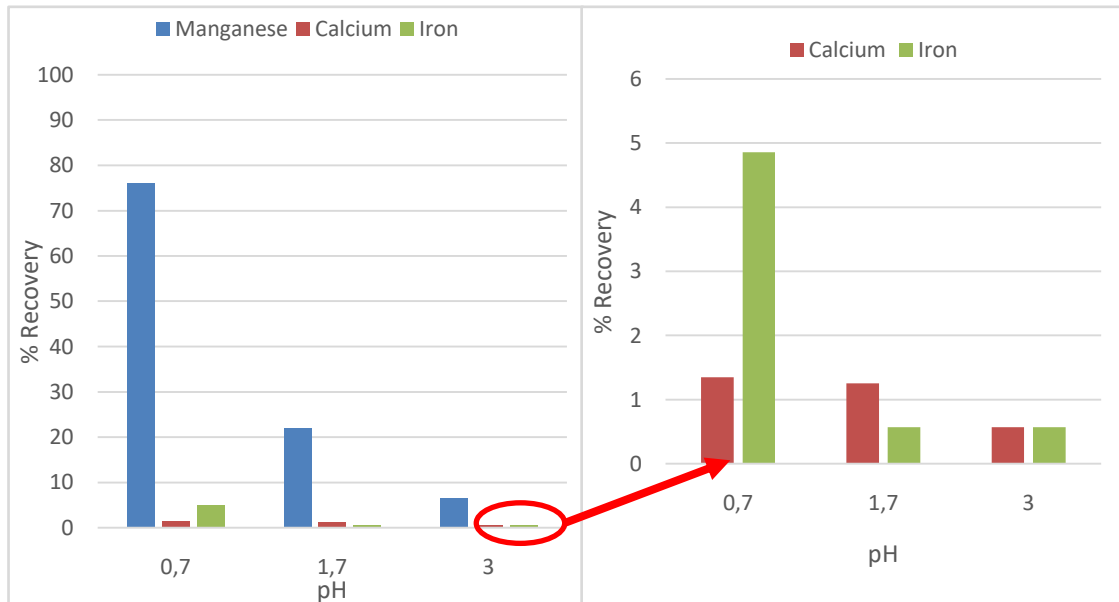


Figure 6. Effect of acid pH on the leaching in the range of 0.7-3 (leaching temperature 80 °C, stirring speed 400 rpm, the average particle size at -200 mesh and solid-to-liquid ratio of 20 % (w/v))

3.2.3 The effect of particle size

The effect of particle size on the leaching rate was investigated using two different particle size fractions in the range of (-70+100)- (-200) mesh and keeping other parameters constant: temperature at 80 °C, stirring speed 400 rpm, acid pH of 0.7 and solid-to-liquid ratio of 20 % (w/v). There was no effect particle size ore with results manganese, calcium and iron recovery of leaching. The results are summarized in Figure. 7. Showed that recovery of manganese, calcium, and iron were extracted from Kulon Progo manganese ore when 0.7 pH of acetic acid but only 76.08 % of manganese recovery, 1.38 % of calcium recovery, and 4.83 % of recovery of Iron. The results adjusted that acetic acid selective with manganese ion.

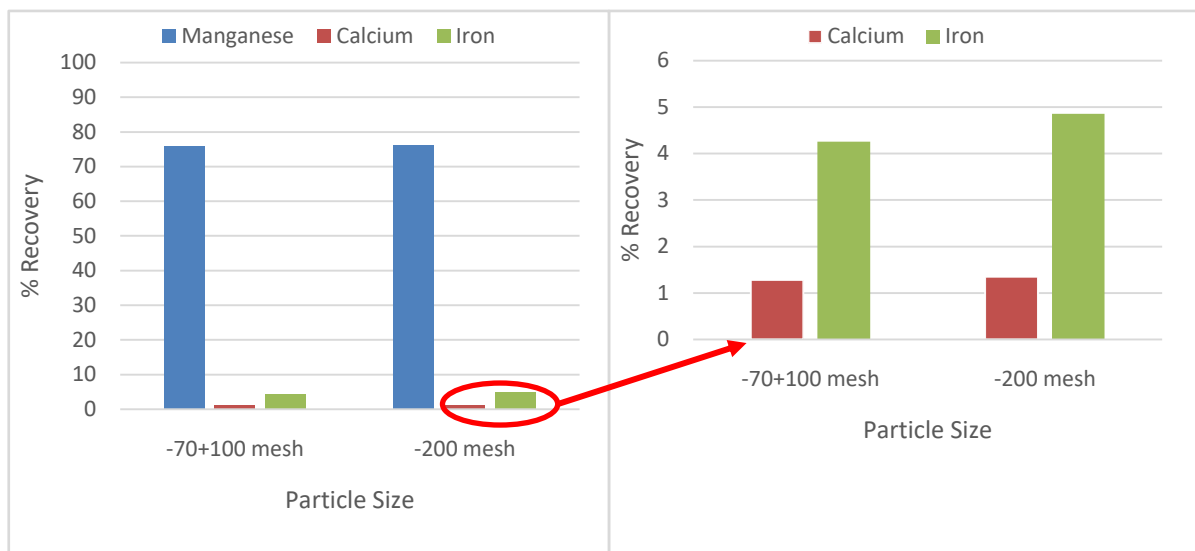


Figure 7. Effect of particle size onl (temperature at 80 °C, stirring speed 400 rpm, acid pH of 0.7 and solid-to-liquid ratio of 20 % (w/v))

3.2.4 Dissolution behavior of different metal ions

Kulon Progo manganese ore is assumed to be incorporated in Calcite, Sphalerite, Chromite, Alumina, Rutile, and Quartz in Kulon Progo; therefore, manganese dissolution must always coincide with the dissolution of the other metals contained in these minerals, particularly calcium and iron. Sphalerite particles (0.7 m²/g) have smaller surface area than calcite (3.82 m²/g) and pyrolusite (1223.9 m²/g) particles [10], [11], [12]. The data in Table 1 showed that calcite is the first dominant mineral in this ore, pyrolusite is second dominant mineral in this ore, and sphalerite is minor mineral in this ore. From Figure 3, we obtained that pyrolusite are on the outside layer in this ore. Because of pyrolusite have a big surface area and located on the outside layer in sample ore, it makes manganese ion easy to dissolve in acetic acid. However, sphalerite have small surface area so that it is very difficult to dissolve in atmospheric leaching even with acid solutions of small pH of acetic acid. Calcite have slightly moderate surface area, so it is relatively difficult to dissolve in atmospheric leaching even with acid solutions of small pH of acetic acid. From Figure 5, 6, and 7 it is observed that manganese recovery is much higher than calcium and iron. Accordingly, it can be predicted that the manganese originates in separated mineral with other mineral and not associated with other element in same mineral. In conclusion, it is very easy to dissolve than calcium and iron.

4. Conclusions

The leaching of Kulon Progo low grade manganese ore was investigated, with the parameters having the ranges: temperature of 30-80 °C; acid pH of 0.7-3, and average particle size of (-70+100) and (-200) mesh. It was observed that the leaching of Kulon Progo low grade manganese ore increased with increasing reaction temperature and decreasing acid pH. It was obtained that the ore particle size has no effect on Mn recovery. The recovery of 76.08 % was obtained with significant low extraction of iron and calcium below 10%. The finding showed the manganese selectivity from its impurities when acetic acid applied.

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