

Effect of Direct and Indirect Pre-Oxidation of Gold Ore from Doup North Sulawesi using Ozone Gas on the Gold Extraction in the Cyanidation Process

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Abstract. Refractory gold ore is a type of gold ore that is difficult to process when treated through a conventional cyanidation process. Pre-oxidation using ozone gas is one of the pre-treatment methods that can be used to improve gold recovery from sulfide-type refractory ore. This study used gold ore samples from Doup, North Sulawesi, Indonesia, to study the effect of direct and indirect pre-oxidation using ozone gas on gold recovery and subsequently treated by a cyanidation process. Direct and indirect pre-oxidation experiments were carried out at different pHs and using two raw materials for ozone generation (air and O₂). The slurry obtained from the pre-oxidation experiments was filtered, and the filtrate was analyzed for the concentration of dissolved Cu, Fe, and Zn using atomic absorption spectroscopy (AAS); meanwhile, the residue from each pre-oxidation experiment was leached by cyanidation to obtain a pregnant leaching solution (PLS), which was analyzed for its gold concentration using AAS. The percentages of dissolved Cu, Fe, and Zn during pre-oxidation increased with the pre-oxidation time when the acidity was maintained at pH 2, using pure O₂ as the ozone raw material. The direct pre-oxidation process at pH 2 using air as the ozone raw material increased gold extraction from 79.08% to 82.78% in the cyanidation process. The pre-oxidation experiments performed without controlling the pH resulted in lower gold dissolutions than the pre-oxidation conditions at pH 2. Possible causes of the lower gold dissolution were discussed.

1. Background

According to data from the World Gold Council^[1], global gold demand in the first quarter of 2022 increased by 34% compared to the same quarter in 2021 on a year-on-year basis. This surge in demand was primarily driven by inflows into Exchange-Traded Funds (ETFs) due to high inflation, as investors sought gold as a safe-haven asset to preserve or even increase their assets during periods of economic downturn. On the other hand, McKinsey & Company^[2] predicted that gold production from refractory ores will continue to grow faster, at 1.4%, compared to gold production from non-refractory ores, which was at 0.3% until 2023.

According to Crowson, the availability of free-milling gold ores has declined over time, leading researchers to shift their focus towards refractory gold ores, which are less economically viable to process using conventional cyanidation methods^[3]. Refractory gold ores are difficult to process and yield less than 95% gold recoveries and even lower than 50% for highly refractory categories when processed with conventional cyanidation, as shown in Table 1.1^[4].

Refractory gold ore requires pre-treatment with certain methods before performing conventional

cyanidation processes to release the gold particles and obtain a high percentage of gold extraction. Although it requires additional processes before cyanidation, according to McKinsey & Company^[2], the average overall cost of producing per troy ounce of gold from refractory ore was 19.1% cheaper in 2019, and it was estimated to be 16.2% cheaper in 2023 than non-refractory ore. This is because, on average, the gold head grade of the refractory ore is 86% higher than that of the non-refractory ore. Therefore, there are opportunities, but at the same time, challenges exist in extracting gold from the refractory ore.

Table 1.1. Gold ore classification according to its recovery^[4]

Classification	Au Recovery
Free-milling	More than 95%
Mildly refractory	80-95%
Moderately refractory	50-80%
Highly refractory	Less than 50%

Various pre-treatment methods to enhance gold recovery from refractory ore have been developed in the world, including roasting processes, oxidation at temperature and high pressure in an autoclave, bacterial

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(bio-oxidation), nitric acid and chlorine gas pre-treatment, as well as the further development of the use of ozone gas as an oxidant^[6-16,18-20]. The pre-oxidation processes can be carried out using oxygen-containing air or enriched oxygen gas to oxidize sulfur from sulfide minerals so that gold that is encapsulated in sulfide minerals can be released. This process has a weakness, where it produces emissions of SO₂ and other harmful gases, such as As₂O₃, if the ore contains arsenic sulfide minerals. The process of pre-treatment of refractory gold ore at high temperature and pressure using an autoclave also has its drawbacks: relatively higher capital costs and relatively more complicated operations^[10]. Other pre-treatment processes, such as the use of bacteria for the bio-oxidation process of refractory gold ore, can provide relatively cheaper capital-cost alternatives. However, the process takes longer and requires special attention to control the behavior of iron and sulfur-oxidizing bacteria^[11]. Other pre-treatment methods, using of HNO₃ as an oxidant, are sufficiently effective for oxidizing ore or gold concentrates with a very high sulfide mineral content (highly complex)^[6,12]. However, the pre-oxidation process with HNO₃ produces emissions of NO gases and arsenic gases, in which this gas mixture needs to be phase separated first by precipitating the arsenic gas, then the remaining NO gas is scrubbed with O₂ so that the NO₂ gas is easily soluble in water and produces HNO₃^[6]. Cl₂ gas oxidants injected into leaching reactors can also effectively deactivate carbonaceous elements in ore or concentrate at the pH range of 3 to 5^[6,13]. However, the use of chlorine gas is not economical when it is used to oxidize sulfide ore due to its high consumption^[6]. In addition to the oxidants mentioned above, ozone gas can be used as an oxidant alternative because it has a high standard reduction potential, namely 2.07 V versus SHE, higher than hydrogen peroxide (1.77 V vs SHE) and chlorine gas (1.36 V vs SHE)^[14].

Ozone gas has been studied for pre-oxidation processes as well as for the extraction of metals from ore or concentrated with sulfide-dominant minerals^[14-18]. Pre-oxidation methods using ozone gas can generally be done directly and indirectly^[14-16]. Pre-oxidation is carried out directly by contacting the ore/concentrate in the form of slurry with the ozone gas injected and circulated continuously. Meanwhile, in an indirect pre-oxidation, ozone gas is injected into the water without ore or concentrate, which is then the ozonated water used to leach the ore/concentrate^[14-16]. The size of the ozone gas bubble has a relationship with the efficiency of the oxidation process^[17]. Sukamto^[17] showed that the use of Mazzei injectors for oxidative leaching of sphalerite concentrates could provide a much higher percentage of Zn extraction compared to the use of ozone diffusers because Mazzei injectors were able to produce ozone gas with a finer bubble size on a micrometer scale. The use of ozone gas as a refractory gold oxidator was found to be able to increase the percentage of gold extraction from highly refractory ore/concentrate in the cyanidation process^[14-16,18-20]. The increase in the percentage of gold extraction depends on the mineralogy and the degree of refractory of the

ore/concentrate^[18-19]. Therefore, it is necessary to conduct a diagnostic examination first to know the gold department found in each type of mineral^[19,21,22].

