


## Article

# Comparative Analysis of the Recovery of $\text{Cu}^{2+}$ and Au from Washing Solution of Pyrite Concentrate Slag by Two Processes

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**Abstract:** A large amount of pyrite concentrate slag washing solution is produced in China every year, and this contains valuable components such as  $\text{Cu}^{2+}$  and Au. The traditional treatment method not only pollutes the environment but also wastes metal resources. For the washing solution containing  $\text{Cu}^{2+}$  437 mg/L and Au 0.13 mg/L, two new processes comprehensive recovery schemes were developed and compared in this paper, namely iron powder replacement pore filtration and neutralization precipitation pore filtration. When the iron powder replacement pore filtration process was adopted,  $\text{Cu}^{2+}$  and Au were mainly comprehensively recovered in the form of a mixture of sponge copper and particulate gold. The test results showed that the replacement optimal conditions involved a pH of 3.0, iron powder dosage of 6 g/L, and replacement time of 3.0 h. After replacement, the filter cloth with below 1  $\mu\text{m}$  pore size was used for filtration. The recovery rate of  $\text{Cu}^{2+}$  in the washing solution was 98.13 and the total recovery rate of Au was 95.83%. Otherwise, when the neutralization precipitation pore filtration process was adopted,  $\text{Cu}^{2+}$  and Au were mainly comprehensively recovered in the form of a mixture of copper hydroxide and particulate gold. The test results showed that sodium hydroxide was used as the precipitant and the optimum neutralization pH value was 6.5. After precipitation, the filter cloth with a below 1  $\mu\text{m}$  pore size was used for filtration. The recovery rate of  $\text{Cu}^{2+}$  in the washing solution was 97.35% and the total recovery rate of Au was 93.54%. The economic benefit estimation of the two processes showed that the neutralization precipitation pore filtration process had the advantages of low material consumption, low cost and high economic benefit.

**Keywords:** pyrite concentrate slag; washing solution; iron powder replacement; neutralization precipitation; micropore filtration



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## 1. Introduction

Pyrite slag, also known as sulfuric acid slag, is a waste residue produced when pyrite concentrate is used as a raw material to produce sulfuric acid [1,2]. Pyrite concentrate slag is discharged in a quantity of nearly ten million tons in China every year, accounting for about 1/3 of the total amount of chemical waste [3]. At present, for the comprehensive utilization of resources and the treatment of pyrite, most gold enterprises at home and abroad have adopted the method of boiling furnace oxidation roasting—water washing pretreatment—gold leaching, and the roasting temperature is generally higher at about 750–900 °C. In addition, pyrite is mainly composed of  $\text{Fe}^{2+}/3+$  and contains small amounts of  $\text{Cu}^{2+}$ , Au, Ag,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and other elements [4,5]. After roasting, the grade of pyrite is increased, which has a serious harmful effect on the direct leaching of gold. In order to eliminate the effect, the roasting slag is pretreated with water washing. The pretreatment water solution contains water-leaching copper, zinc, and residual trace ultra-fine gold, which can be used to make wires, conductors, electrodes, and other materials [6–8] and

has a high recycling value for gold mining enterprises. Taking a gold smelter in Yunnan Province, China as an example, the washing slag obtained from the pyrite concentrate slag after washing was used for cyanide gold extraction. During the washing process, a large amount of the washing solution is produced, with a daily output of 2600 m<sup>3</sup>/d, in which the concentration of Au is 0.13 mg/L and the concentration of Cu<sup>2+</sup> is 437 mg/L. If the washing solution adopted the traditional process of 'neutralization precipitation-concentration-neutralization water reuse', the Cu<sup>2+</sup> and a small amount of Au in the washing solution were finally precipitated in the neutralization slag and could not be recovered. When high calcium-neutralized water was reused, the problem of calcium sulfate blocking the pipeline often occurred. At the same time, a large amount of it was transported to the yard and stored in the open air, which had great management and environmental protection risks [9,10]. It can be easily dissolved due to moisture, rain oxidation, alkaline changes, etc., resulting in the secondary pollution of the environment, posing a significant environmental risk. Therefore, the question of how to develop a new comprehensive recovery process for Cu<sup>2+</sup> and Au from the washing solution is of great significance.

