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EFFECT OF OXIDIZING AGENTS IN EXTRACTING GOLD FROM ANODE SLIME

PENGARUH OKSIDATOR DALAM MENGESTRAKSI EMAS DARI LUMPUR ANODA

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ABSTRACT

Anode slime is a byproduct collected from electro refining copper process. The valuable metals present in the slime are Au, Ag, Pt, Pd and Pb. Yet, the slime has not been processed in Indonesia but sent to another country. Extracting the gold from anode slime had been attempted in the laboratory by applying wet chlorination method. Sodium hypochlorite (NaOCl) and hydrogen peroxide (H_2O_2) served as the oxidizing agents. Effects of various parameters such as solvent concentration, leaching time and temperature on the percent extraction of gold were studied. The optimum recovery of gold with NaOCl is 98.86 % Au at leaching temperature of 40°C, solvent concentration 5 M, NaOCl 5 mL and 20% solid after 120 minutes leaching time. Silver loss under this condition is 2–3%. Leaching the gold by H_2O_2 provided the highest gold extraction of 99.99% Au at 7M HCl concentration, temperature 60°C, H_2O_2 0.5 M, leaching time 180 minutes, and 20% solid. The silver loss under this condition is only 0.6%.

Keywords: anode slime, wet chlorination, extraction, gold, oxidation, oxidizer

SARI

Lumpur anoda merupakan produk samping proses pemurnian elektrolisis tembaga yang di dalamnya masih terkandung logam-logam berharga seperti Au, Ag, Pt, Pd dan Pb dalam jumlah signifikan. Hingga saat ini, pengolahan lumpur anoda untuk mengekstrak logam-logam berharga belum dilakukan di Indonesia tetapi di luar negeri. Proses ekstraksi emas dari lumpur anoda skala laboratorium dilakukan dengan cara klorinasi basah menggunakan oksidator natrium hipoklorit (NaOCl) dan hidrogen peroksida (H_2O_2*). Parameter-parameter yang mempengaruhi proses ekstraksi dan diamati dalam percobaan adalah konsentrasi pelarut, waktu pelindian dan suhu. Persen ekstraksi optimum menggunakan NaOCl adalah 98,86% pada konsentrasi pelarut 5 M, suhu 40 °C, NaOCl 5 mL, waktu 120 menit dan 20% padatan. Kehilangan Ag pada proses ini 2–3 %. Penggunaan *H_2O_2* menghasilkan persen ekstraksi emas tertinggi 99,99% pada konsentrasi HCl 7 M, suhu 60°C, *H_2O_2* 0,5 M, waktu 180 menit dan 20% padatan. Kehilangan Ag pada kondisi ini hanya 0,6%.*

Kata kunci : lumpur anoda, klorinasi basah, ekstraksi, emas, oksidasi, oksidator

INTRODUCTION

Anode slime, a by product collected from electro refining copper, contains valuable metals such as Au, Ag, Pt, Pd, Se. The metallic substances are collected from the bottom of electrolytic cells during refining the copper (Hait et al., 2002). There are two different slimes that depend on the sources from which they are obtained. The first one produced during processing the copper

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concentrate. It contained relatively high gold, silver, tellurium and selenium. The second one produced during processing the recycled scrap that performed higher lead, copper, tin and silver content (Amer, 2002). Chemical composition of the first type slime depends on the composition of copper concentrates (Wang et al., 2003).

Technology that has been used for the valuable metals extraction from anode slime is pyrometallurgical and hydrometallurgical route processes. Pyrometallurgical process developed by Outokumpu Technology in Boliden Swedia. Anode slime is smelted using Top Blown Rotary Converter type of Kaldo furnace. The processing steps in Kaldo furnace are smelting, slag separation, converting and refining consecutively. During smelting and formation lead (Pb) slag, would be oxidized to PbO changed into slag by injecting the oxygen at temperature of 1200 °C. The valuable metals of anode slime (such as Au, Ag, Pt, Pd and Pt) remain in the bottom as doré bullion to be purified using Moebius electrolysis cell for silver and Wohlwill electrolysis cell for gold (Ludvigson and Lasson, 2003). Lead oxidation and slag formation process are the critical stage because it can entrap gold and silver into slag.