The present study investigated the influence of the pre-oxidation processes, directly and indirectly, using ozone on the percentage of gold recovery from the Doup gold ore. Doup is a gold ore deposit operated by PT J Resources Asia Pacific Tbk in Bolaang Mongondow County, North Sulawesi. The department of gold on the Doup ore sample was determined by conducting a diagnostic leaching experiment using some type of acid solution followed by cyanidation. A series of direct and indirect pre-oxidation experiments were also conducted to study the effects of pre-oxidation time, pH regulation, and ozone source input gases on the dissolution of Cu, Fe, and Zn during the Doup gold ore pre-oxidation process, which resulted in comparison with the results of previous studies^[20].

2. Material and method

2.1. Material

PT J Resources Asia Pacific Tbk supplied the gold ore samples used in this study from their Doup Mine Project, Panang ISE Domain, North Sulawesi. The sodium cyanide used in the experiment was reagent grade, while the other chemical reagents used in this study were analytical reagent grade. Distilled water was used to dilute the chemical reagents when necessary.

2.2. Experiment Method

The experimental procedure includes diagnostic leaching, pre-oxidation, and cyanidation experimental procedures. Initially, the sample was prepared by grinding up to 100 percent -200 mesh sizes (<74 microns). The ground sample was then homogenized and sampled using coning and quartering. After preparation, the gold ore samples were used for diagnostic leaching, pre-oxidation, and cyanidation experiments.

2.2.1. Diagnostic leaching experiment

The diagnostic leaching test was performed on gold ore samples of the Doup Mine twice (duplicated). The process consists of four stages. The first stage was cyanidation to extract free milling gold contained in the ore. Cyanidation was carried out in a chemical glass of 500 ml. The cyanidation parameters used in the diagnostic leaching experiment were a cyanide concentration of 1500 mg/L, pH in the range of 10.5–11.5, solid/liquid ratio (S/L) = 1/1, and an agitation rate of 700 rpm for 24 hours. After 24 hours, the slurry was filtered and rinsed, and the first-stage residue was dried in an oven at 105 °C for 12 hours for further processing.

In the second stage of the diagnostic leaching, leaching with a solution of Na₂CO₃ 60 g/L at a temperature of 90 °C for 2 hours was carried out for the first stage residue. The S/L ratio used was 1/10, and the agitation was performed at a speed of 500 rpm. After

that, the slurry was filtered, then the residues were further leached with 12% chloric acid (HCl) and an S/L ratio of 1/2 at 60 °C for 8 hours. After that, the slurry was filtered again and dried with the same parameters as before. After drying, the acid-leaching residues in the second phase were cyanidized with the same parameters as cyanide in the first phase, then filtered, rinsed, and dried, thus obtaining cyanide-bearing residue. This second-stage diagnostic purifier was aimed at breaking oxides and carbonates matrices, such as minerals calcite, dolomite, and goethite, as well as some other types of minerals, such as gypsum, arsenates, galena, and pyrrhotite. The particles of gold encapsulated within the mineral-mineral matrix were hoped to be released so that the cyanidation process could dissolve them.

Next, in the third phase, leaching with a 48% sulphuric acid (H₂SO₄) solution at a temperature of 80°C for 5 hours was carried out using the cyanidation residues of the previous phase. The slurry was then filtered, and the residues were leached with a 33% nitric acid (HNO₃) solution at a temperature of 60°C for 6 hours. Both of these bottle roll tests used an equal S/L ratio of 1/2 and an agitation speed of 500 rpm. After leaching with these two acids, cyanidation with the same parameters as the previous process was carried out to extract gold that had been released from the lattice of mineral-mineral sulfides, such as pyrite, marcasite, sphalerite, and arsenopyrite that were destroyed by H₂SO₄ and HNO₃.

In the final stage, the cyanidation residue from the third stage was roasted in a muffle furnace to break the carbonaceous material present in the ore, releasing the previously adsorbed gold particles. The roasting was carried out at a temperature of 700°C for 6 hours, before the roasted residue was subjected to cyanidation with the same parameters as before. After cyanidation for 24 hours, the slurry was filtered, rinsed, and then dried. Each filtrate resulting from the cyanidation was collected, and solvent extraction with diisobutyl ketone (DIBK) was carried out to increase the concentration of gold and analyze its soluble gold content using AAS. In the meantime, the cyanidation residues of the final stage of this diagnostic purification were subjected to fire assay to analyze the concentration of residual gold, in which the remaining gold was the gold that could not be leached due to being trapped in the silicate mineral lattice^[21,23].

2.2.2. Pre-oxidation experiment

Pre-oxidation experiments with ozone gas were carried out using a Mazzei injector as a slurry injection system. The process was carried out in a double jacket reactor with a half-inch hole below for slurry circulation and had five necks. The middle neck hole was used for the impeller, the four necks next to each were used for the slurry inlet that has been in contact with the ozone, for the ozone residual gas discharge pipes, for measuring the pH and oxidation-reduction potential (ORP) profiles, and, for the last hole with the largest diameter, for the inlet of distilled water and ore samples and for the measurement of temperature, dissolved O₂ (DO₂) and dissolved O₃ (DO₃). Through the outer jacket of the

reactor, cooling water was circulated continuously to control the temperature. Schematically, the set of equipment for pre-oxidation is shown in Figure 2.1.

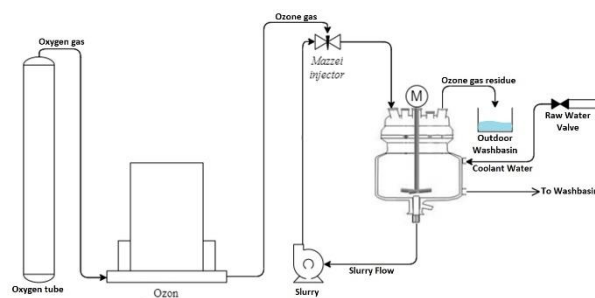


Fig. 2.1. Schematic experiment of ore pre-oxidation using ozone gas

The pre-oxidation experiments were performed using direct and indirect methods. Two experimental variables were studied. The first variable tested was the slurry pH, which had two levels: pH as is (without pH adjustment) and pH 2. The fixed variable was air, which was used as the raw material to produce ozone in the ozone generator. The selection of pH 2 was based on various literature reports that the lower the pre-oxidation pH, the higher the percentage of gold extraction in the cyanidation process^[14,18,19]. The second variable tested was the ozone raw material, either ambient air or pure O₂. The reason why the type of input gas as a raw material varies is to know how significant the change in the percentage of gold extraction in the cyanidation process is when pure O₂ is used compared to ambient air as the raw material of ozone gas. In addition, it will be related to economic considerations for the commercial application of the technique.