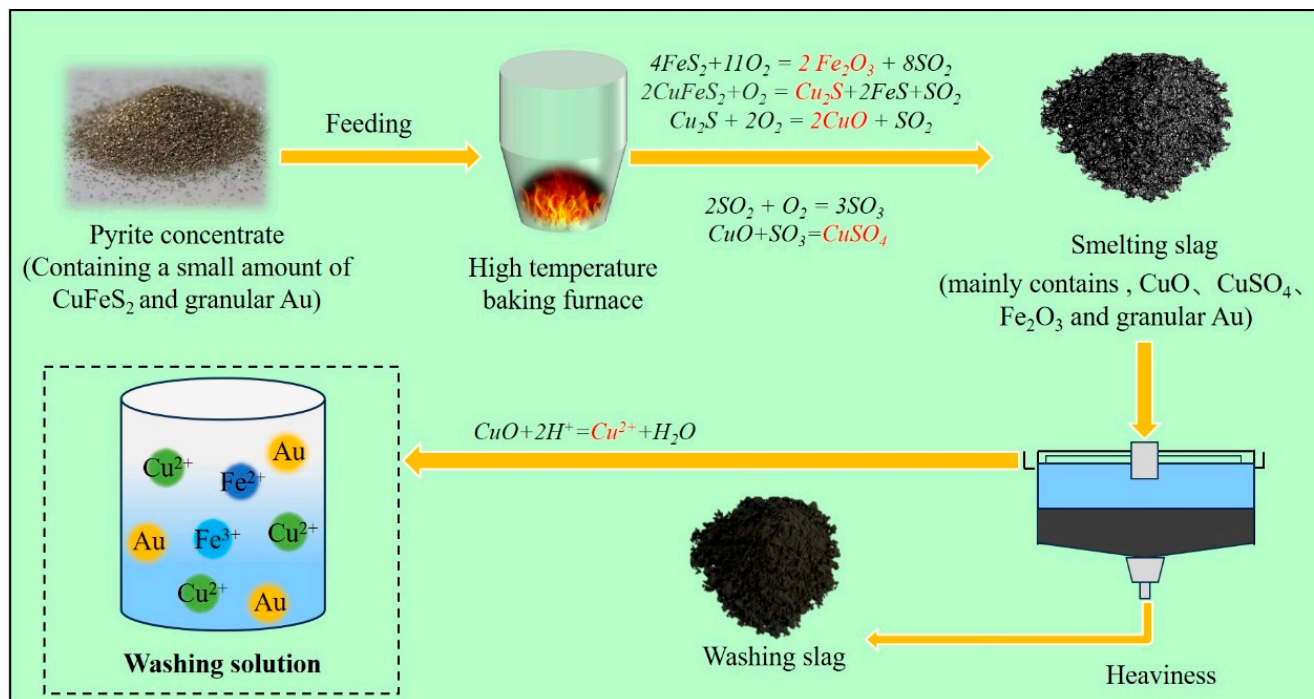
At present, domestic copper ore adopts the bioleach solvent extraction electrodeposition (BL-SX-EW) wet copper extraction process, but Fe in the leaching solution ions and suspended particles cause severe interfacial emulsion during solvent extraction. Moreover, the mass concentration of copper in the leaching solution is much lower than what is stated in the requirements of the process design, which significantly affects the subsequent extraction and electrodeposition processes. The treatment methods of Cu<sup>2+</sup> in wastewater include reduction, neutralization precipitation, and physicochemical and biological methods [11–13]. The Cu<sup>2+</sup> in wastewater is mainly studied by the chemical precipitation, iron powder replacement, and electrolysis methods [14–18]. The iron powder replacement method and neutralization precipitation method are widely used because of their simple operation, good replacement effects, small material consumption, and obvious economic benefits [19,20]. The earliest method used to extract gold from the solution involves cyanide, but because cyanide is highly toxic, improper use not only seriously pollutes the ecological environment but also can be harmful to human health. So far, scholars at home and abroad have studied a variety of non-cyanide gold extraction methods, including halogenation (chlorine, bromine, iodine) and through thiourea, thiosulfate, aqua royalty, stone sulfur mixtures, etc., but because thiosulfate stability is poor, it is easy for it to be oxidized and decomposed in solution, resulting in a large consumption of thiosulfate. There are many methods to recover Au from wastewater, mainly including adsorption and micropore filtration [21,22]. Micropore filtration mainly selects a filter material with an appropriate pore size and the Au in the wastewater can be effectively filtered and intercepted. Compared with other methods, micropore filtration is widely used because of its effective separation of solid and liquid, high filtration accuracy, simple operation, and good treatment effect [23,24]. In this paper, based on the principle of recovery of Cu<sup>2+</sup> and Au in a washing solution, combined with the occurrence states of Cu<sup>2+</sup> and Au in the washing solution, the comparative test analysis of two processes, namely iron powder replacement pore filtration and neutralization precipitation pore filtration, was carried out to achieve the efficient recovery of Cu<sup>2+</sup> and Au in the washing solution.

## 2. Materials and Methods

### 2.1. Source of the Washing Solution

The test material was taken from a gold smelter's pyrite concentrate slag washing solution in Yunnan Province, China. The slag of pyrite concentrate (containing a small amount of CuFeS<sub>2</sub> and granular Au) is obtained by high-temperature desulfurization roasting, which is porous and fluffy. A small amount of sulfur in the slag remains in the form of SO<sub>3</sub>, which reacts with water to produce dilute sulfuric acid when washed, which is the main reason for the weak acidity of the water solution. The main components of the slag are iron oxide, a small amount of copper oxide, copper sulfate, gold particles, etc. Copper oxide and copper sulfate in the slag react with dilute sulfuric acid and water to

form  $\text{Cu}^{2+}$ , which is the main form of copper in the water lotion. At the same time, the gold is in a granular form in the water lotion and does not participate in the reaction, and so, the washing solution containing a small amount of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and granular gold can be obtained. The source of washing solution is shown in Figure 1.



**Figure 1.** Source diagram of washing solution.

## 2.2. Analysis of the Washing Solution

The compositional analysis results of the washing solution are shown in Tables 1 and 2.

**Table 1.** The element concentrations in the washing solution.

Element	Au	Ag	$\text{Cu}^{2+}$	$\text{Fe}^{3+}$	$\text{Fe}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$	$\text{As}^{3+/5+}$	pH
Content/mg/L	0.13	0.03	437	127	144	0.09	0.11	0.07	3.5

**Table 2.** The proportions of Au with different particle sizes in the washing solution.

Particle Size/ $\mu\text{m}$	+50	−50~+10	−10~+2	−2~+1	−1	Total
Percentage/%	5.67	6.78	8.96	72.34	6.25	100.00

It can be seen from Table 1 that the washing solution mainly contains Au (0.13 mg/L),  $\text{Cu}^{2+}$  (437 mg/L),  $\text{Fe}^{2+/3+}$  (271 mg/L), and small amounts of other elements. Au and  $\text{Cu}^{2+}$  are the main valuable elements in the washing solution, and these have high recovery value. The analysis in Table 2 shows that Au exists in the form of fine particles in the washing solution and the particle size is between 1 and 50  $\mu\text{m}$ . Most of Au exists in the form of 1–2  $\mu\text{m}$  particles.

