

Article

Selective Separation Recovery of Copper and Arsenic from the Leaching Solution of Copper Soot

Zhizhao Yang ¹, Yongbing Zhang ¹, Hepeng Zhou ^{1,2,*}, Xianping Luo ^{1,2}, Xuekun Tang ¹ and Zishuai Liu ¹¹ Jiangxi Province Key Laboratory of Mining and Metallurgy Environmental Pollution Control, Jiangxi University of Science and Technology, Ganzhou 341000, China² Engineering Research Center for High-Efficiency Development and Application Technology of Tungsten Resources, Jiangxi University of Science and Technology, Ministry of Education, Ganzhou 341000, China

* Correspondence: zhp0919@163.com

Abstract: Through the main chemical reaction of metal ions and S^{2-} , a new type of sulfide precipitant was first prepared and used to realize the selective separation recovery of copper and arsenic from the leaching solution of copper soot. It is proven by experimental results that the prepared sulfide precipitant could realize the efficient separation recovery of copper and arsenic. Indeed, the copper sulfide slag with Cu grade of about 47% and arsenic trisulfide slag with As operation recovery of about 98% could be obtained. The results of chemical reaction energy calculation analysis and SEM images analysis illustrate that the selective separation recovery of copper and arsenic mainly depended on the chemical reactions of sulfide precipitation. The ions of S^{2-} and HS^- produced by the prepared sulfide precipitant could react with Cu^{2+} and arsenic components to form CuS and As_2S_3 , respectively, in the copper and arsenic recovery procedure. In addition, the smaller solubility of CuS and the lower rate of S^{2-} engendered by the sulfide precipitant were key to achieving the efficient separation and recovery of copper and arsenic.

Keywords: copper; arsenic; leaching solution; separation recovery; sulfide precipitant



Citation: Yang, Z.; Zhang, Y.; Zhou, H.; Luo, X.; Tang, X.; Liu, Z. Selective Separation Recovery of Copper and Arsenic from the Leaching Solution of Copper Soot. *Metals* **2022**, *12*, 1983. <https://doi.org/10.3390/met12111983>

Academic Editor: Daniel Assumpcao Bertuol

Received: 18 October 2022

Accepted: 16 November 2022

Published: 20 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Copper is widely used in electronic, machinery manufacturing, construction, national defense and marine industries due to its advantages of good conductance, thermal conductivity and ductility [1,2]. In the consumption of nonferrous metal materials in China, it is second only to aluminum [3]. Generally speaking, the technological process steps of mining, flotation, smelting and electrolysis are required to obtain cathode copper with high purity from copper ore [4,5]. However, a large amount of copper soot will be produced in the smelting process [6], which not only has a high reclaim value due to its high copper content but will lead to grievous environmental pollution owing to its high arsenic content [7]. In the context of tremendous demand for copper metal and green ecological development in China [8], it is crucial to recover copper and safely solidify arsenic from copper soot.

Over the past few decades, scholars have carried out lots of research work on the selective separation and recovery of copper and arsenic from copper soot [9–13]. Copper soot was usually leached and converted into a leaching solution containing copper and arsenic [14,15]. The method of acid leaching was widely used due to its high efficiency and low cost [16,17]. In order to separate and recover copper and arsenic from acid leaching solution, the most common methods were chemical precipitation, adsorption, extraction and ion exchange [18–21]. The sulfide precipitation method in the chemical precipitation method has the advantages of simple operation and low production cost [22]. For example, monoclinic pyrrhotite was used to selectively precipitate sulfide of copper ions from arsenic wastewater; more than 96% copper ions were removed and a copper product of 20.2% Cu and 0.7% As could be obtained [23]. A gas–liquid sulfidation reaction was proposed and applied to the separation of copper and arsenic from acidic wastewater,

where CuS was the main phase in the precipitate in which copper content was 63.38% in a mass fraction [24]. The key to the separation and recovery of copper and arsenic by the sulfide precipitation method is to convert copper and arsenic into copper sulfide and arsenic trisulfide, respectively [25]. More importantly, the solubility product of copper sulfide is much smaller than that of arsenic trisulfide in the entire pH range [26]. However, sodium sulfide or sodium hydrosulfide was mostly used as the sulfide precipitant in the sulfide precipitation method [27,28]. Although the separation and recovery of copper and arsenic can be realized, the problems of low separation efficiency, large amounts of H₂S gas escaping and large dosages remain [29,30]. Therefore, it is still a significant challenge to selectively separate and recover copper and arsenic from the leaching solution of copper soot without H₂S gas pollution when using the sulfide precipitation method [31].