The pre-oxidation experiment began with the preparation of distilled water and contacting it with the ozone gas in the double jacket reactor system for 15 minutes. After that, the pre-oxidation procedure continued depending on whether a direct or indirect method was used. In the direct method, after the distilled water was in contact with the ozone gas for 15 minutes, a sample of 300 grams of ore was slowly inserted into the same reactor system. H₂SO₄ was added periodically to keep the condition of the slurry stable at pH 2. Agitation in the reactor was carried out at a speed of 300 rpm. Temperature profiles, pH, ORP, DO₂, and DO₃ were measured and recorded every 0, 15, 30, 60, 120, and 240 minutes. The ozonation process was carried out for 240 minutes by sampling in the 30th, 60th, and 120th minutes. Sampling was performed with a volumetric pipette. After the last sampling, the ozone generator and pump were turned off; the injector gap was removed from the reactor and directed into a two-liter chemical glass to accommodate the slurry. The ozonation slurry was then filtered with a vacuum filtration pump, and the filtrate was stored. After that, the residues were rinsed with distilled water and then dried in the oven at a temperature of 105 °C for 12 hours.

In the indirect method, after the distilled water was in contact with the ozone gas for 15 minutes, the water was removed from the reactor system and inserted into a two-liter reactor glass. Next, a sample of 300 grams of

ore was inserted, and the agitator was turned on with a speed of rotation set at 800 rpm. The H₂SO₄ solution was added periodically to keep the condition of the slurry stable at pH 2. Like the direct method, temperature profiles, pH, ORP, DO₂, and DO₃ were measured and recorded every 0, 15, 30, 60, 120, and 240 minutes. After the experiment was finished, the slurry was filtered, rinsed, and dried.

2.2.3. Cyanidation experiment

The cyanidation experiment was carried out using a bottle roll machine inside a two-litre glass bottle. The experiment was carried out by keeping the pH parameters in the range of 10.5–11.5, the NaCN concentration of 500 ppm, 30% solid, and the rotation speed of the bottle roll machine at 60 rpm. No adjustment was performed for temperature and DO₂. The cyanidation process was carried out for all pre-oxidation residues that have been dried, as well as for ore cyanidation without pre-oxidation, for comparison. The cyanidation process in this experiment began with 210 grams of solid and 490 mL of distilled water prepared and put into the bottle. Then, some CaO was added to the bottle and slowly matched until the pH entered the specified range. After that, roll the bottle for 15 minutes so that the slurry system and the pH in the bottle become homogeneous. After that, a pH measurement was performed again to ensure that the pH remained within the specified range before the initial amount of 500 mg/L of sodium cyanide (NaCN) was added. The bottle was then placed on the bottle roll machine for the cyanidation process. Cyanidation was carried out for 24 hours with sampling at 1, 2, 4 and 8 hours. The sample was taken using a volumetric pipette and then filtered using a vacuum filtration pump to obtain 50 mL of pregnant leach solution (PLS). The solid residue taken was returned to the bottle. 10 mL of the 50 mL PLS sample was used to determine the free cyanide concentration by titration method using AgNO₃.

When the 24th hour was reached, the entire slurry was filtered, rinsed, and dried in an oven at a temperature of 105°C for 12 hours while the PLS was stored. PLS for each sampling time and each variation was analyzed using AAS. Meanwhile, the residual gold content in each cyanidation residue was analyzed using the fire assay method.

3. Results and Discussion

3.1. Gold ore from Doup mine characterization result

Gold ore samples in this study were initially characterized using X-ray diffraction (XRD) to identify the crystalline minerals, X-ray fluorescence (XRF) to identify the chemical composition, and fire-assay to quantify the Au grade of the ore. Based on the results of the XRD characterization presented in Figure 3.1, the gold ore sample contains quartz (SiO₂), pyrite (FeS₂), muscovite (KAl₂(AlSi₃O₁₀)(F,OH)₂), spangolite

(Cu₆Al(SO₄)(OH)₁₂Cl•3H₂O), albite (NaAlSi₃O₈), and gypsum (CaSO₄•2H₂O).

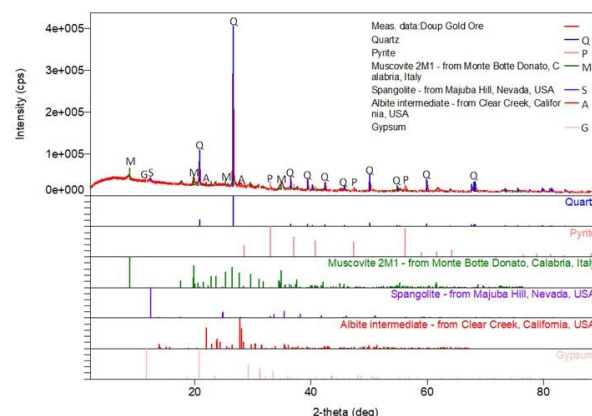


Fig. 3.1. Doup gold ore XRD characterisation result

The XRF characterization results, presented in Table 3.1, showed that the gold ore sample contained Cu, Fe, Zn, and S at 0.107%, 10.4%, 0.701%, and 4.2%, respectively.

Table 3.1. Doup gold ore XRF element and oxide quantitative characterisation result

Element	Result	Oxide	Result
Cu	0.107%	CuO	0.0443%
Fe	10.4%	Fe ₂ O ₃	5.42%
Zn	0.701%	ZnO	0.287%
Pb	0.564%	PbO	0.196%
S	4.2%	SO ₃	4.72%
Mg	0.667%	MgO	0.773%
Al	17.5%	Al ₂ O ₃	21.7%
Si	48.5%	SiO ₂	57.6%
K	0.56%	K ₂ O	5.6%
Ca	3.5700%	CaO	1.98%
Mn	1.0200%	MnO	0.484%

The gold content in the Doup mine analyzed using the fire assay method showed an average Au grade of 1.995 ppm.

3.2. Analysis of gold distribution in Doup gold ore from diagnostic leach results

The results of the diagnostic leach experiments are presented in Figure 3.2, which showed that as much as 1.29 ppm Au, or 80.06% of the gold in ore, was extracted in the first phase of cyanidation, indicating that most of the gold in ore Doup is free-milling gold. In the second stage, the residues of the first stage leaching that have been dried are then leached with sodium carbonate and hydrochloric acid, followed by the cyanidation of the leached residue obtained after drying. From the second stage of this diagnostic leaching, the Au extraction was 2,09% or about 0.0336 ppm Au. The gold extracted from the second stage of this diagnostic leaching is categorized as gold associated with the mineral group carbonate, oxide, sulfate, and less soluble sulphide. Furthermore, 2.76% of the total gold in the ore,

or 0.0444 ppm Au, was extracted after the destruction of mineral-mineral sulfides with sulphuric acid and nitric acid reagents in the third phase of diagnostic leaching. From the results of the fourth stage of diagnostic leaching, it was found that there was no gold adsorbed by carbon material in the ore. Furthermore, the final residues fire assay analysis showed that as much as 15.10% of gold in ore or 0.243 ppm Au was trapped in silicate minerals that were not destroyed at the previous stages of diagnostic leaching.