## 2.3. Test Methods

### 2.3.1. Iron Powder Replacement Micropore Filtration Test

In this study, the process of iron powder replacement microporous filtration was used to recover  $\text{Cu}^{2+}$  and Au in the washing solution.

The recovery test of  $\text{Cu}^{2+}$  in the washing solution was mainly replaced with iron powder (Aladdin Biochemical Technology Co., Ltd., 7439-89-6, Aladdin Reagent, Shanghai, China), because the amount of iron powder, replacement time, and pH value will affect the replacement rate of  $\text{Cu}^{2+}$  in the washing solution, and so the influence of three factors was discussed. In each test, washing solution was taken (1 L) in a beaker and we added iron powder and stirred it with a magnetic stirrer (Boda Jingke Biotechnology Co., Ltd., HMS-901, Shenzhen, China) at stirring speed of 600 rpm under control certain reaction conditions at 25 °C. After the reaction was completed, the washing solution was filtered, and the contents of  $\text{Cu}^{2+}$  and Au in the filtrate were determined by atomic absorption spectrometer (Beifen Ruili Analytical Instrument Co., Ltd., WFX-220A, Beijing, China). After the displacement reaction, the solution was passed through filter cloths with different apertures (2  $\mu\text{m}$ , 1  $\mu\text{m}$ , <1  $\mu\text{m}$ ) (Bolian Filtration Co., Ltd., polyester filter cloth, 404AX, Tieling, China). Due to the small apertures on the filter cloths, the Au particles would be trapped on the filter cloths and the solution would leak out through the filter holes.

### 2.3.2. Neutralizing Precipitation–Micropore Filtration Test

In this study, the process of neutralization precipitation porous filtration was used to recover  $\text{Cu}^{2+}$  and Au in the washing solution.

The washing solution was taken (1 L) in a beaker and we added a certain amount of NaOH (Nanjing Chemical Reagent, 1310-73-2, Nanjing, China, 30% concentration) to control the pH of the solution and to ensure the precipitation of  $\text{Cu}^{2+}$  as much as possible. After the neutralization and precipitation reaction was complete, the washing solution was passed through the filter cloths of different apertures (Bolian Filtration Co., Ltd., polyester filter cloth, 404AX, Liaoning, China). Due to the small apertures in the filter cloths, the Au particles would be trapped on the filter cloth and the solution would leak out through the filter holes. Atomic absorption spectroscopy (Beifen Ruili Analytical Instrument Co., Ltd., WFX-220A, Beijing, China) was used to determine the Au and  $\text{Cu}^{2+}$  content in the filtrate and the recovery rate was calculated sequentially.