Hydrometallurgical route that has been applied in industry is known as Hoffman process. In this process, anode slime is leached by hydrochloric acid. Some metals is oxidized using Cl_2, followed by gold separation using DBC (dibutyl carbitol) as well as selenium and tellurium reduction using SO_2 and silver reduction using dextrose (Hoffman, 1990). Hydrometallurgical process of anode slime is relatively new compared to the possible extension pyrometallurgical process that is many innovations in the extraction process. Many hydrometallurgical processes were reported for extracting the valuable metals; among them are cyanidation (Hoffman, 1991; McClincy, 1990) and thiourea leaching (Schulze, 1984). In its development, it is showed that thiourea is more effective to extract silver (Ag) than that of cyanide because of its simplicity to form complex compounds. Some researchers (Kusnierov et al., 1993; Kucha, 2001) reported that thiourea was very effective for recovering valuable metals from copper concentrates. Composition that is suitable for treating anode slime by thiourea are lead concentrations <15% and Ag <0.5%. Thiourea leaching has been performed in hydrochloric, sulfuric and nitric acid media. Dissolution of gold and silver up to 97% was reported in a solution containing 20 g/dm^3 HCl, 0.2 g/dm^3 H_2O_2 and 100 g/dm3 thiourea (Amer, 2002). Hait et al., 2002 extracted valuable metals such as copper (Cu), selenium (Se) and tellurium (Te) using sulfuric acid by adding MnO_2. The combination of MnO_2 and NaCl provided higher recovery for these metals. Bard and Sobral (2008) had conducted a research to replace Cl_2 by hydrogen peroxide (H_2O_2). The result of experiments showed that the H_2O_2 is more effective to dissolve the valuable metals than that of sodium chlorate.

This paper discusses gold (Au) extraction from anode slime through hydrometallurgical process by replacing Cl_2 oxidizer with sodium hypochlorite (NaOCl) and H_2O_2. The NaOCl is expected to change into Cl_2 gas because Cl_2 reacts with strong oxidizing agents such as HCl produces ion ClO^- and ClO^{3-} which is strong enough to dissolve Au, Ag, and Cu. Anode slime obtained from PT. Smelting has a distinctive characteristic that is too high lead concentration (approximately >50% Pb). Based on these characteristics, it is necessary to seek the best processing route. The first process is separating Pb in ammonium acetate solution before extracting the Au. A large amount of lead in anode slime would seriously affect the low recovery of precious and other valuable metals. Hydrometallurgical process of this gold extraction has advantages namely providing higher recovery not only for gold and silver, but also platinum and palladium because the possibility of gold and the other metal losses to the slag as normally happened in pyrometallurgical route can be avoided. Moreover, the fact that hydrometallurgical route requires lower energy consumption (below 100°C) is also an advantage.

METHODOLOGY

In this research work, gold extraction was conducted by wet chlorination process using NaOCl and H_2O_2 after removing lead from the slime by second-stage leaching in ammonium acetate solution (Rodliyah et al., 2011). The parameters studied in wet chlorination process included hydrochloric acid concentration that ranged from 1 to 7 molar, leaching time 15 to 180 minutes and temperature 20 to 80°C. The experiment was started by leaching lead residue, followed by separating its filtrate and residue. The residue was then dried in an oven. The filtrate and residue were analyzed using atomic absorption spectrophotometer (AAS) to identify the leached gold.

Leaching apparatus consisted of 250-mL flasks equipped with magnetic stirrer. 5 grams of 150 mesh slime was reacted in glassed flask with HCl solution. The flask was connected to a funnel for slowly H_2O_2 and NaOCl addition. Cl_2, generated during reaction, flowed into $NaOH^-$ containing solution to neutralize the Cl_2 into NaCl. Leaching experiments with wet chlorination method is shown in Figure 1.

RESULTS AND DISCUSSION

The chemical content of representative anode slime is given in Table 1.

Prior to extracting the gold, experiments of Pb leaching from anode slime had been conducted (Rodliyah et al., 2011). Results of chemical analysis for residue of lead leaching is shown in Table 2 from the table, it is clear that the contents of Au, Ag, Se, Te and Sb increase; while Pb and Cu decrease if compared to Table 1. The lead is not too high, about 13.54%. Rodliyah (2011) reported that metal could be leached by ammonium acetate solution resulted in the highest of total Pb extracted is 94.9%.