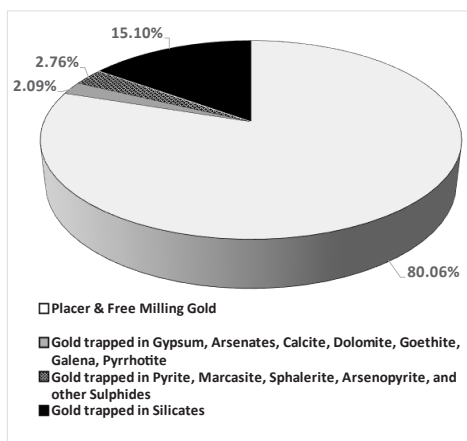


Fig. 3.2. Doup gold department pie chart

3.3. Analysis of temperature, pH, dissolved ozone (DO₃), dissolved oxygen (DO₂), oxidation-reduction potential (ORP) during pre-oxidation

Temperature profiles for any variation of pre-oxidation with ozone gas (ozonation) directly and indirectly are shown in Figure 3.3. The measurement results show that the indirect method provided a lower temperature during pre-oxidation than the direct method in all variations. This is because, in the indirect method, the slurry was not in contact with the ozone gas as in the direct method, so that the ozone solubility decreases significantly over time. Notably, for all variations on the direct method, temperature decreases can occur because cooling water was added through the outer reactor layer/jacket, so that the temperature can be kept constantly below 36 °C after the first 30 minute. If no cooling water was added into the outer layer of the reactor, the actual temperature of the slurry can reach 58 °C, which can significantly reduce the dissolving ozone gas due to the very rapid decomposition of ozone at high temperatures^[19,25].

The pH profile during the direct and indirect ozonation process is shown in Figure 3.4. In the direct method without pH adjustment (pH as is), the pH decreased from 6.59 before the reaction slowly to 5.94 in the 240th minute. This was owing to the oxidation reaction of mineral sulfides that produce H⁺ ions^[6,20]. Meanwhile, in the indirect method without pH regulation, the measurement results showed an increase in pH along with the pre-oxidation time. This was owing to the limited solubility of dissolved ozone and the decomposition of ozone to form radicals and oxygen. The generated oxygen may help the oxidation process of sulfide minerals, in which O₂ in near neutral pH as an

oxidator will undergo a reduction process to produce hydroxide ions (OH⁻) according to the following reaction equation^[6,24] :

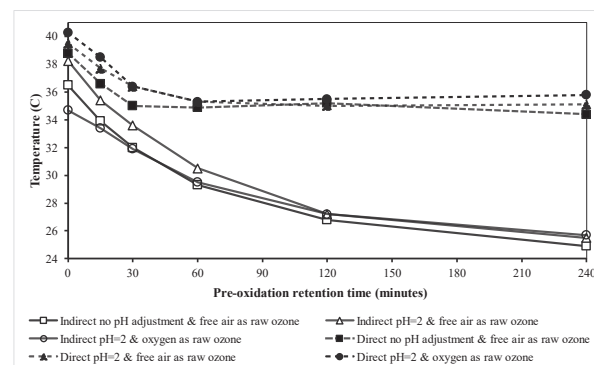


Fig. 3.3. Profile of temperature change with pre-oxidation process time

The side-product of hydroxide ions caused the slow increase in pH in the indirect pre-oxidation method, as presented in Figure 3.4. Ozone and dissolved oxygen profile data on indirect methods presented in Figure 3.5 (a) and (b) also indicate this phenomenon. A decrease in the concentration of dissolved ozone from 0.11 mg/L to 0.01 mg/L at the end of the pre-oxidation process corresponds to an increase in the concentrated oxygen from 5.4 mg/L at the beginning to 8.1 mg/L at the end of the pre-oxidation experiment, indicating the occurrence of the decomposition of the O₃ gas into the O₂ gas as one of its reaction products.

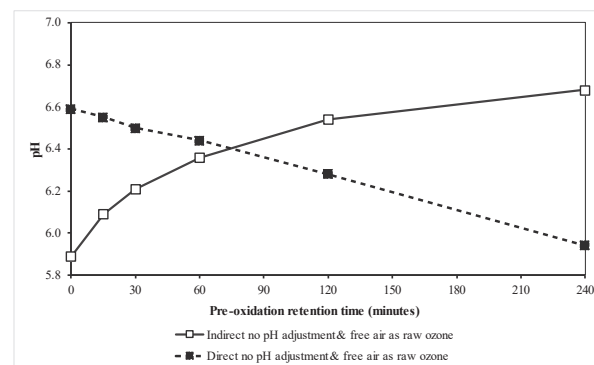


Fig. 3.4. Profile of pH change with pre-oxidation process time

Based on the data of the dissolved oxygen profile in Figure 3.5 (b), in a direct method with a pH of 2 that used O₂ as the raw material of ozone, the dissolution oxygen profile was much higher than the rest of the experiments and tended to be constant above 16 mg/L. This high oxygen solubility is consistent with the ORP profile in Figure 3.5 (c), wherein the ORP increased monotonically to 1066 mV (vs SHE) after 4 hours of ozonation. This indicated that the process of ozone gas formation with the ozone generator tool used in this experiment runs effectively with O₂ gas as the input raw material for ozone production. For comparison, the results of a study conducted by Mashifana et al. ^[18] showed that a slurry ORP of 1032 mV (vs SHE) was achieved in 3 hours of the ozonation process at pH 2.

According to the theory, the lower the pH, the higher the ozone solubility due to the slower ozone decomposition rate^[24,25]. Dissolved ozone parameters for all variations in pH 2 were not detected on the DO₃ meter because it

was suspected that the dissolved ozone exceeded the detection limit of DO₃ meters used in this study, that was 9.99 mg/L.