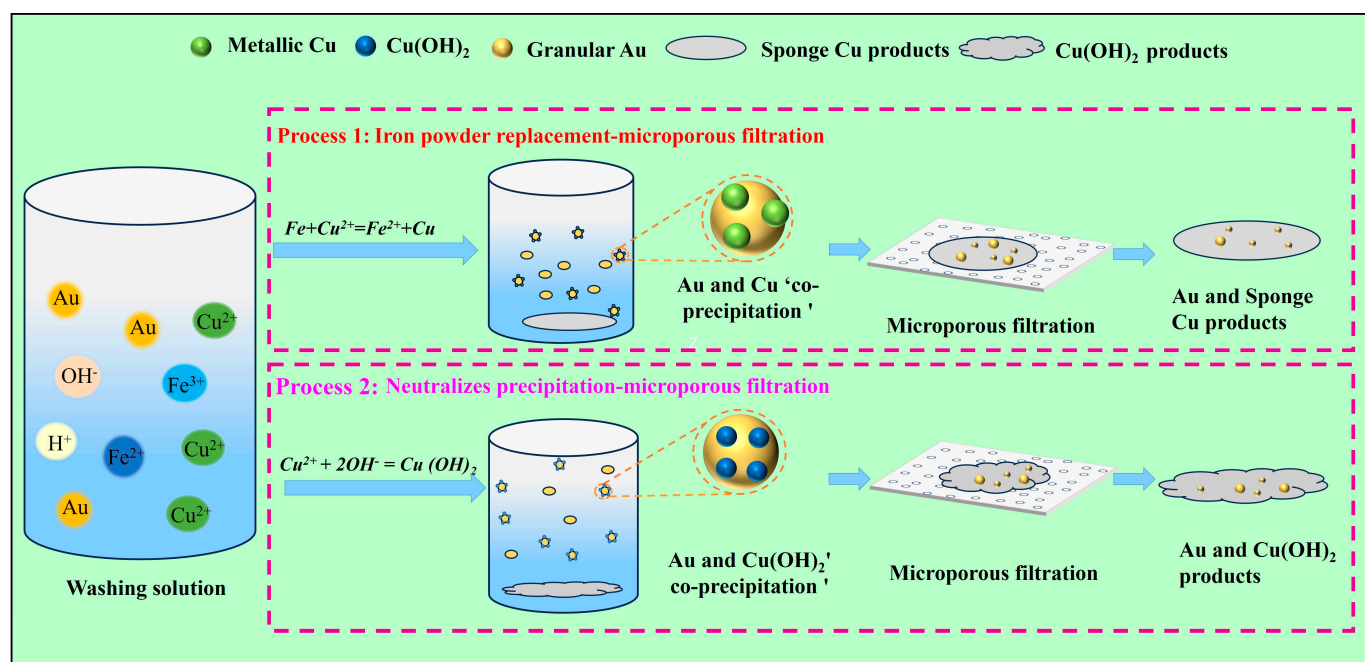
## 3. Results and Discussion

### 3.1. Recovery Mechanism of $\text{Cu}^{2+}$ and Au in the Washing Solution

In this study, two processes of iron powder replacement porous filtration and neutralization precipitation porous filtration were adopted to comprehensively recover  $\text{Cu}^{2+}$  and Au in the washing solution. When recovering  $\text{Cu}^{2+}$  and Au from the washing solution by iron powder replacement, one metal is used to replace another metal ion from the solution. At this time, the metal element as the replacement agent is oxidized and enters the solution in the form of ions while the metal ions are reduced to a metal state and precipitated. In the displacement reaction, iron is the more reactive metal and copper is the less reactive metal. The iron powder and the copper ions in the water solution undergo redox reaction, in which the iron itself oxidizes and the copper ions are reduced to copper metal. In this way, the formed metal copper exists in the form of fine particles in the water solution. In the process of iron powder replacement porous filtration, the  $\text{Cu}^{2+}$  was reduced to sponge Cu by iron powder replacement. The formation of fine gold precipitation is due to the low solubility of gold; gold cannot be completely dissolved in water in a displacement reaction, so it is suspended in the solution in the form of particles and gradually precipitated down with the reaction. At the same time, in this study, the fine Au and sponge Cu particles could be ‘co-precipitated’ by mutual adsorption, then the granular Au and sponge Cu products were recovered by a microporous filtration process.

In the process of neutralization precipitation pore filtration, metal ions were mainly adopted to react with  $\text{OH}^-$  to form  $\text{A}(\text{OH})_x$  precipitates, which were insoluble and whose solubility varied greatly. Therefore,  $\text{Cu}^{2+}$  could be precipitated as much as possible by controlling the pH of the solution. At the same time, Au was suspended in the solution in the form of particles. The fine particles of Au and  $\text{Cu}(\text{OH})_2$  could be ‘co-precipitated’ by mutual adsorption, then the granular Au and  $\text{Cu}(\text{OH})_2$  products could be recovered

through the microporous filtration process; the mechanisms of the two processes to recover  $\text{Cu}^{2+}$  and Au in the washing solution are shown in Figure 2.



**Figure 2.** Diagram showing recovery mechanism of  $\text{Cu}^{2+}$  and Au from washing solution achieved by two processes.

### 3.2. Recovery of $\text{Cu}^{2+}$ and Au by Iron Powder Replacement–Micropore Filtration

In this part, the recovery of  $\text{Cu}^{2+}$  and Au in a washing solution by the iron powder replacement pore filtration process was studied. The effects of the pH value, iron powder dosage, replacement time, and pore size of the filter cloth were investigated.

#### 3.2.1. Effect of pH

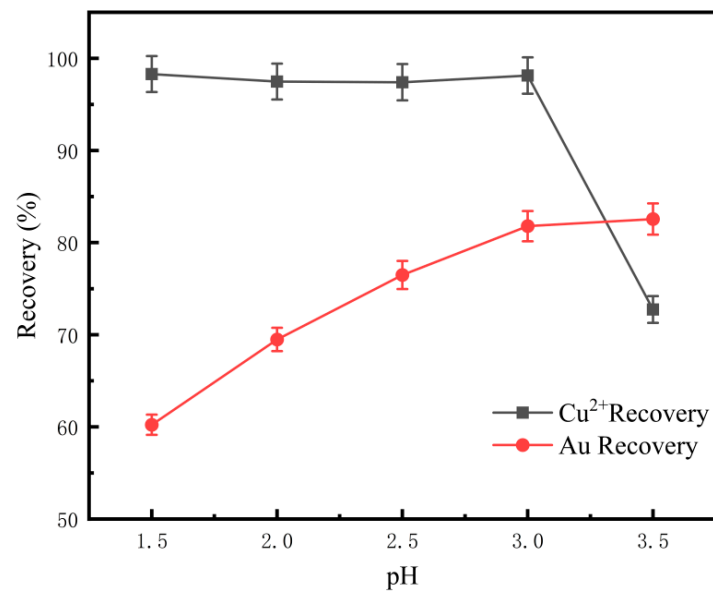
Thermodynamically, a more positive metal in solution can only be replaced by a more negative metal. The solution of pyrite slag water mainly contains metal ions such as copper and iron and also contains a small amount of granular gold. The standard redox potentials ( $\Delta E^\theta$ ) of these metals in an acidic solution are shown in Table 3 [25]. According to Table 3, the standard redox potential of iron is more negative than that of other metals, and it can be replaced from a solution. The standard redox potential of gold is the largest, but it exists in a granular form in the water solution and does not react with iron powder. When adding iron powder to the water solution, the following reactions mainly occur:



**Table 3.** Standard redox potentials of metals in acidic solutions.

Element	$2\text{H}^+/\text{H}_2$	$\text{Cu}^{2+}/\text{Cu}$	$\text{Au}^{3+}/\text{Au}$	$\text{Fe}^{2+}/\text{Fe}$
$\Delta E^\theta / \text{V}$	0.000	+0.342	+1.498	−0.447

The stirring speed in the test was 600 rpm and the temperature was 25 °C, the pH value in the washing solution was adjusted from the beginning value of 3.5 to the final value of 1.5, and the pH effect of washing solution on the recovery rate of  $\text{Cu}^{2+}$  and Au during the iron powder replacement process is shown in Figure 3.