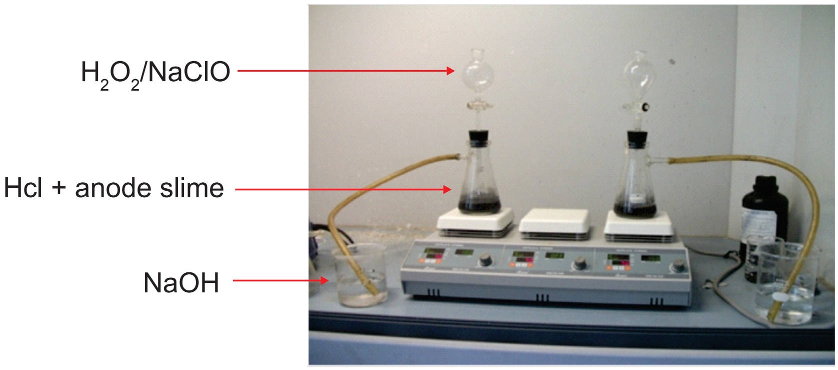

Figure 1. Experiments of gold leaching using wet chlorination method

Table 1. Chemical content of anode slime used in the experiment

No.	Element	Quantity (%)
1.	Au	1.57
2.	Ag	4.52
3.	Se	8.83
4.	Pb	52.58
5.	Cu	0.49
6.	Te	0.12
7.	Bi	4.10
8.	As	1.74
9.	Sn	0.17
10.	Sb	0.12
11.	Ni	0.02
12.	Fe_2O_3	0.01
13.	Al_2O_3	0.15
14.	SiO_2	0.45
15.	SO_3	14.43
16.	Cl	1.42
Total		94.78

Table 2. Chemical content of Pb leach residue

No.	Element	Quantity (%)
1.	Au	2.47
2.	Ag	7.1
3.	Se	13.23
4.	Pb	13.54
5.	Cu	0.09
6.	Te	0.15
7.	Sb	0.16

Gold Leaching by NaOCl

Preliminary experiments of gold leaching were carried out by hydrochloric acid solution using NaOCl oxidizer. The observed parameters consisted of the HCl concentration (1 to 4 molar) and the amount of oxidizer 20% (v/v). Leaching temperature as well as leaching time were fixed at 60°C and 120 minutes respectively. The results can be seen in Figure 2.

Figure 2 reveals that percent extraction of gold increases with the increase of HCl concentration, whereas percent extraction of silver significantly decreases with the increase of HCl concentration. However, silver is significantly still disolved at about 44.47%. The extracted gold seems to be low (approximately 59.19%) due to the applied temperature is rather high (60°C) that may affect on Cl_2 solubility from the reaction between NaOCl and HCl, so the ability in oxidizing Au turns ineffective. According to Hoffman (1990), the solubility of Cl_2 gas and absorption rate decrease when temperature is increased until 60 °C. Therefore, effect of temperature and concentration of HCl need to be studied to attain higher percent extraction of gold.

Next experiment was studying the effect of oxidizer amount on the percent of Au and Ag extractions. The experimental results presented in Figure 3 shows that gold extraction increases with the increase of amount NaOCl, while the silver decreases. The more NaOCl addition, the more Cl_2 gas production to oxidize and disolve gold. However, the percent of Au extraction in these experiments is inadequate (75.85%), while the silver is likely still dissolved into filtrate as much as 27.23%.

Effort to improve percent of Au extration and decrease the silver was performed by varying

