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Study of Sulfuric Acid and Hydrochloric Acid as Acid Wash Reagents to Remove Ag, Cu and Fe

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Abstract

In Indonesia there are several areas that have gold deposit reserves, one of which is located in Bakan Village, North Sulawesi. Gold ore in Bakan Village is extracted by heap leaching method by PT. J Resources Bolaang Mongondow. This study aims to analyze and compare 1 M sulfuric acid (H_2SO_4) and 3% hydrochloric acid (HCL) as acid wash reagents to remove Ag, Cu and Fe. This acid wash study was carried out using the bottle roller test method using two different reagents, sulfuric acid and hydrochloric acid. The results of the research on the acid wash process The results showed that the effective reagent in dissolving base metals was 1 M sulfuric acid (H_2SO_4) with the solubility percentage of each element as follows Ag 0.3%, Cu 20.2%, Fe 60.4%. Meanwhile, 3% hydrochloric acid was only able to dissolve Ag 0.4%, Cu 4.3% and 4.3% Fe.
Keyword: *Extractive Metallurgy, Acid washing, Sulfuric Acid, Hydrochloric Acid*

Introduction

PT. JRBM J holds a contract of work located in North Sulawesi, specifically in Bakan and North Lanut (Diputra, 2022).Located in the southern part of North Sulawesi, to be more precise, about 25 km to the southeast from Kotamobagu, North Sulawesi, Indonesia (Surahmad, Inung, Adnyano, & Purnomo, 2021).Bakan is the 6th generation Contract of Work owned by PT J Resources Nusantara which was acquired from PT. Avocet(Ode Muhamad Razak et al., 2023) PT. JRBM is a company engaged in gold mining (Haryati, Kopa, & Prabowo, 2018)

The extraction of gold ore at from ore at PT. JRBM is carried out using the heap leach method. which is well-suited for the specific characteristics of low grade mineral ore in the Bakan Site, This ore has a low gold grade, high porosity, and is classified as oxide ore, high porosity, and is a type of oxide ore.

Processing of ore for the extraction of valuable metals such as gold and silver is a complex and very important process in the mining industry. One of the crucial steps in the extraction process is elution, which involves separating the valuable metal ions adsorbed on the ion exchange resin.

This elution process enables high quality recovery of valuable metals from the resin surface. However, in practice, there are often challenges associated with high concentrations of base metals, such as copper, silver or iron, in the acid wash step which is in preparation for the elution process.

This problem can occur because the processed ore contains various base metals which are also adsorbed during the adsorption process

High metal-base concentrations can have a negative impact on gold and silver extraction processes. These base metals can react with the reagents used in the extraction process, inhibiting the ability of these reagents to interact with precious metals. In addition, high base-metal concentrations can also lead to the formation of unwanted by-products, which can affect the quality and final yield of the extracted precious metal (Marsden & House, 2006)

In the heap leaching method, The leaching solution in the is NaCN, taking advantage of the properties of cyanide ions in NaCN which can bind gold and create a complex known as NaAu $(CN)_2$. This gold binding process occurs through the following reaction (Fungene, Groot, Mahlangu, & Sole, 2018)

$$8NaCN + 4\ Au + O_2 + H_2O \rightarrow 4\ [Au(CN)_2^-] + 4\ NaOH$$

The rich solution known as the pregnant leach solution from leaching will then be transferred to the recovery units using a pump will be transferred using a pump to the units recovery. heap leach method it self has several advantages compared to other extraction processes, including not going through intensive stages crushing, and grinding, no solid/liquid separation required after processing, low capital and operating costs and suitable for ores low grade (*Nurkhamim*, n.d.)

In general, the hydrometallurgical process includes two main stages namely leaching and recovery. At this stage of leaching, a carefully chosen dissolution process is implemented to efficiently certain precious metals in the ore, minimizing the presence of impurities (Marsden & House, 2006).

The next subsequent is the recovery stage, which involves extracting metals from leaching solutions in the form of pure metals or compounds. This recovery stage takes place within an equipment called an elution column, which is particularly designed for the desorption process of gold from loaded resin using an eluate solution.