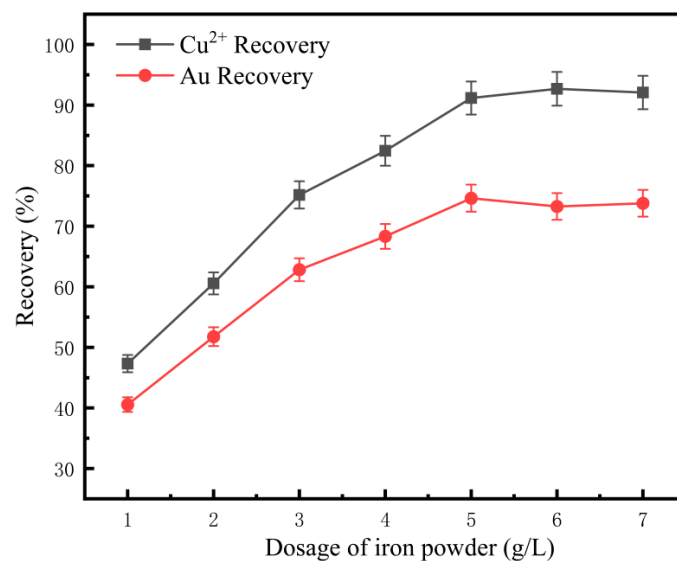


**Figure 3.** Effect of pH value on recovery of Cu<sup>2+</sup> and Au in washing solution.

As can be seen from Figure 3, when the pH value of the washing solution was 1.5–3.0, the Cu<sup>2+</sup> replacement rate was maintained at about 98%, and the recovery rate of Au gradually increased with the increase in the pH value from 60.23% at the beginning to 82.56%. Overall, Cu<sup>2+</sup> recovery stabilized at pH 1.5–3.5 and then declined while Au recovery showed an upward trend. Comprehensively considered, the pH value of the water wash in the test was 3.0, the recovery rate of Cu<sup>2+</sup> was 98.13%, and the recovery rate of Au was 81.79%.

### 3.2.2. Effect of Iron Powder Dosage

Due to the presence of impurity ions in a washing solution, a certain amount of iron powder will be consumed in the process of iron powder replacement. Therefore, the amount of iron powder needs to be increased in actual operation. For each test, the washing solution was taken in a quantity of 1 L in a beaker with stirring speed of 600 rpm, temperature of 25 °C, and pH value of 3 and the effects of iron powder dosage on the recovery rates of Cu<sup>2+</sup> and Au in the washing solution are shown in Figure 4.



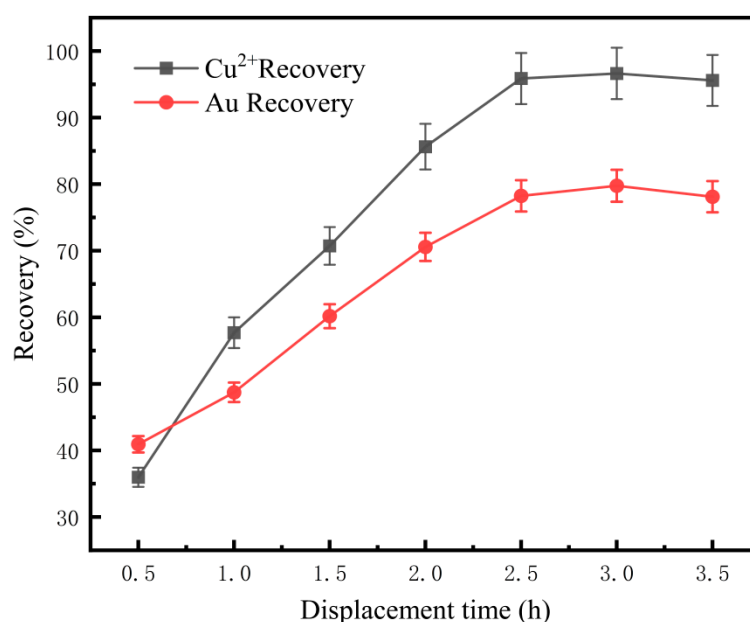
**Figure 4.** Effects of iron powder dosage on the recovery of Cu<sup>2+</sup> and Au in washing solution.



It can be seen from Figure 4 that with the increase in iron powder, the rate of replacement of  $\text{Cu}^{2+}$  by iron powder gradually increased and the replacement rate of  $\text{Cu}^{2+}$  increased from 47.32% to 92.68%. The granular Au in the washing solution would be “co-precipitated” with the replaced metal Cu, so the recovery rate of Au would gradually increase. When the amount of iron powder was between 5 and 7 g/L, the recovery rate of  $\text{Cu}^{2+}$  was basically stable at about 92%, and the recovery rate of Au was basically stable at about 73%. However, in terms of cost saving, the iron powder dosage in the follow-up test was selected to be 6 g/L, the replacement rate of  $\text{Cu}^{2+}$  reached 92.68%, and the recovery rate of Au reached 73.27% under this condition.

### 3.2.3. Effect of Displacement Time

When the pH value was 3, the iron powder dosage was 6 g/L, the temperature was 25 °C, the stirring speed was 600 rpm, and the replacement time was 0.5–3.5 h, and the replacement test was carried out under different time conditions for the washing solution, and the test results are shown in Figure 5.



**Figure 5.** Effect of replacement time on the recovery of  $\text{Cu}^{2+}$  and Au in washing solution.

It can be seen from Figure 5 that the recovery rates of  $\text{Cu}^{2+}$  and Au were only 35.97% and 40.93% at the reaction time of 0.5 h. With the increase in the replacement time, the recovery rate of  $\text{Cu}^{2+}$  and Au first increased and then stabilized. When the displacement time was 2.5–3.5 h, the  $\text{Cu}^{2+}$  replacement rate was basically stable at about 95%, and the recovery rate of Au was stable at about 78%. After the displacement time of 2.5 h, the recovery rates of  $\text{Cu}^{2+}$  and Au did not change much. Therefore, the iron powder replacement time was selected for 3.0 h, the recovery rate of  $\text{Cu}^{2+}$  was 96.63%, and the recovery rate of Au was 79.76%.