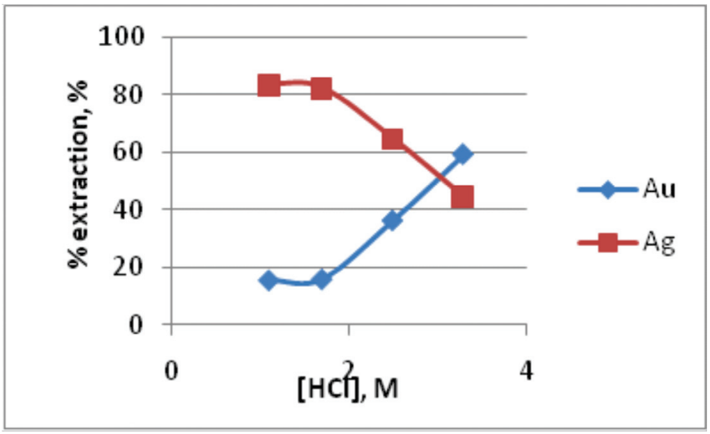

Figure 2. Effect of HCl concentration on % extraction of Au and Ag

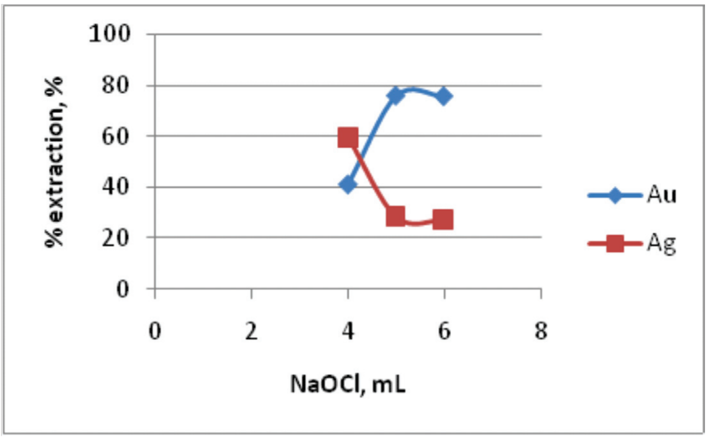

Figure 3. Effect of NaOCl amount on % extraction of Au and Ag

the temperature and reaction time as well as increasing the concentration of HCl. The result is shown in Figure 4. The figure confirms that the Au can be improved significantly to 98.86% at 40 °C with leaching time of 120 minutes. This suggests that the solubility of Cl_2 gas increases by lowering temperature leaching from 60 to 40°C. However, percent extraction of Au would drop to 94.63% when the temperature was lowered to room temperature (25°C). So, it can be infered that the 40°C is the optimum condition that provides the highest percent extraction.

A small amount of silver (about 2-3%) is still dissolved in the filtrate of Au leaching as can be seen in Figure 5. This phenomenon indicates low solubility of Ag in HCl and the Ag may be precipitated in the form of AgCl.

Leaching of Gold Using H_2O_2

Effect of leaching time and temperature can be shown in Figure 6. Experiment was conducted using parameters as follows: 5 M HCl, percent solid 20, 0.5 M H_2O_2 and 30 – 150 minutes leaching time. Percent extraction of Au base on leaching time and temperature variation is shown in Figure 6.

It is shown that when the temperature is raised up to 60°C the extracted of Au tends to increase from 2.3 to 30.89%. However, raising temperature up to 80°C results in significant decrease of the extracted gold about 13.1%. According to Hoffman (1990), to leach Au by HCl and H_2O_2 oxidizer could apply temperature up to 70°C without reagent loss. This relates to present experiment