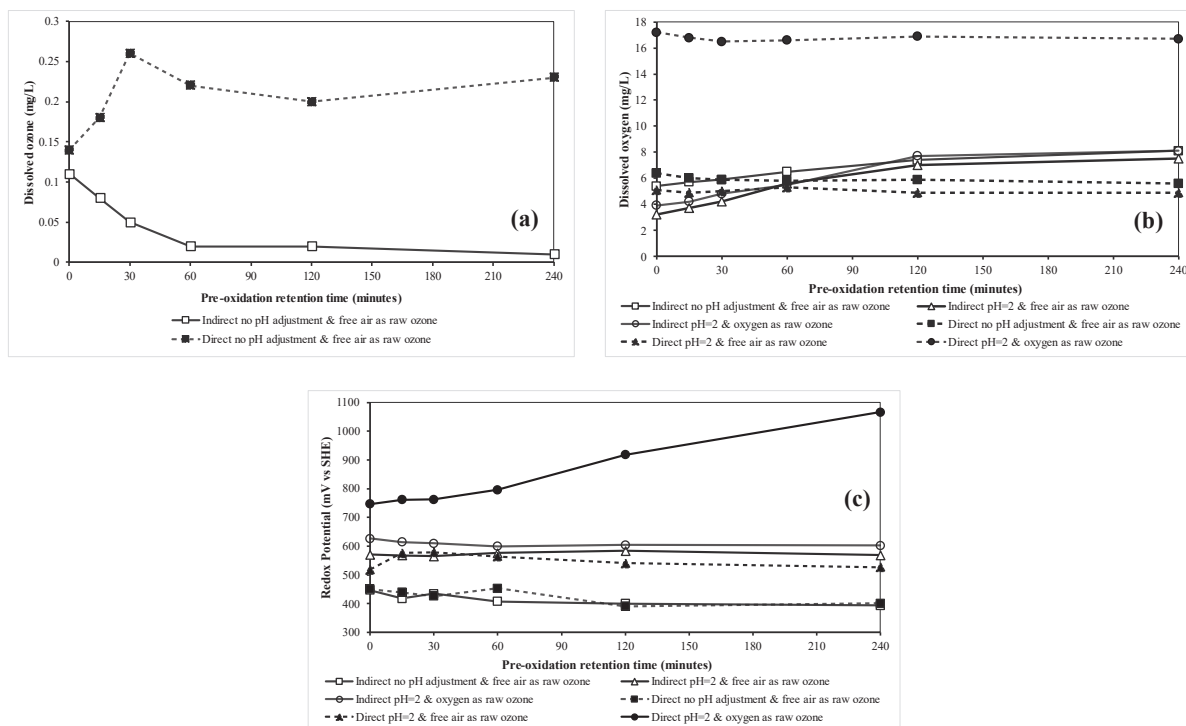


Fig. 3.5. (a) Profile of dissolved ozone (DO₃) change with pre-oxidation process time; (b) Profile of dissolved oxygen (DO₂) change with pre-oxidation process time; (c) Profile of oxidation-reduction potential (ORP) change with pre-oxidation process time.

3.4. Analysis of retention time, pH, and raw material gas variation effect on dissolved Cu, Fe, and Zn during pre-oxidation

The percentage of Cu, Fe, and Zn dissolution in the pre-oxidation experiment was used as a parameter to evaluate the continuity of the sulfide mineral oxidation process. The variations studied for their influence on the solubility percentage of these three base metals include pre-oxidation time, pH, and the type of raw material to generate ozone.

3.4.1. Analysis of pre-oxidation retention time variation effect on dissolved Cu, Fe, and Zn

The pre-oxidation process was carried out for 240 minutes, for which 240 minutes were sampled in the 30th, 60th and 120th minutes. Percentage profiles of Cu, Fe, and Zn dissolved as functions of pre-oxidation process time are shown in Figure 3.6 (a), (b), and (c), respectively. Generally, it can be seen that the percentage of Cu, Fe, and Zn extraction continues to increase with the course of pre-oxidation time, especially on the direct method. With longer duration, the contacts between ore particles and the oxidants were more extended, resulting in an increase in the percentage

of Cu, Fe, and Zn dissolved through the metals' sulfide mineral oxidation process^[6,19,20].

3.4.2. Analysis of pH variation effect on dissolved Cu, Fe, Zn during pre-oxidation

In each direct and indirect method, pH variation is performed at two levels of variation, namely, without pH adjustment (neutral) and adjustment at pH 2. In this variation experiment, free air was used as a raw material for ozone generation.

The comparison of dissolved Cu, Fe, and Zn profiles from pre-oxidation without pH regulation and pre-oxidation at pH 2 is shown in Figure 3.7 (a), (b), and (c). Based on the data obtained, pre-oxidation without pH adjustment was unable to dissolve the elements Cu, Fe, and Zn when compared to preoxidation performed at pH 2. When it is analysed from the pH and ORP profiles during pre-oxidation, the pre-oxidation process without pH regulation (pH about 6.5), in theory, based on their Eh-pH diagrams, Cu, Fe, and Zn are stable within the solid phase of the oxide and its hydroxide. The highest dissolved elements of Cu, Fe, and Zn were obtained in the pre-oxidation process by the direct method, namely 82.46%, 46.84%, and 78.68%, respectively.

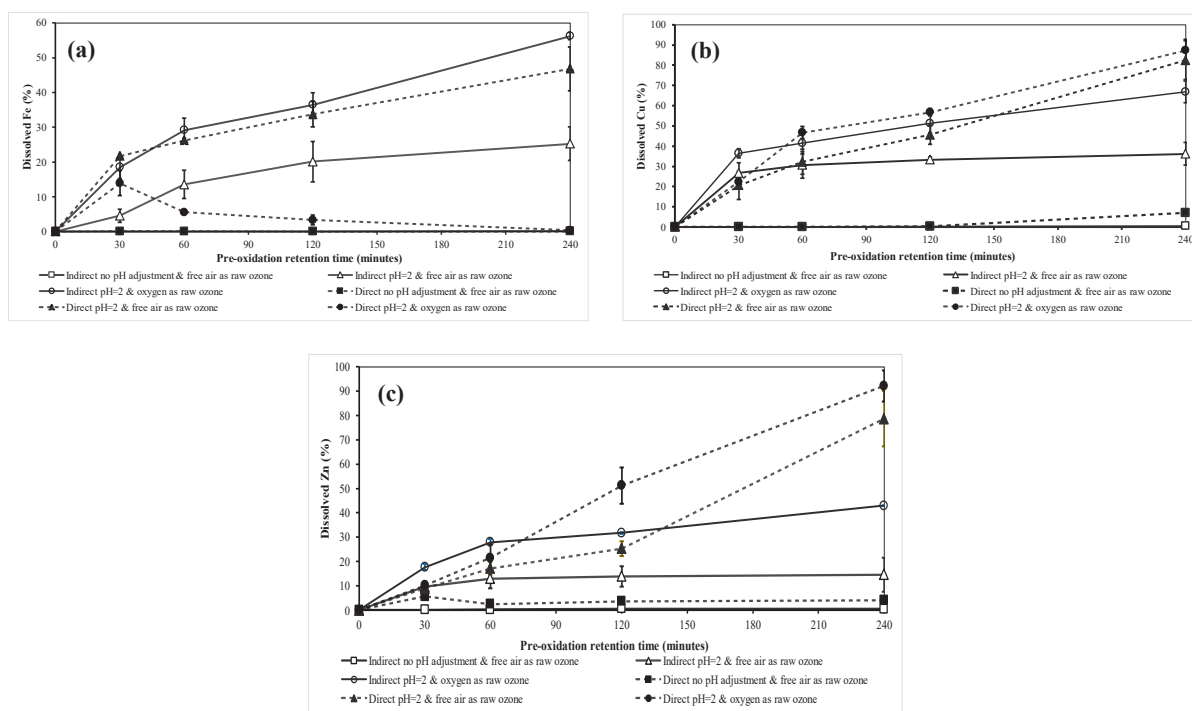


Fig. 3.6. (a) Pre-oxidation process time effect on dissolved Cu; (b) Pre-oxidation process time effect on dissolved Fe; (c) Pre-oxidation process time effect on dissolved Zn.