According to Sections 3.2.1–3.2.3, the optimum parameters for iron powder replacement had a pH value of 3, iron powder dosage of 6 g/L, and replacement time of 2.5 h and the washing solution was comprehensively utilized with a recovery rate of  $\text{Cu}^{2+}$  of 98.13% and recovery rate of Au of 81.79%. The contents of  $\text{Cu}^{2+}$  and Au in the washing solution before and after iron powder replacement are shown in Table 4.

**Table 4.** Contents of  $\text{Cu}^{2+}$  and Au in the washing solution before and after iron powder replacement.

Element	Original Washing Solution (mg/L)	Washing Solution after Replacement (mg/L)	Recovery (%)
$\text{Cu}^{2+}$	437.00	8.172	98.13
Au	0.13	0.024	81.79

### 3.2.4. Effect of Microporous Filtration on Au Recovery in the Washing Solution after Iron Powder Replacement

Microporous filtration uses the evenly distributed pore size on a filter cloth; according to the particle size of the Au in the washing solution, researchers reasonably select the size of the filter cloth pores to intercept the tiny solid particles in a solution so that they cannot be removed through the filter cloth. The filter cloth is made of cellulose or a polymer composite material, which is a highly refined filter material with a pore size of 0.1~75  $\mu\text{m}$  and a film thickness of 120~150  $\mu\text{m}$ , and the separation effect of the filter cloth is determined by its own structure, that is, by the shape and size of each pore.

Since Au is “co-precipitated” with the Cu metal replaced by this iron powder, most of the granular Au was recovered according to Section 3.2.3, and this section focuses on the Au content of the washing solution after the iron powder was replaced (see Table 4). In the comparison test involving 2  $\mu\text{m}$ , 1  $\mu\text{m}$ , and below 1  $\mu\text{m}$  filter cloth filtration for the remaining Au particles in the washing solution, the interception of Au in the washing solution after iron powder replacement with filter cloths of different apertures was achieved and is shown in Table 5.

**Table 5.** Interception of Au particles in the washing solution after iron powder replacement with filter cloths of different apertures.

Washing solution after replacement Au 0.024(mg/L)	Filter Cloth Pore Size ( $\mu\text{m}$ )	2 $\mu\text{m}$	1 $\mu\text{m}$	<1 $\mu\text{m}$
	Au in filtrate (mg/L)	0.014	0.008	0.001
	Au recovery rate (%)	44.66	66.67	95.83

It can be seen from Table 5 that in the washing solution, after the replacement of iron powder, filtered with a filter cloth with a pore size of 2  $\mu\text{m}$ , the retention recovery rate of gold was less than 50%, but as the micropores of the filter cloth became smaller, the interception of Au was higher. When the filter aperture was less than 1  $\mu\text{m}$ , the fine Au could be effectively recovered with a recovery rate of 95.83%.

### 3.3. Recovery of $\text{Cu}^{2+}$ and Au by Neutralization Precipitation–Micropore Filtration

In this part, the recovery of  $\text{Cu}^{2+}$  and Au in the washing solution by the neutralization precipitation–micropore filtration process was studied. The effects of pH value in the washing solution and the pore size of the filter cloth were investigated.

#### 3.3.1. The pH Required for Metal Precipitation in the Washing Solution

Sodium hydroxide was used in the test; if lime was used, in addition to the acid–base neutralization reaction, a large amount of calcium sulfate precipitate would be generated, the pipeline would be blocked, and the neutralization slag would be solid waste, so the safety and management risks were large. According to the main metal ions,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Fe}^{2+}$  molar concentration; the  $\text{M}(\text{OH})_n$  solubility products of the main metal ions of the washing solution; the initial precipitation concentration of each ion; and the pH of complete precipitation were calculated. The pH of the solution was controlled to ensure the precipitation of  $\text{Cu}^{2+}$  as much as possible and reduce the precipitation of  $\text{Fe}^{2+}$  /  $\text{Fe}^{3+}$  ions to



achieve the purpose of recovering Au and  $\text{Cu}^{2+}$ ; the pH value required for each metal ion to start and completely precipitate is shown in Equations (3)–(5) and Table 6.

$$\text{Molarity (mol/L)} = \frac{\text{Substance number of solutes (mol)}}{\text{Volume of solution (L)}} \quad (3)$$

$$\text{Start precipitation pH} = 14 + \frac{1}{n} \text{Lg} \frac{\text{Ksp}}{\text{Molarity}} \quad (4)$$

$$\text{Complete precipitation pH} = 14 + \frac{1}{n} \text{Lg} \frac{\text{Ksp}}{1 \times 10^{-5}} \quad (5)$$

**Table 6.** The pH required for metal ion precipitation in the washing solution.

Title	Concentration (mg/L)	Molarity (mol/L)	Hydroxide Ksp	Start Precipitation pH	Complete Precipitation pH
$\text{Cu}^{2+}$	437	0.00682	$2.2 \times 10^{-20}$	5.25	6.67
Au	0.130	-	-	-	-

It can be seen from Table 6 that  $\text{Cu}(\text{OH})_2$  began to precipitate at pH 5.25 and all of it precipitated when the solution pH value was 6.67.

### 3.3.2. Analysis of Neutralization Precipitation Test Results

The neutralization precipitation test was carried out according to different pH conditions. The test results are shown in Table 7.