Based on the principle of step sulfide precipitation, a new type of sulfide precipitant which can slowly release S^{2−} and slow down the reaction rate was prepared in this work to replace the traditional sulfide precipitant. The purpose is to reduce the concentration of S^{2−} in acid leaching solution, improve the selective separation efficiency of copper and arsenic and avoid the escape of H₂S gas. Firstly, the effects of the dosage of sulfide precipitant, pH value and reaction time on the selective separation and recovery of copper and arsenic were investigated. Secondly, the process and mechanism of selective separation and recovery of copper and arsenic were revealed through the calculation of chemical reaction energy. On the whole, we want to prepare a new type of sulfide precipitant to selectively and efficiently separate and recover copper and arsenic from the leaching solution of copper soot, and present the mechanism of selective separation and recovery of copper and arsenic in this study.

2. Experimental

2.1. Materials and Reagents

The acid leaching solution of copper soot was taken from Western Mining Co., Ltd. (Qinghai Copper Co., Ltd., Xining, China) in Qinghai Province, China, the contents of copper and arsenic in which were about 28 g/L and 15 g/L, respectively, and the original pH value was 1.4. The strong acidity and the high content of copper and arsenic manifested were suitable for the study of selective separation and recovery of copper and arsenic from the leaching solution of copper soot.

FeCl₂·4H₂O, FeCl₃·6H₂O, MnSO₄·H₂O, ZnSO₄·7H₂O, and Na₂S·9H₂O required for the preparation of sulfide precipitant were purchased from Shanghai McLean Biochemical Technology Co., Ltd. The pH regulator H₂SO₄ was produced by Xilong Science Co., Ltd. All reagents needed in the experiment were analytical grade.

2.2. Preparation of Sulfide Precipitant

FeCl₂·4H₂O, FeCl₃·6H₂O, MnSO₄·H₂O and ZnSO₄·7H₂O were used as metal ions sources of Fe²⁺, Fe³⁺, Mn²⁺ and Zn²⁺, respectively, and Na₂S·9H₂O was used as a sulfur source to provide S^{2−} and react with metal ions. First, the molar ratio of FeCl₂·4H₂O:FeCl₃·6H₂O:MnSO₄·H₂O:ZnSO₄·7H₂O:Na₂S·9H₂O of 2:2:1:1:6 should be dissolved and mixed, and the concentration of metal ions could be kept between 0.5 and 1 mol/L. Then, the sulfide precipitant could be obtained after sulfide ions reacted with metal ions for 30 min at 50 °C. Figure 1 shows the SEM images of the preparation of sulfide precipitant. According to the principle of chemical reaction, the preparation of sulfide precipitant should be a mixed nano micron metal sulfide of FeS, Fe₂S₃, MnS and ZnS.

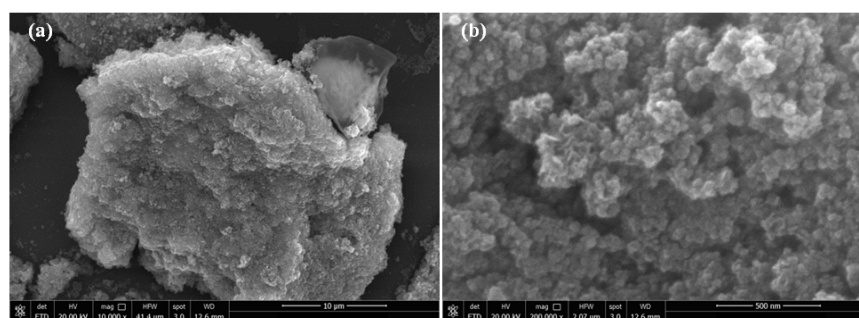


Figure 1. SEM images of the prepared sulfide precipitant. (a) 10,000×; (b) 200,000×.

2.3. Separation Recovery of Copper and Arsenic Experiments

In each experiment, 100 mL of copper soot acid leaching solution was taken and the pH value was adjusted using a certain concentration of H_2SO_4 . Next, the leaching solution was transferred to a three-necked flask and mixed with the prepared sulfide precipitant according to the designed molar ratio. Continuous stirring was performed for preferential separation and recovery of copper at 50 °C. The copper sulfide slag and arsenic filtrate were obtained by filtration when the reaction was completed. Then, the arsenic-containing filtrate pH was adjusted with a certain concentration of H_2SO_4 and should be returned to the three-port flask. The prepared sulfide precipitant was added and mixed with arsenic-containing filtrate according to the designed molar ratio at 50 °C. After the reaction of arsenic separation and recovery ended, the arsenic trisulfide slag and filtrate were obtained by filtration. XRF analysis was performed after the copper sulfide slag and arsenic trisulfide slag were dried; the filtrate was analyzed by ICP. Finally, the recovery of copper and arsenic was calculated by the weight of precipitate slag and analysis results. The schematic diagram of the experimental setup is shown in Figure 2.