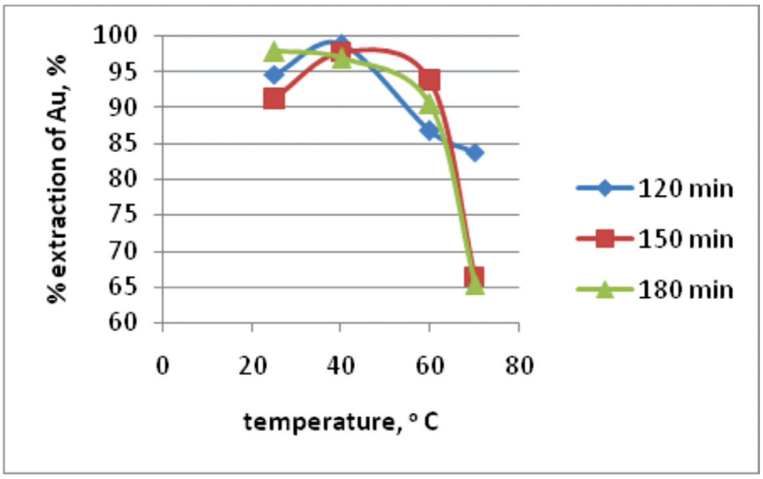

Figure 4. Effect of temperature on % extraction of Au

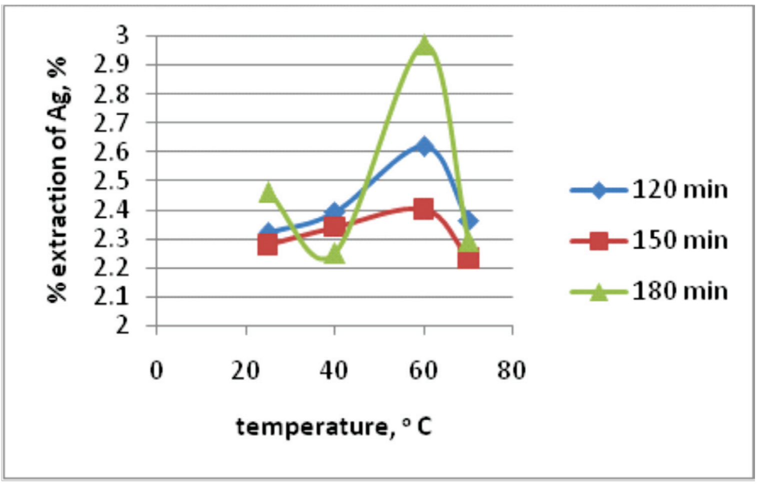

Figure 5. Effect Temperature on % extraction of Ag

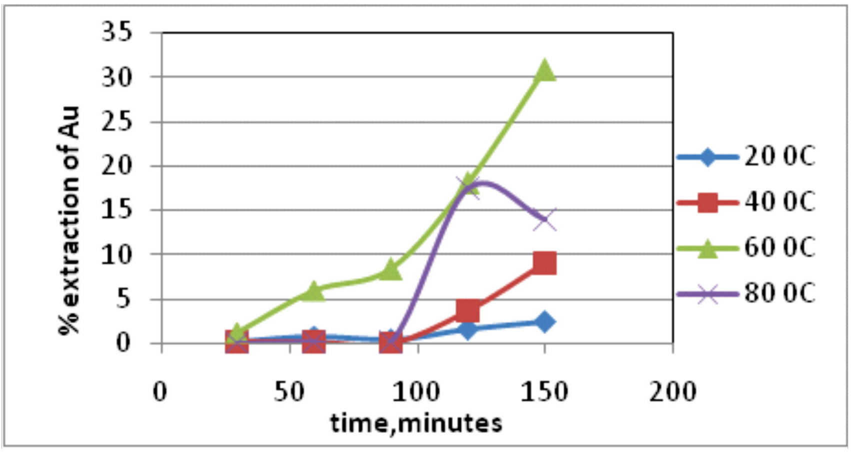

Figure 6. Effect time on percent extraction of Au with temperature variations

results that are carried out at temperature of 80°C and shows significant decrease of the extracted gold. The H_2O_2 is decomposed due to its ability as an oxidizer is in adequate. The highest extracted gold can be achieved at temperature of 60°C.

Study on the effect of HCl concentration to extract Au was conducted at 60°C, percent solid 20%, 0.5 M H_2O_2 and leaching time for 30 - 180 minutes in 30 minutes intervals. From the experiment results (Figure 7), it seems that the highest percent extraction is 99.99% and obtained at 7 M HCl during 180-minute leaching time. The extracted Au increases when the concentration HCl increases because gold dissolution reaction of Au is likely more effective through oxidation of Au to Au^+ by H_2O_2 and $AuCl^{4-}$ complex formation.

The leached Au in Pb leached residues ensures that the highest percent extraction of gold is 99.99% which is obtained at 7M HCl concentration, 60 °C leaching temperature, 180-minute leaching time, 20% percent solid, 0.5M H_2O_2 concentration. Silver is not expected to dissolve during the leaching, but it turns out to a certain extent of soluble silver, causes a certain amount of silver loss. Figure 8 shows that the higher HCl concentration, the more losses the silver. The maximum loss (about 0.6% Ag) is achieved at 7M HCl concentration.

Figure 9 indicates that the temperature does not significantly affect the percent of dissolved Ag. The average loss Ag is about 0.3%. Effect of HCl concentration and leaching temperature on the