**Table 7.** Effects of pH on  $\text{Cu}^{2+}$  and Au recovery in the washing solution.

pH	Elemental Concentrations(mg/L)		Recovery (%)	
	$\text{Cu}^{2+}$	Au	$\text{Cu}^{2+}$	Au *
5.0	225.54	0.054	48.38	58.46
6.0	105.37	0.041	75.89	68.46
6.5	11.54	0.031	97.35	76.15
7.0	12.19	0.032	97.21	75.38
8.0	11.89	0.030	97.27	76.92

\* Part of the granular Au and  $\text{Cu}(\text{OH})_2$  ‘co-precipitation’ occurred.

It can be seen from Table 7 that when the pH value was 5, the recovery rate of  $\text{Cu}^{2+}$  was only 48.38%, accompanied by the value of 58.46% for finely granular Au and  $\text{Cu}(\text{OH})_2$  ‘co-precipitation’. With the increase in the pH, the recovery rates of  $\text{Cu}^{2+}$  and Au gradually increased and then stabilized, and the recovery rate of  $\text{Cu}^{2+}$  fluctuated around 97% at pH 6.5–8, and the recovery rate of Au fluctuated around 75%. The optimum recovery of Au and  $\text{Cu}^{2+}$  was obtained at a pH of 6.5.

According to Section 2.3.2, when the pH value was 6.5, the recovery rate of  $\text{Cu}^{2+}$  was 97.35% and the recovery rate of Au was 76.15%, and the contents of the  $\text{Cu}^{2+}$  and Au elements in the washing solution before and after neutralization precipitation are shown in Table 8.

**Table 8.**  $\text{Cu}^{2+}$  and Au in the washing solution before and after precipitation.

Element	Original Washing Solution (mg/L)	Washing Solution after Precipitation (mg/L)	Recovery (%)
$\text{Cu}^{2+}$	437.00	11.540	97.35
Au	0.13	0.031	76.15

### 3.3.3. Effect of Microporous Filtration on the Recovery of Au in the Washing Solution after Neutralization Precipitation

The content of Au was 0.031 mg/L (Table 8) after the neutralization of precipitation in the washing solution. In the comparison test involving Au particles filtered by 2  $\mu\text{m}$ , 1  $\mu\text{m}$ , and less than 1  $\mu\text{m}$  filter cloths, the interception of Au particles in the precipitation in the washing solution with different filter cloth apertures is shown in Table 9.

**Table 9.** Interception of Au particles in the washing solution after neutralizing precipitation with filter cloths of different apertures.

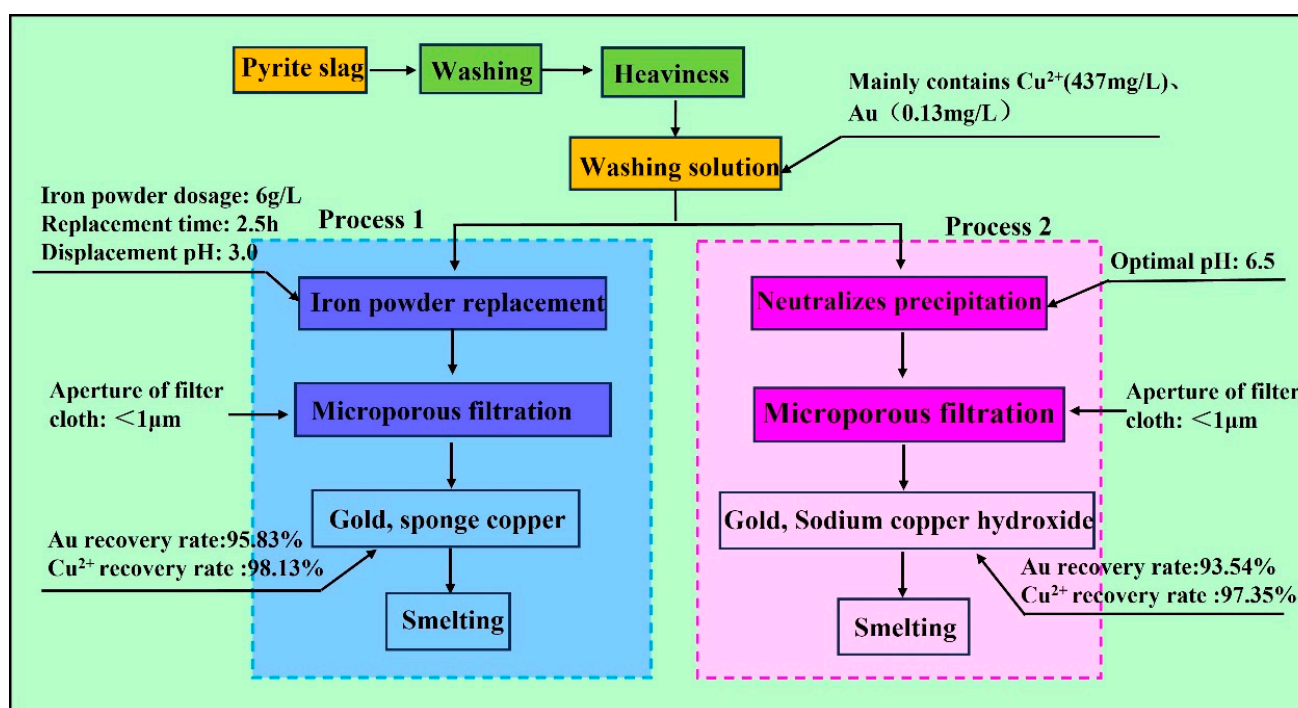
Washing solution after precipitation Au 0.031(mg/L)	Filter Cloth Pore Size ( $\mu\text{m}$ )	2 $\mu\text{m}$	1 $\mu\text{m}$	<1 $\mu\text{m}$
	Au in filtrate(mg/L)	0.017	0.011	0.002
	Au recovery rate (%)	45.16	64.51	93.54

It can be seen from Table 9 that when the filter cloth aperture was 2  $\mu\text{m}$ , the recovery rate of Au was 45.16%. With the decrease in aperture, the recovery rate of gold was getting better and better. When the aperture of filter cloth was less than 1  $\mu\text{m}$ , the recovery rate of Au was 93.54%.