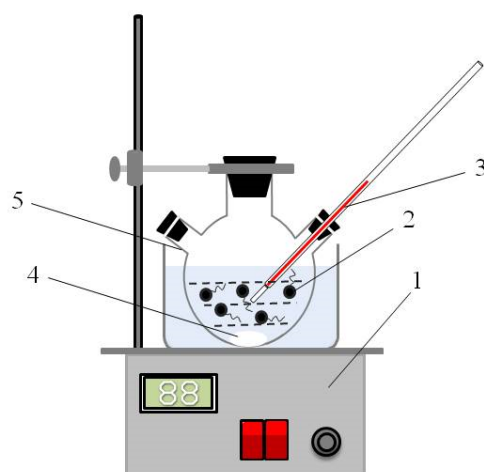


Figure 2. Schematic diagram of copper precipitation recovery experiment setup: 1—water bath thermostat, 2—the prepared of sulfide precipitant, 3—thermometer, 4—magnetic rotor and 5—three mouth flask.

2.4. Chemical Reaction Energy Calculation

The software of Gaussian View 6.0 was used to calculate the energy in the process of separation and recovery of copper and arsenic about related chemical reactions. The structural model of the compound or ion should be established first. Afterwards, the structural model was optimized based on the density functional theory. Finally, the energy of a compound or ion could be obtained by calculating the frequency with the optimal structure. In addition, the ΔG of the chemical reaction equation was the difference between the sum of the calculated product energy and the sum of the original substance's calculated energy.

2.5. SEM Images Analysis

The instrument model of MLA650F field emission scanning electron microscope was used to analyze the prepared sulfide precipitant, copper sulfide slag, and arsenic trisulfide slag. To begin with, the round cell climbing sheet with a diameter of 6 mm should be stuck in the copper plate with conductive adhesive. After that, a few samples to be measured should be mixed with absolute alcohol in a beaker. Further, a small amount of sample should be transferred to the round cell climbing sheet. The sample must be sprayed with gold to enhance the conductivity before SEM image analysis.

3. Results and Discussion

3.1. Copper Recovery from the Leaching Solution of Copper Soot

3.1.1. Effect of Dosage

Figure 3 shows the relationship between the dosage of sulfide precipitant and the effect of copper preferential recovery. As can be seen from the graph, the recovery of Cu and As gradually increased as the dosage of sulfide precipitant improved, but the Cu grade of copper sulfide slag gradually reduced. For the Cu grade and recovery of copper sulfide slag, the recovery increased from 86.75% to 96.42% and the grade kept at about 47% when the molar ratios of sulfide precipitant to copper increased from 1:1 to 1.1:1. However, with further increase in the sulfide precipitant dosage, the recovery of Cu could not be significantly improved, but the grade of Cu descended quickly. As for the As recovery of copper sulfide slag, it increased from 8.78% to 20.64% with improved molar ratios of sulfide precipitant to copper. This was mainly caused by the reaction between the excessive sulfide precipitant and arsenic in the leaching solution. This demonstrates that the effect of copper arsenic separation and recovery was more terrible with the increased sulfide precipitant dosage. In order to better realize the preferential separation and recovery of copper from the leaching solution, the optimum molar ratio of sulfide precipitant to copper should be 1.1:1.

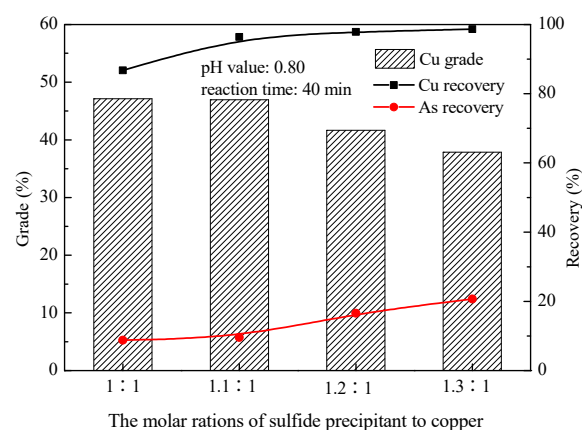


Figure 3. Effect of different molar ratios of sulfide precipitant to copper-on-copper selective recovery.

3.1.2. Effect of pH

The relationship between the pH value of the leaching solution and the effect of copper selective recovery is presented in Figure 4. On the whole, the Cu grade and As recovery of copper sulfide slag were significantly affected by pH value. On the one hand, the grade of Cu gradually increased to about 47% and the recovery of Cu maintained more than 94% in the pH range of 1.4 and 0.8. This showed that the prepared sulfide precipitant can realize the separation and recovery of copper at a very low pH value, which had great significance for industrial production and application. However, at pH 0.6, the Cu grade and As recovery reduced rapidly compared with a pH value of 0.8. On the other hand, the pH value had an important influence on the reduction in As recovery in the copper sulfide slag. The recovery rate of As decreased by approximately ten percentage points

when the pH was gradually adjusted from 1.4 to 0.8. The copper sulfide slag with a Cu grade of 46.85%, a Cu recovery of 96.11% and an As recovery of 9.24% could be obtained at pH 0.8. Hence, the leaching solution pH value should be adjusted to 0.8 for a better effect of copper selective recovery.