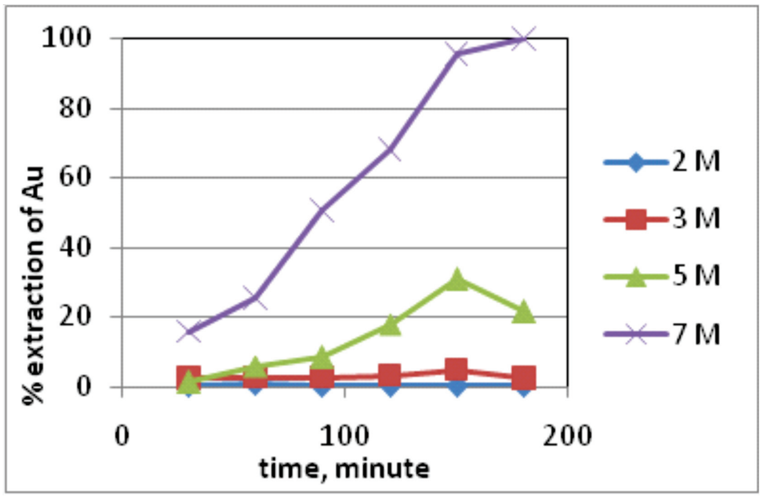

Figure 7. Effect of time on extracted Au

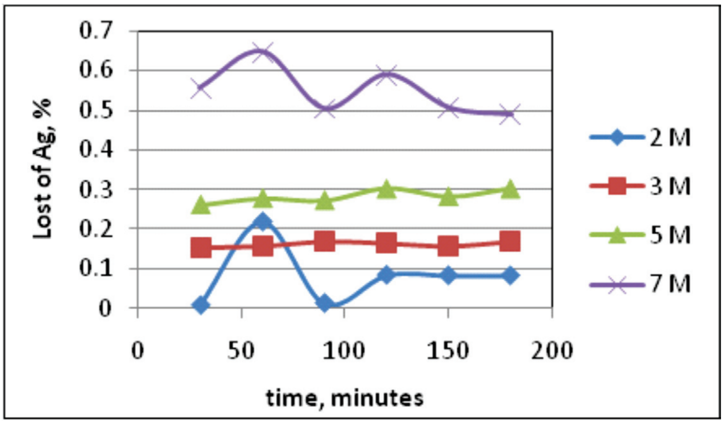

Figure 8. Loss of Ag on time at variations of HCl concentration

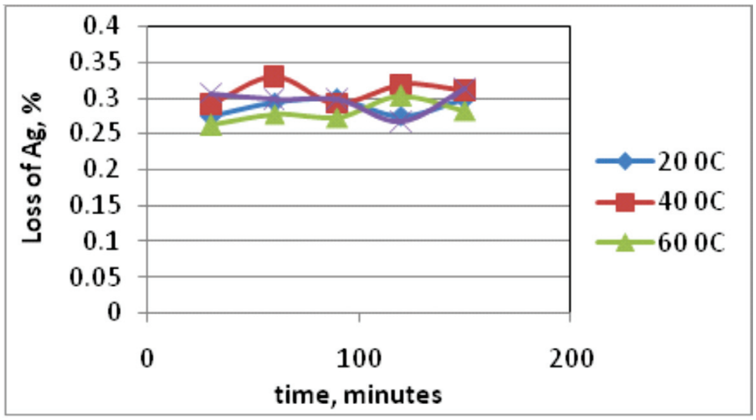

Figure 9. Ag loss due to time at temperature variation

dissolved Ag is not significant. It is only 0.6%.

From a series of Au leaching experiments using HCl solution with H_2O_2 and NaOCl oxidizer, it can be compared several parameters to the effectiveness of Au leaching as presented in Table 3. The leaching process using HCl solution and H_2O_2 as oxidizer provides higher extracted Au (99.99%) if compared to the leaching using HCl solution and NaOCl oxidizer (98.86%). The differences in extracted Au from both oxidizers seem small but as the extracted metal is a noble one such figures (approximately 1.12%) provide high economic value and significant difference in revenue from the gold sale. The fact that the price H_2O_2 is cheaper than NaOCl, leaching gold from anode slime using H_2O_2 is more effective compared to the use of NaOCl.

Table 3. The best condition for gold leaching using HCl solution and H_2O_2 and NaOCl as oxidizers

Condition	H_2O_2	NaOCl
Temperature (°C)	60	40
[HCl] (M)	7	5
Leaching time (minute)	180	120
Loss of Ag (%)	0,6	2-3
Percent extraction (%)	99.99	98.86

CONCLUSION

Both sodium hypochlorite (NaOCl) and hidrogen peroxide (H_2O_2) can be used as good oxidizer to generate Cl_2 in Hoffman process and its do efectual for dissolving valuable metals from anode slime that is capable of disolving gold more than 98%. However H_2O_2 does more effective compare to NaOCl in dissolving the valuable metals in anode slime. The chlorination process using NaOCl and H_2O_2 as oxidizers is also highly selective for the extraction of gold, because silver is dissolved is very small.

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