3.4.3. Analysis of raw gas for ozone generation's effect on dissolved Cu, Fe, Zn during pre-oxidation

A variation in the type of raw material of the ozone input gas generator, i.e. free air and pure O₂, was carried out to study the influence of the raw material type for this generation of ozone on the percentage of Cu, Fe, and Zn dissolved from the pre-oxidation process. In addition to the technical aspect, this variation would also be considered in the economic aspect if these pre-oxidation techniques with ozone gas would be commercially applied. Experiments with variation of the type of raw material of the ozone generation were carried out at pH 2. Based on Figures 3.8 (a), (b), and (c), in the indirect methods, there was a significant increase in the proportions of Cu, Fe, and Zn dissolved from 36.14%, 25.26%, and 14.69% to 66.78%, 56.22% and 42.99%, respectively, if pure oxygen was used as the raw material of ozone.

In pre-oxidation experiments with direct methods, the use of pure O₂ as ozone raw material was able to increase the extraction of soluble Cu and Zn, respectively from 82.46% and 78.68% to 87.41% and 92.13%. There was a decrease from 46.84% to 0.35% for dissolved Fe extraction. In the direct pre-oxidation experiments with pure O₂ as the raw material of this ozone generation, a dissolved Fe increase occurs at the beginning of the pre-oxidation process up to the 30th minute; it then decreases monotonically until the end of pre-oxidation time. When it is analysed from its ORP change profile (Figure 3.5 (c)), redox potential increases

also occurred from the 30th minute. Considering the Eh-pH diagram of the Fe-S-H₂O system, it appeared that the redox potential of the system entered the FeOOH stability area. The reduction of dissolved Fe occurs probably because dissolved Fe precipitated out into ferric hydroxide^[6].

3.5. Analysis of gold extraction during cyanidation

The results of gold extraction from the cyanidation process for any pre-oxidation variation were compared to the result of ore cyanidation without pre-oxidation. It aims to evaluate whether each method and variation of pre-oxidation using ozone gas can provide enhanced gold extraction. The results of dissolved gold during the cyanidation process with variations in pH regulation and ozone gas raw materials, respectively, are shown in Figures 3.9 (a) and (b).

Figure 3.9 (a) shows that the indirect and direct pre-oxidation without pH regulation gave a lower percentage of dissolved gold extraction compared to pre-oxidation conditions at pH 2. These results are the same as those presented by Bazhko et al. ^[19], wherein pre-oxidation at pH ≥ 3 did not result in better gold extraction. This may be owing to the formation of a passive layer of ferric hydroxide on the surface of sulfide minerals that was not reacted during the pre-oxidation process discussed in the previous section. This iron hydroxide can inhibit the subsequent oxidation of sulfide minerals and inhibit the release of gold particles^[6,19].

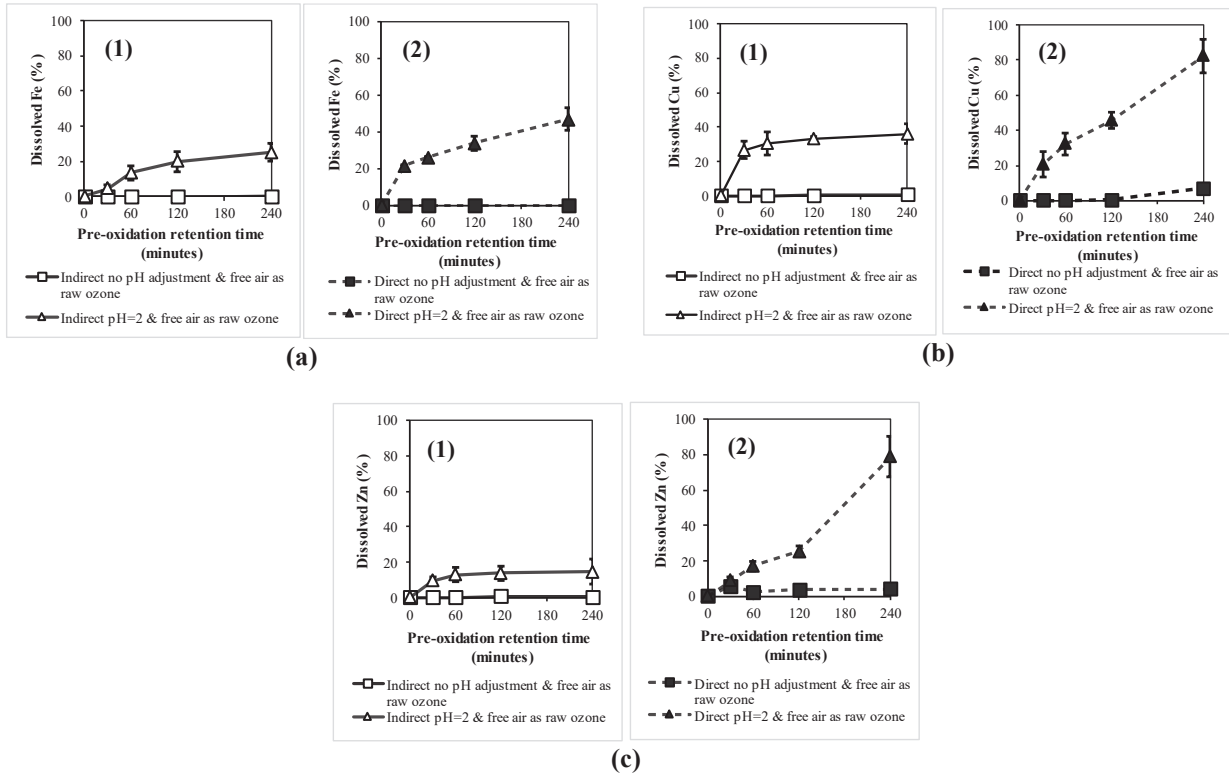


Fig. 3.7. Comparison of dissolved Cu (a), Fe (b), and Zn (c) profile without pH adjustment and with adjustment at pH 2: (1) Indirect method; (2) Direct method.