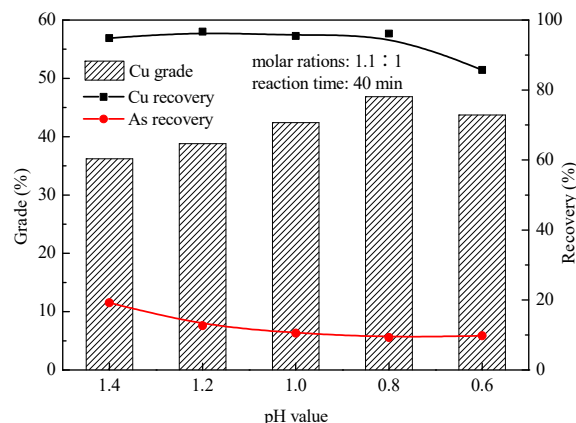


Figure 4. Effect of different pH values on copper selective recovery.

3.1.3. Effect of Reaction Time

As shown in Figure 5, the reaction time had a great influence on the copper sulfide slag of Cu recovery and Cu grade. The recovery and grade of Cu gradually improved to about 97% and 46.5%, respectively, when the reaction time was over 40 min. It is worth noting that the recovery of As rose to 18.56% and then gradually decreased to 9.21% as the reaction time increased. This may be attributed to the replacement reaction between As_2S_3 and copper ions, as the As_2S_3 formed in the earlier stage could react with copper ions to form CuS due to the smaller solubility of CuS . Therefore, the recovery of As in the copper sulfide slag gradually reduced with the increased reaction time. Copper sulfide slag with a Cu grade of 46.54%, a Cu recovery of 97.22% and an As recovery of 9.68% could be obtained when the reaction time was 40 min. Consequently, the optimum reaction time should be set to 40 min to achieve the selective recovery of copper from the leaching solution of copper soot.

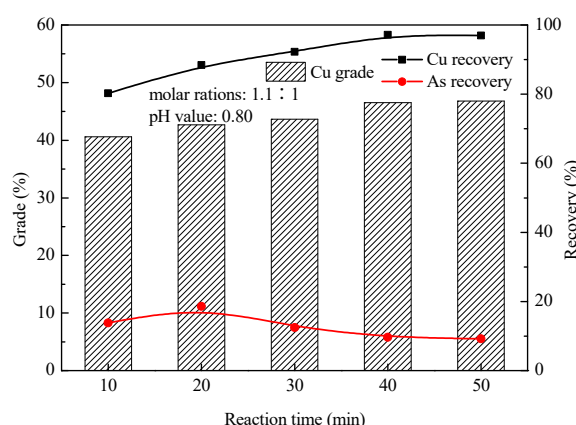


Figure 5. Effect of different reaction times on copper selective recovery.

3.2. Arsenic Recovery from the Leaching Solution of Copper Soot

3.2.1. Effect of Dosage

Figure 6 shows the relationship between the dosage of sulfide precipitant and the effect of arsenic selective recovery. Obviously, the operation recovery of As improved from 60.70% to 98.15% when the molar ratios of sulfide precipitant to arsenic increased from 1:1 to 3:1, and the operation recovery rate of As increased by approximately forty percentage

points. This illustrates that the effect of arsenic recovery was tremendously affected by the dosage of sulfide precipitant. In addition, the As grade of arsenic trisulfide slag always kept over 24% when the molar ratios of sulfide precipitant to arsenic increased between 1:1 and 3:1; it was less affected by the dosage of sulfide precipitant. Especially when the molar ratios of sulfide precipitant to arsenic reached 2:1, the arsenic trisulfide slag with an As grade of 29.98% and an As operation recovery of 97.94% could be obtained. The results indicate that the recovery of arsenic from arsenic-containing filtrate could be realized by using this sulfide precipitant, and the optimum molar ratio of sulfide precipitant to copper should be 2:1.

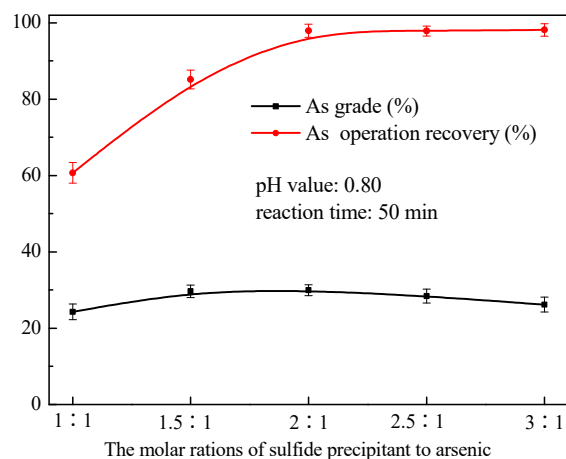


Figure 6. Effect of different molar ratios of sulfide precipitant to arsenic on arsenic selective recovery.