Eluate solution utilized in PT. JRBM consists of thiourea with a concentration of 60-80 gpl and H_2SO_4 at 0.6-1 Molars. Excessive sulfuric acid concentration can lead to rapid resin deterioration.

Prior to elution, the resin underwent an of the acid washing process is to eliminate precipitates (scales) such as carbonate from the resin's pores. This process aims to reopen the micro-pores of the resin, thereby increasing its active surface area. Consequently, the contact between the thiourea solution and the resin's surface, which contains the Au complex, is facilitated (Marsden & House, 2006).

Washing with acid is also intended to remove a certain amount of base metal which is also adsorbed (Naufal, Pratama, & Yushandiana, n.d.). In this process, release is desired base metal as high as possible, so that later during the stripping process consumption of thiourea by base metal can be minimized. The resin used in PT. JRBM is strong base anion resin with the trademark Minix-Dowex, reagents that can be used to regenerate resin include hydrochloric acid (HCL) and sulfuric acid (H_2SO_4) (Prayitno & Sardjono, 2002)

This study aims to compare sulfuric acid and hydrochloric acid in removing Fe, Ag and Cu. In this context, research and innovation are continuously being carried out to reduce the problem of metal-base concentration in the acid washing process of gold and silver extraction by testing reagents that are effective in dissolving Ag, Cu and Fe.

By overcoming these problems, it is hoped that the precious metal extraction process can run more efficiently, produce higher quality products, and contribute to the implementation of the metal mining and processing industry.

Several types of organic acids have been reported to remove Ag, Fe and Cu.

Sulfuric acid with concentrations ranging from 0.3 to 1 M exhibits superior performance in the removal of Cr, Cu, and Ni (Lin, Chien, & Liang, 2012)In addition to H_2SO_4 with a concentration of 0.5-1 M demonstrates effective desorption of Fe. (Taha et al., 2020)

Use of hydrochloric acid at this concentration is based on its effectiveness in Cd, Pb, Cu, Zn, Ni and As. (Zhang, Xu, Kanyerere, Wang, & Sun, 2022)hydrochloric acid with Concentrations ranging from 1 M - 6 M Has the ability to dissolve Fe and Ti. (Hernández, García, Cruz, & Luévanos, 2013)

Research Methods

The research methodology employed in this study involved direct research at the SGS JRBM unit. SGS is a contractor company providing testing, verification and inspection services. The research procedure consisted of obtaining 120 ml sample of Minix-Dowex resin samples and preparing reagents for acid washing and manufacture eluate stripping.

The acid washing reagent used was sulfuric acid (H_2SO_4) with a concentration of 1M, and hydrochloric acid with a concentration of 3%. Other chemical solutions that can be used acid washing reagents include hydrochloric acid (HCl), sulfuric acid (H_2SO4), nitrate acid (HNO_3), and phosphoric acid (H_3PO_4) oh(Oh, Bade, Lee, Choi, & Shin, 2015)According to calculations, 3% hydrochloric acid (HCl) is equivalent to 1 M hydrochloric acid (Zhang et al., 2022)

Then the acid wash process was carried out using the bottle roller test medium for 30 minutes and stripping for 5 hours.

Preparation of 3% HCl Acid Wash Solution From 36.5% HCl

Pour 164 ml of 3% HCl in a beaker glass, then add a little distilled water to a 2000 ml volumetric flask, and shake the solution until it is homogeneous.

Solution Making Acid Wash H_2SO_4 1 M From H_2SO_4 98%

Pour 946 ml of distilled water into a beaker, then add 54 ml of 98% H_2SO_4 into a 1 litre volumetric flask, then shake the flask until the solution is homogeneous.

Solution Manufacture Eluate Stripping

35 gram of thiourea was prepared into a beaker, next 54 ml of 1M H_2SO_4 was prepared into a beaker then 35 gram of thiourea was put into a 500 ml volumetric flask. 1 M H_2SO_4 solution was added to the meniscus line and the solution was shaken until homogeneous. Titration of thiourea solution with $AgNO_3$ is used to determine the concentration of thiourea.