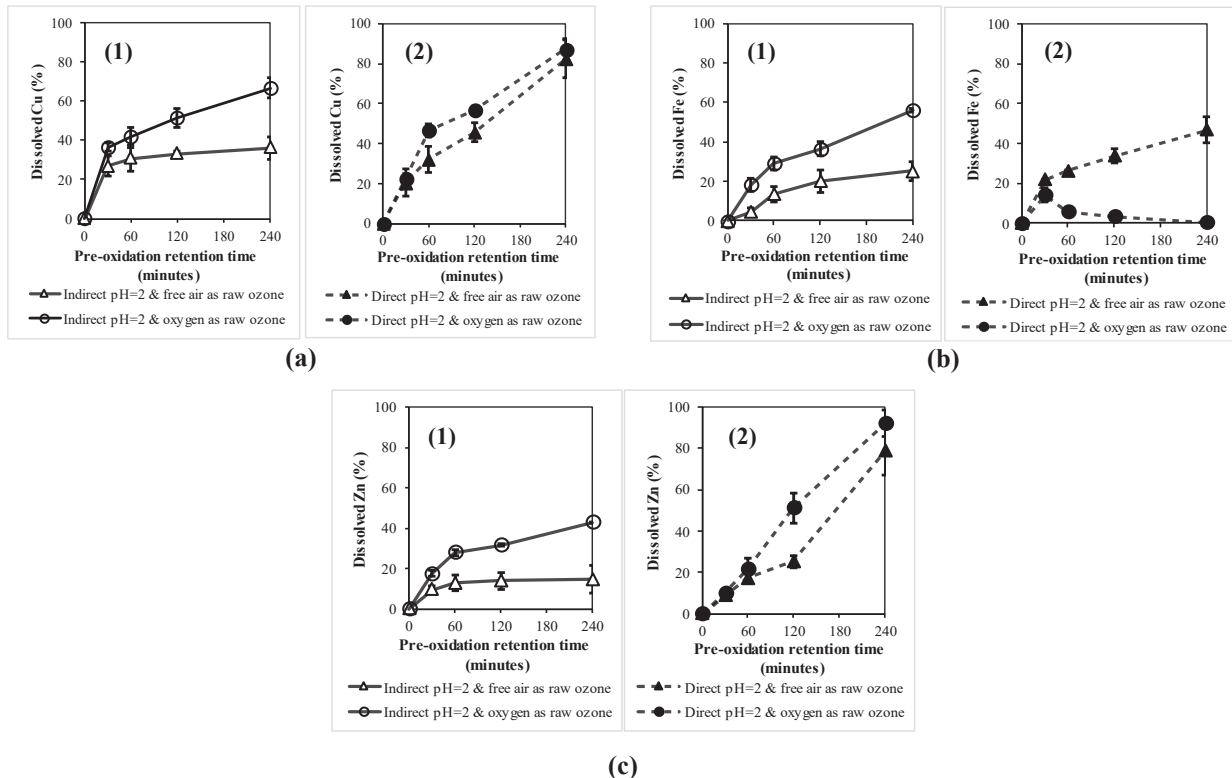


Fig. 3.8. Comparison of dissolved Cu (a), Fe (b), dan Zn (c) profile using free air and oxygen as a raw gas for ozone generation: (1) Indirect method; (2) Direct method.

The occurrence of formation of ferric hydroxide can also occur in pre-oxidation by the method of using O₂ as the raw material of ozone, in which iron that has been dissolved from sulfide minerals is precipitated into ferric hydroxides according to the predicted stability

area of the Eh-pH diagram of the Fe-S-H₂O system at pH 2. The conditions of pre-oxidation with O₂ gas as a source of ozone provide a lower percentage of gold extraction compared to the conditions where air is used as the raw material for ozone. As shown in Figure 3.9 (b), the use of O₂ gas as an ozone raw material provides

only a slight percentage increase in gold extraction compared to that using air as an ozone raw material. That is, the use of O₂ gas as an ozone raw material did not have much impact on the increase in the percentage of gold extraction for ore from the Doup Mine compared to the utilization of air as an ozone raw material. This indicates that the process does not need to use expensive gas as the raw ozone material, and the air can be directly used.

As can be seen in Figure 3.10, the best gold extraction was achieved with pre-oxidation conditions at pH 2 and by using air as an ozone raw material, which gave 82.78% gold extraction. The percentage of the

dissolved gold extraction was 3.7% higher when compared to the cyanidation conditions of the ore without the pre-oxidation process, which was 79.08%. Based on the results of SEM analysis presented in Figure 3.11, pre-oxidation under conditions that result in increased gold extraction, produces pre-oxidized residues with a more porous surface morphology with many fractures. Porous structures with many of these cracks were also reported by Li et al. [8]. The resulting pores may liberate gold, allowing it to react with cyanide in the cyanidation process, thereby increasing the percentage of gold extraction.

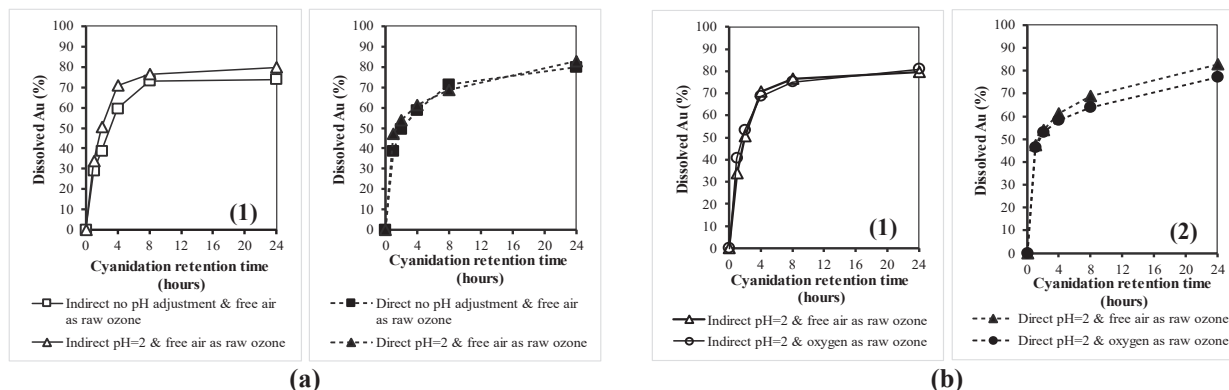


Fig. 3.9. Gold extraction profile during cyanidation from pre-oxidation residue (a) with no pH adjustment and adjustment to pH 2 variation; (b) free air and oxygen variation as raw gas for ozone generation : (1) Indirect method; (2) Direct method.