3.2.2. Effect of pH

The relationship between the pH value and the effect of arsenic selective recovery is presented in Figure 7. As seen in Figure 7, the pH value of arsenic-containing filtrate had a significant effect on As grade of arsenic trisulfide slag. The As grade of arsenic trisulfide slag increased from 12.64% to 30.15% when the pH value was adjusted to gradually reduce from 0.9 to 0.3. The operation recovery of As always kept over 91% in the pH range of 0.9 to 0.2. This indicates that arsenic could be effectively recovered in a wide pH range, but the solution pH should be reduced as far as possible to obtain the arsenic trisulfide slag with a higher grade. Especially at pH 0.3, the grade and operation recovery of As were 30.15% and 97.09%, respectively. Hence, the pH value of arsenic-containing filtrate should be adjusted to 0.3 to achieve a better effect of arsenic recovery.

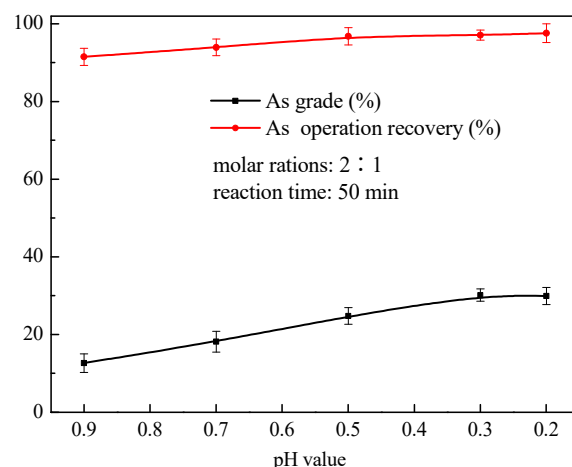


Figure 7. Effect of different pH value on arsenic selective recovery.

3.2.3. Effect of Reaction Time

Figure 8 presents the relationship between the reaction time and the effect of arsenic selective recovery. The sulfide precipitant could gradually dissolve and ionize S^{2-} and HS^- to react with arsenic ions to form As_2S_3 . Therefore, enough chemical reaction time should be guaranteed to improve the effect of arsenic recovery. As presented in Figure 8, the operation recovery of As gradually increased from 79.93% to 98.09% when the reaction time increased from 20 min to 60 min. More attention should be paid to the fact that the difference between the operation recovery and grade of As was very small when the reaction time was 50 and 60 min. Moreover, the operation recovery and grade of As were 97.45% and 29.36% when the reaction time was set to 50 min, respectively. Therefore, the optimum reaction time should reach 50 min to realize the efficient recovery of arsenic from arsenic-containing filtrate.

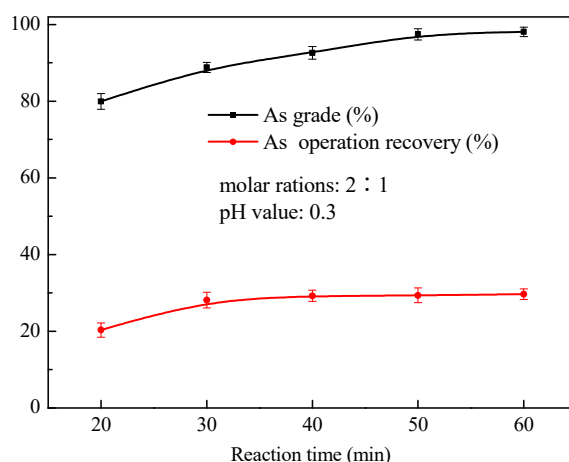


Figure 8. Effect of different reaction times on arsenic selective recovery.

3.3. Chemical Reaction Energy Calculation Analysis

The preparation process of sulfide precipitant mainly takes place alongside the reaction of sulfide precipitation. Primarily, the reaction process necessitates that the S^{2-}/HS^- should react with Fe^{2+} , Fe^{3+} , Mn^{2+} and Zn^{2+} to form a large number of metal sulfide particle precipitation of FeS , Fe_2S_3 , MnS and ZnS . Moreover, the selective separation recovery of copper and arsenic process mainly takes place alongside the reaction of the S^{2-}/HS^- with Cu^{2+} and arsenate-ion-containing components to form CuS and As_2S_3 . The sulfide precipitant preparation process of possible chemical reaction equations and the ΔG calculation results are shown in Table 1. The possible chemical reaction equations and the ΔG calculation results in the selective separation recovery of copper and arsenic process are shown in Tables 2 and 3, respectively.