### 3.4. Comparative Analysis of $\text{Cu}^{2+}$ and Au in Washing Solution by Two Different Processes

#### 3.4.1. Comparison of Indicators of $\text{Cu}^{2+}$ and Au in the Washing Solution

When the two processes were used to recover  $\text{Cu}^{2+}$  and Au in the washing solution, the recovery rate of  $\text{Cu}^{2+}$  was 98.13% and the recovery rate of Au was 95.83% for the iron powder replacement–micropore filtration process. On the other hand, the recovery rate of  $\text{Cu}^{2+}$  was 97.35% and the recovery rate of Au was 93.54% for the neutralization precipitation–micropore filtration process. From the perspective of the overall recovery rate, the process index of iron powder replacement–micropore filtration was better than that of neutralization precipitation–micropore filtration and the different process flows of recovering  $\text{Cu}^{2+}$  and Au in the washing solution are shown in Figure 6.



**Figure 6.** The process flow diagram of recovering  $\text{Cu}^{2+}$  and Au from the washing solution.

### 3.4.2. Economic Benefit Analysis of Recovering $\text{Cu}^{2+}$ and Au from the Washing Solution

The indexes, investment, profit, safety, and environmental protection risks of two different process routes of the washing solution were compared as shown in Table 10.

**Table 10.** The economic benefit estimation of  $\text{Cu}^{2+}$  and Au in the washing solution for the two processes (a gold smelter in Yunnan, China).

Metric Name		Iron Powder Replacement—Micropore Filtration	Neutralize Precipitation—Micropore Filtration
Washing solution components	Output ( $\text{m}^3/\text{d}$ )	2600	2600
	Au ( $\text{g}/\text{m}^3$ )	0.13	0.13
	Cu ( $\text{g}/\text{m}^3$ )	437	437
Metal recovery	Au	95.83%	93.54%
	Cu	98.13%	97.35%
Production costs	Agent consumption ( $\text{g}/\text{m}^3$ )	Iron powder 2294	NaOH 820
	Agent price (CNY/g)	0.0065	0.003
	Agent cost (CNY/ $\text{m}^3$ )	14.91	2.46
Sales revenue	Au price (CNY/g) *	458	458
	Cu price (CNY/g)	0.048	0.048
	Au income (CNY/ $\text{m}^3$ )	59.08	58.64
	Cu income (CNY/ $\text{m}^3$ )	20.58	20.49
	Product sales (CNY/ $\text{m}^3$ )	79.66	79.13
Profit	Profit (CNY/ $\text{m}^3$ )	64.75	76.67
	Annual profit (million CNY)	$64.75 \times 2600 \times 330 \div 10,000 = 5555$	$76.67 \times 2600 \times 330 \div 10,000 = 6578$

\* London Au prices are as of 28 August 2023.

It can be seen from Table 10 that from the perspective of the metal recovery rate, the recovery of  $\text{Cu}^{2+}$  and Au by the iron powder replacement–micropore filtration process was better than that by the neutralization precipitation–micropore filtration process, but from the perspective of the production cost, the consumption of iron powder was larger than that of sodium hydroxide, and the benefits of Au and  $\text{Cu}^{2+}$  recovered from the washing solution by the process of neutralization precipitation–micropore filtration amounted to 65.78 million CNY, which was 10.23 million CNY more than the iron powder replacement–micropore filtration process, and the economic benefits were obvious.

## 4. Conclusions

(1) The daily output of pyrite concentrate slag washing solution in China is large, and the main valence elements are Au (0.13 mg/L) and  $\text{Cu}^{2+}$  (437 mg/L), which have high recovery values. The two new processes of iron powder replacement–micropore filtration and neutralization precipitation–micropore filtration have achieved the efficient recovery of Au and  $\text{Cu}^{2+}$  in a washing solution.

(2) In terms of thermodynamics, the standard redox potential of iron is negative than that of other metals and other metals can be replaced from the solution. Gold particles and replaced metal copper “co-precipitate” to form “sponge copper” products. The best process conditions in this study included a pH of 3.0, iron powder dosage of 6 g/L, replacement time of 3.0 h, and filter hole diameter of less than 1  $\mu\text{m}$ . The recovery rates of  $\text{Cu}^{2+}$  and gold were 98.13% and 95.83%, respectively.

(3) When the washing solution adopted the neutralization precipitation–micropore filtration process, due to the adsorption effect between the fine particles, Au could display the “co-precipitation” phenomenon with the precipitated  $\text{Cu}(\text{OH})_2$  to form a “copper hydroxide” product. The optimal process condition included a pH value of 6.5; at this time, the filter cloth with a pore size less than 1  $\mu\text{m}$  was intercepted, and the recovery rate of  $\text{Cu}^{2+}$  was 97.35%. The total recovery of Au was 93.54%.

(4) Compared with the two processes, the iron powder replacement–microporous filtration process had the advantage of a high recovery rate and the neutralization precipitation–microporous filtration had the advantages of low material consumption, low processing cost, and obvious economic benefits. This process was expected to be popularized and applied in similar gold enterprises.

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