The results of the cyanidation process after the pre-oxidation process in this study had a good correlation with the results of diagnostic leaching. Between pre-oxidation and the cyanidation of ore and the first stage of diagnostic leaching is the same for dissolving gold that has already been released without pre-treatment, where the dissolved gold extraction obtained is almost the same, namely 79,08% and 80,06%, respectively. After a series of stages of diagnostic leaching, residues were obtained with an unextractable gold content — locked in silicate minerals^[19,22,23] — of 15.10%. Of all the results of pre-oxidation residual cyanidation, none also yielded the extraction of dissolved gold >84.90%.

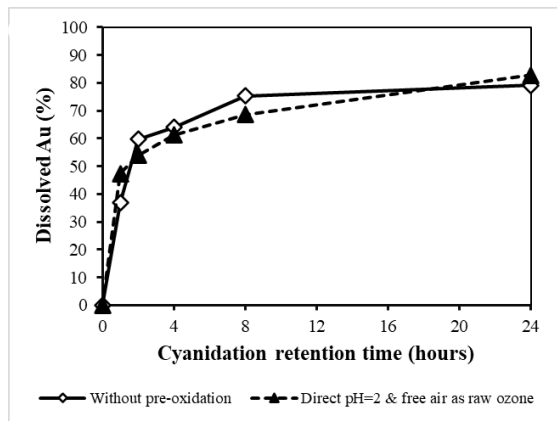


Fig. 3.10. Gold extraction during cyanidation comparison between without pre-oxidation and pre-oxidation with highest gold extraction

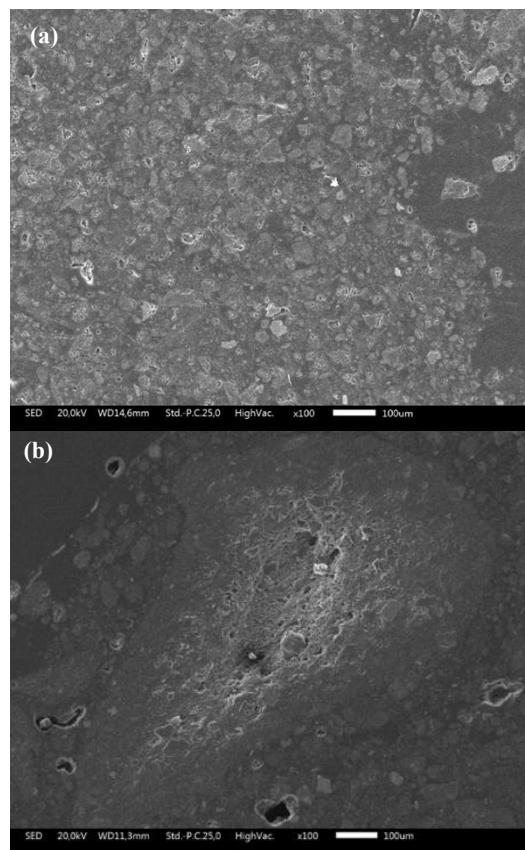


Fig. 3.11. SEM analysis results: (a) untreated Doup gold ore; (b) Pre-oxidation residue that provides highest gold extraction during cyanidation

3.6. Analysis of cyanide and calcium oxide consumption during cyanidation process

Data from the calculation of cyanide consumption presented in Figure 3.12 (a) generally shows that pre-oxidation with ozone directly produces residues that consume more cyanides than the indirect method and cyanidation of ore without pre-oxidation. Cyanide is required 1.81 times more than the cyanidation process without pre-oxidation in the experimental conditions that provide the best gold extraction percentage. This is related to the analysis discussed in the previous section on the possibility of the formation of elemental sulfur in the residues of the pre-oxidation process. Previous investigators on pre-oxidation of sulfide ore or refractory concentrate showed that elemental sulfur can be formed and reacts with cyanide to form thiocyanate ion (SCN^-) in the cyanidation process according to the following reaction equation^[6,11,16,19] :



For comparison Bazhko et al.^[19] found that with the same retention time and pH parameters in direct pre-oxidation, the cyanide consumption in the cyanidation process increases by 2.375 times when compared to direct cyanidation.

The calcium oxide (CaO) consumption profile used as a reagent to increase the pH for various experimental variations is shown in Figure 3.12 (b). In a pre-oxidation experiment at pH 2 for each indirect and direct method, the CaO required to raise the pH toward a cyanidation pH condition (pH 10.5–11.5) increased compared to the pre-oxidation variation without pH regulation because increasing the pH of the preoxidation residue from 2 requires more CaO than the pre oxidation residues without a decrease in the pH that has a pH of about 6.

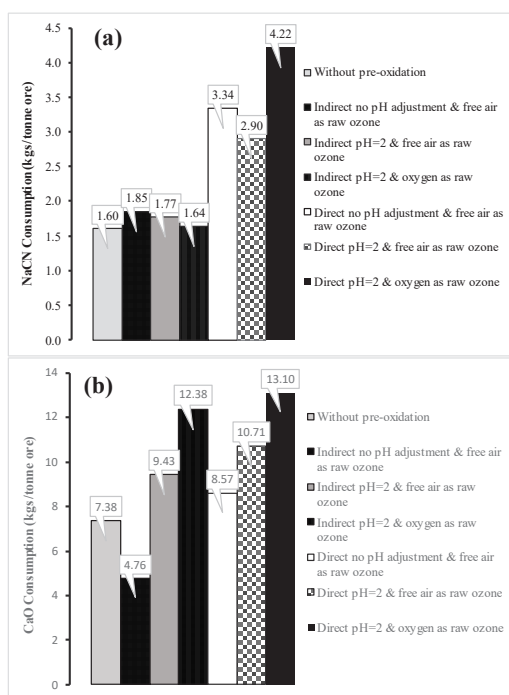


Fig. 3.12. The consumption profile (kgs/tonne ore) of NaCN (a) and CaO (b) during cyanidation for all experiment variation

4. Conclusions

The profiles of temperature, pH, dissolved ozone (DO₃), dissolved oxygen (DO₂), and oxidation-reduction potential (ORP) can be used to predict the species forming and reactions occurring during pre-oxidation processes. The percentage of Cu, Fe, and Zn dissolved in the pre-oxidation process increased with the longer pre-oxidation time, lower pH, and the use of O₂ gases as raw ozone materials. Pre-oxidation using ozone gas, directly and indirectly, increased the gold extraction in the cyanidation process. Gold extraction of 82.78% was obtained by pre-oxidation method directly at pH 2 and using air as the raw material of ozone. The percentage of gold extraction increased by 3.7% compared to cyanidation of ore without pre-oxidation with 79.08% gold extraction. Cyanide consumption with pre-oxidation conditions that provide the best gold extraction percentage for direct and indirect methods increased 2.375 and 1.025 times, respectively, compared to non-pre-oxidated cyanidation. The consumption of calcium oxide for cyanidation depends on the residual pH of the pre-oxidation residue.

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