Table 1. The possible chemical reaction equations and the calculation result of ΔG in the sulfide precipitant preparation process.

Number	Chemical Reaction Equations	ΔG (kJ/mol)
1	$S^{2-} + Fe^{2+} = FeS$	−2893.28
2	$2HS^- + Fe^{2+} = FeS + H_2S$	−2278.89
3	$S^{2-} + Mn^{2+} = MnS$	−2738.16
4	$2HS^- + Mn^{2+} = MnS + H_2S$	−2123.73
5	$S^{2-} + Zn^{2+} = ZnS$	−2437.23
6	$2HS^- + Zn^{2+} = ZnS + H_2S$	−1822.85
7	$6S^{2-} + 4Fe^{3+} = 2FeS + S + Fe_2S_3$	−24,988.57
8	$18HS^- + 6Fe^{3+} = Fe_2S_3 + 9H_2S + 2S + 4FeS$	−31,268.39

Table 2. The possible chemical reaction equations and calculation result of ΔG in the selective recovery of copper process.

Number	Chemical Reaction Equations	ΔG (kJ/mol)
1	$\text{FeS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Fe}^{2+}$	−598.22
2	$\text{MnS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Mn}^{2+}$	−753.38
3	$\text{ZnS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Zn}^{2+}$	−1054.26
4	$\text{Fe}_2\text{S}_3 + 4\text{H}^+ = 2\text{H}_2\text{S} + 2\text{Fe}^{2+} + \text{S}$	−173.51
5	$\text{S}^{2-} + \text{Cu}^{2+} = \text{CuS}$	−2720.36
6	$2\text{HS}^- + \text{Cu}^{2+} = \text{CuS} + \text{H}_2\text{S}$	−2105.98
7	$\text{S}^{2-} + 2\text{H}^+ = \text{H}_2\text{S}$	−3491.49
8	$\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}$	−1438.55

Table 3. The possible chemical reaction equations and calculation result of ΔG in the selective recovery of arsenic process.

Number	Chemical Reaction Equations	ΔG (kJ/mol)
1	$\text{FeS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Fe}^{2+}$	−598.22
2	$\text{MnS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Mn}^{2+}$	−753.38
3	$\text{ZnS} + 2\text{H}^+ = \text{H}_2\text{S} + \text{Zn}^{2+}$	−1054.26
4	$\text{Fe}_2\text{S}_3 + 4\text{H}^+ = 2\text{H}_2\text{S} + 2\text{Fe}^{2+} + \text{S}$	−173.51
5	$14\text{H}^+ + 4\text{S}^{2-} + 2\text{AsO}_3^{2-} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−25,383.30
6	$10\text{H}^+ + 4\text{HS}^- + 2\text{AsO}_3^{2-} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−19,224.48
7	$12\text{H}^+ + 4\text{S}^{2-} + 2\text{HAsO}_3^{2-} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−20,668.79
8	$8\text{H}^+ + 4\text{HS}^- + 2\text{HAsO}_3^{2-} = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−14,509.96
9	$10\text{H}^+ + 4\text{S}^{2-} + 2\text{H}_2\text{AsO}_3^- = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−16,792.22
10	$6\text{H}^+ + 4\text{HS}^- + 2\text{H}_2\text{AsO}_3^- = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−10,633.40
11	$8\text{H}^+ + 4\text{S}^{2-} + 2\text{H}_3\text{AsO}_3 = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−13,976.47
12	$4\text{H}^+ + 4\text{HS}^- + 2\text{H}_3\text{AsO}_3 = \text{As}_2\text{S}_3 + 6\text{H}_2\text{O} + \text{H}_2\text{S}$	−7817.65

As shown in Table 1, the sulfide precipitant was mainly composed of metal sulfide generated by the reaction of metal ions with S^{2-} or HS^- . Meanwhile, a small amount of H_2S gas generated in the process of preparation was dissolved in the solution. On the whole, the binding capacity of S^{2-} and metal ions was greater than that of HS^- and metal ions, which proclaimed that metal ions will react with the S^{2-} to form the corresponding metal sulfide preferentially. This is critical to avoid H_2S gas escaping into the air during the preparation of sulfide precipitant.

As shown in Table 2, two processes were needed for the selective separation and recovery of copper from the acidic leaching solution of copper soot. First, the metal sulfide of FeS , Fe_2S_3 , MnS and ZnS contained in the sulfide precipitant should react with H^+ to produce H_2S gas, and subsequently be absorbed into the solution to produce the ions of S^{2-} and HS^- . Afterwards, the S^{2-} and HS^- could combine with Cu^{2+} to form a large number of copper sulfide slag. Meanwhile, a part of S^{2-} and HS^- could react with H^+ to produce H_2S gas, but it could not escape into the air due to the dissolution. From the ΔG calculation results of the chemical reaction, the binding capacity of S^{2-} and Cu^{2+} was greater than that of HS^- and Cu^{2+} . This illustrates that achieving the selective separation and recovery of copper mainly depended on the chemical reaction of S^{2-} with Cu^{2+} [32].