Acid Wash Procedure

Place 120 ml of dry resin in a 480 ml bottle of 3% HCL, perform a bottle roll test for 30 minutes, then take a sample of ± 100 ml solution and 20 ml resin for sampling.

Procedure *Stripping*

- Stripping Preparation
  Place 400 ml of thiourea solution in a glass beaker and heat with a magnetic stirrer at 55-57 ^oC for 5 hours at 200 rpm.
- Stripping Proccess
  100 ml of ion exchange resin is placed in a glass beaker containing thiourea solution and stripped for 5 hours at a constant temperature of 55-57°C. After 5 hours the sample is re-sampled.

Head Resin

Prior to the Acid Wash process, the resin head was tested using the AAS test, based on data from the analysis of Atomic Absorption Spectrophotometry (AAS) tests carried out at the Société Générale De Surveillance De Surveillance (SGS) PT. JRBM. Data head resin is data that explains the content of elements in the resin sample before the process is done acid wash. The table of head resin data can be seen in table 1.

Sampel ID	**Ag (ppm)**	**Cu (ppm)**	**Fe (ppm)**
1	70	1780	800
2	70	1800	830
3	80	1810	800
Average	73	1,797	810

Table 1. Head Resin Data
Source: PT. JRBM

Solution Acid Wash

This data is the result of sample reading acid wash H_2SO_4 1 M and HCL 3%. The table of solution acid wash data can be seen in table 2.

Variation	Solution Assay Acid Wash		
	Ag (ppm)	Cu (ppm)	Fe (ppm)
H_2SO_4 1M	0,02	32,3	108
HCl 3%	0,03	7,27	3,82

Tabel 2. Solution Acid Wash Data
Source: PT. JRBM.

Solution Results of Stripping

This data describes the percentage of the amount of Au dissolved by the thiourea solution and the percentage base metal dissolved in both reagents acid wash. The table of data solution results stripping can be seen in the table 3.

Variation	Metal Washed Eff%		
	Ag (ppm)	Cu (ppm)	Fe (ppm)
H_2SO_4 1M	87.2%	88.7%	0.8%
HCl 3%	89.2%	93.9%	6.5%

Table 3. Data Solution Results Stripping
Source: PT. JRBM

Results And Discussion

To determine the success rate of the elution process, calculations are carried out which include acid wash efficiency and stripping efficiency

In the analysis of % efficiency for the acid wash at PT. JRBM, two methods are employed: calculating per element base metal and calculating the % efficiency of acid wash. The formula used is the following:

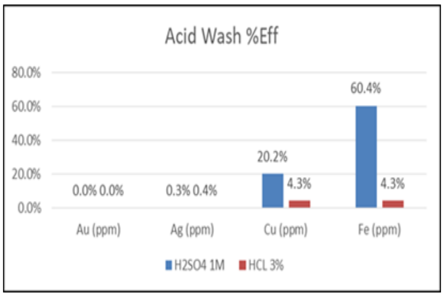
$$\frac{Volume\ Solution\ x\ Base\ Metal\ in\ Solution}{ion\ exchange\ resin\ weight\ x\ Base\ Metal\ in\ Head\ Resin} \text{x100\%}$$

Analysis of the calculation of % for the stripping process at PT. JRBM uses the following formula:

$$\frac{Volume\ Solution\ x\ \ Au\ Dalam\ Solution\ Hasil\ Stripping}{ion\ exchange\ resin\ weight\ x\ Au\ in\ Solution\ before\ Stripping} \text{x100}$$

Comparison of The Effectiveness of Sulfuric Acid (H_2SO_4) 1 M and 3% HCl As Reagentacid Wash

%Efficiency chart for the acid wash of base metal elements is depicted in picture 1.



Picture 1. % Efficiency Chart Acid Wash Element Base Metal

Source: PT. JRBM

Based on Figure 1 reveals during the acid wash process, elemental gold element remains insoluble in both sulfuric acid and hydrochloric acid because gold has an oxidation state of +1 and does not have valence electrons that are easily accepted, so it does not easily react with acids.