It can be seen from Table 3 that the process of arsenic recovery from the arsenic-containing filtrate was similar to the recovery of the copper process. The selective separation and recovery of arsenic realized mainly relied on the chemical reaction of $\text{S}^{2-}/\text{HS}^-$ with AsO_3^{2-} , HAsO_3^{2-} , H_2AsO_3^- and H_3AsO_3 . From the results of chemical reaction energy calculation, small ΔG for generating arsenic trisulfide slag indicated that arsenic is easy to combine with sulfide ion. However, the molar ratios of $\text{S}^{2-}/\text{HS}^-$ to arsenic should be greater than two to better achieve the recovery of arsenic. This is consistent with the experiment results of arsenic recovery dosage.

Therefore, the concentrations of S^{2-} and HS^- should always be kept at a low level in the process of selective separation recovery of copper and arsenic due to the stability of the sulfide precipitant. This was key to improving the selective separation efficiency of copper and arsenic, and it could prevent large amounts of H_2S gas from being generated in a short time. Therefore, the selective separation recovery of copper and arsenic from the leaching solution of copper soot could be efficiently realized by the prepared sulfide precipitant.

3.4. SEM Images Analysis

The SEM images of copper sulfide slag and arsenic trisulfide slag obtained by the sulfide precipitant are presented in Figures 9 and 10, respectively. As shown in Figure 9, the SEM images of copper sulfide slag were mainly flocculence and pancake. From Figure 10, the SEM images of arsenic trisulfide slag were mainly spherical and flaky. Meanwhile, the spherical particle size of arsenic trisulfide slag was much smaller than that of flaky. Hence, it was obvious that there were big differences in the SEM image characteristics between the prepared sulfide precipitant, copper sulfide slag and arsenic trisulfide slag. The results suggest that the sulfide precipitant had a fierce chemical reaction in the separation recovery of copper and arsenic, and a large number of new sediments was generated [33]. According to the analysis results of XRF and chemical reaction energy calculation, the new sediment generated in the process of separation recovery of copper and arsenic should mainly be CuS and As_2S_3 , respectively.

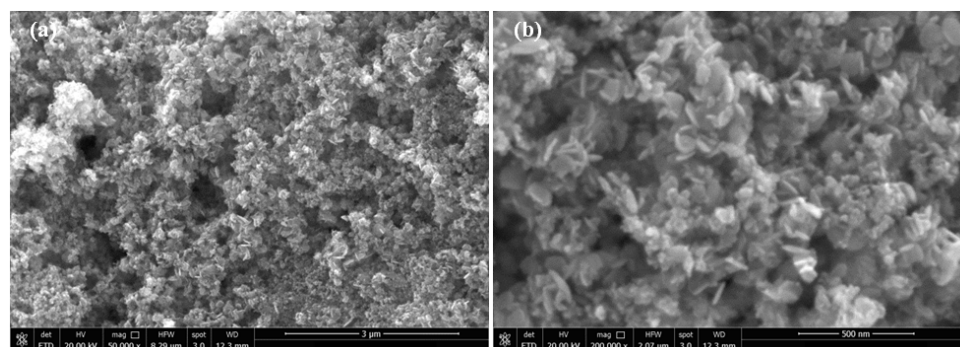


Figure 9. SEM images of copper sulfide slag. (a) 50,000 \times ; (b) 200,000 \times .

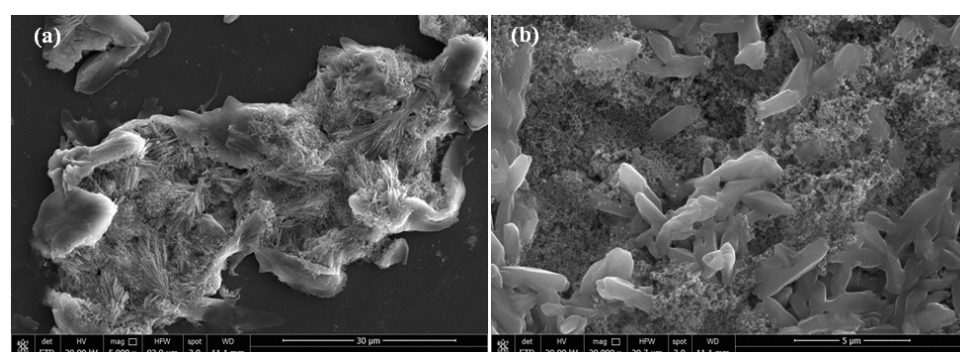


Figure 10. SEM images of arsenic trisulfide slag. (a) 5000 \times ; (b) 20,000 \times .