Next is the amount base metal the least dissolved is silver (Ag) this is due to the low affinity with acid ions in the reagent acid wash thus making it difficult for the reaction to occur between Ag and the acid which causes it to dissolve the metal.

In addition, Ag demonstrates a rate reaction with sulfuric acid, rendering the solution process less effective in dissolving Ag, Ag also additional other chemical reactions such as electrolysis in order to be dissolved optimally.

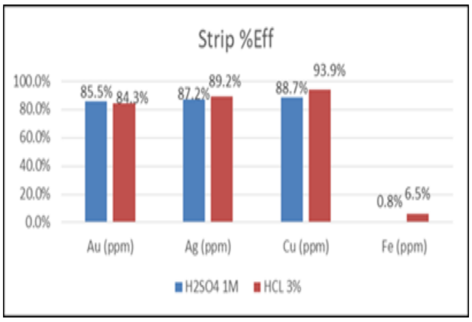
An effective reagent for dissolving Cu is sulfuric acid, this is because sulfuric acid has stronger oxidizing properties. Sulfuric acid can oxidize base metal such as Cu becomes Cu^{2+} while hydrochloric acid has weaker oxidizing properties so that the percentagebase metal low dissolved Cu.

Regarding the dissolution of Fe sulfuric acid is more effective than hydrochloric acid due to its stronger oxidizing properties. Sulfuric acid forms such with Fe which is easily soluble while hydrochloric acid does not form complexes resulting in less Fe being dissolved.

The reaction that occurs is as follows: $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

Comparison of The Effectiveness of Sulfuric Acid (H_2SO_4) 1 M and Hydrochloric Acid (HCL) 3% on Stripping Efficiency

Efficiency stripping can be seen in the picture 2.



Picture 2 Graph of % Stripping Efficiency

Source: PT. JRBM

The graph also reveals that the higher stripping efficiency of sulfuric acid compared to hydrochloric acid is attributed to its greater effectiveness in dissolving base metals. However, the graph also indicates that the amount of dissolved base metals increases over time, which can be attributed to the longer contact time between the reagent and the resin during the stripping process compared to the acid wash procedure.

Based on the graph above it can also be concluded that, the use of hydrochloric acid is more effective than sulfuric acid, this happens because hydrochloric acid has oxidizing properties, which facilitate the base metal separation from the resin by transforming it into more soluble metal ions. (Oh et.all, 2015).

Can also be seen type base metal Cu and Ag dissolved a lot, this is because these two metals have a relatively low oxidation potential, so they are easily oxidized by hydrochloric acid into soluble metal ions. However, Fe has a higher oxidation potential, making it more difficult to oxidize and therefore more difficult to dissolve.

Conclusions

The conclusions of this research work are as follows:

1. On process acid wash sulfuric acid is effective for dissolving Cu this is because sulfuric acid has stronger oxidizing properties. Sulfuric acid can oxidize base metal such as Cu becomes Cu^{2+}.
2. Sulfuric acid is also effective in dissolving Fe, because sulfuric acid has strong oxidizing properties, Sulfuric acid forms complexes with Fe which are easily soluble.
3. Ag is base metal which is the least soluble this is due to the low attachment of acid ions in the reagent acid wash thus making it difficult for the reaction to occur between Ag and the acid which causes it to dissolve the metal.
4. On process acid wash sulfuric acid is effective at dissolving base metal Cu type because sulfuric acid has the advantage of activating hydrogen ions (H^+).
5. On process stripping the use of hydrochloric acid is more effective than sulfuric acid, this happens because hydrochloric acid has oxidizing properties that can separate base metal of resin by changing base metal into more soluble metal ions.
6. Base metal which is dissolved in the process stripping are Cu and Ag this is because these two metals have a relatively low oxidation potential, while Fe has a higher oxidation potential,

making it more difficult to oxidize making it more difficult to dissolve.

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