4. Conclusions

In this study, a new type of sulfide precipitant was prepared to realize the selective separation recovery of copper and arsenic from the leaching solution of copper soot. The experimental results indicate that the obtainable recovery and grade of Cu in the copper sulfide slag were about 97% and 47%, respectively, and the obtainable recovery and grade of As in the arsenic trisulfide slag were about 98% and 30%, respectively. The results of chemical reaction energy calculation analysis and SEM images analysis indicate that the selective separation recovery of copper and arsenic mainly depended on the S^{2-} and HS^-

produced by the prepared sulfide precipitant. In addition, S^{2-} and HS^- could react with Cu^{2+} and arsenic components to form CuS and As_2S_3 , respectively. The smaller solubility of CuS than As_2S_3 and the low rate of S^{2-} and HS^- produced by the sulfide precipitant were integral to achieving the efficient separation and recovery of copper and arsenic. On the whole, the selective separation recovery of copper and arsenic from the leaching solution of copper soot could be realized by using the prepared sulfide precipitant.

Author Contributions: Conceptualization, H.Z. and Z.L.; methodology, Z.Y., Y.Z., H.Z., X.L., X.T. and Z.L.; validation, Z.Y.; formal analysis, Z.Y., Y.Z., H.Z. and X.L.; investigation, Z.Y. and Y.Z.; resources, H.Z.; writing-original draft preparation, Z.Y.; writing-review and editing, H.Z.; visualization, X.L. and X.T.; data curation, Z.Y., Y.Z., H.Z., X.T. and Z.L.; project administration, H.Z.; funding acquisition, H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by National key research and development program (grant no. 2018YFC19016); The Youth Jinggang Scholars Program in Jiangxi Province (grant no. QNJG2020048); and The Program of Qingjiang Excellent Young Talents, Jiangxi University of Science and Technology (grant no. JXUSTQJB2020002).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yang, Z.; Geng, L.; Zhou, H.; Liu, Z.; Xie, F.; Yang, S.; Luo, X. Improving the flotation separation of chalcopyrite from galena through high-temperature air oxidation pretreatment. *Miner. Eng.* **2022**, *176*, 107350. [\[CrossRef\]](#)
2. Zhou, H.; Geng, L.; Zhang, Y.; Yang, Z.; He, K.; Xie, F. Selective flotation separation of chalcopyrite and sphalerite by thermal pretreatment under air atmosphere. *Physicochem. Probl. Miner. Process.* **2021**, *57*, 305–314. [\[CrossRef\]](#)
3. Northey, S.; Mohr, S.; Mudd, G.M.; Weng, Z.; Giurcob, D. Modelling future copper ore grade decline based on a detailed assessment of copper resources and mining. *Resour. Conserv. Recy.* **2014**, *83*, 190–201. [\[CrossRef\]](#)
4. Li, Y.; Zhu, X.; Qi, X.; Shu, B.; Zhang, X.; Li, K.; Wei, Y.; Hao, F.; Wang, H. Efficient removal of arsenic from copper smelting wastewater in form of scorodite using copper slag. *J. Clean. Prod.* **2020**, *270*, 122428. [\[CrossRef\]](#)
5. Ahmad, A.L.; Ooi, B.S. A study on acid reclamation and copper recovery using low pressure nanofiltration membrane. *Chem. Eng. J.* **2010**, *156*, 257–263. [\[CrossRef\]](#)
6. Guo, X.; Chen, Y.; Wang, Q.; Wang, S.; Tian, Q. Copper and arsenic substance flow analysis of pyrometallurgical process for copper production. *T. Nonferr. Metal. Soc.* **2022**, *32*, 364–376. [\[CrossRef\]](#)
7. Guo, L.; Hu, Z.; Du, Y.; Zhang, T.C.; Du, D. Mechanochemical activation on selective leaching of arsenic from copper smelting flue dusts. *J. Hazard. Mater.* **2021**, *414*, 125436. [\[CrossRef\]](#)
8. Yang, B.; Huang, D.; Liu, D.; Zha, G.; Jiang, W.; Kong, X. Research and industrial application of a vacuum separation technique for recovering valuable metals from copper dross. *Sep. Purif. Technol.* **2020**, *236*, 116309. [\[CrossRef\]](#)
9. Al-Abed, S.R.; Jegadeesan, G.; Purandare, J.; Allen, D. Arsenic release from iron rich mineral processing waste: Influence of pH and redox potential. *Chemosphere.* **2007**, *66*, 775–782. [\[CrossRef\]](#)
10. Xue, J.; Long, D.; Zhong, H.; Wang, S.; Liu, L. Comprehensive recovery of arsenic and antimony from arsenic-rich copper smelter dust. *J. Hazard. Mater.* **2021**, *413*, 125365. [\[CrossRef\]](#)
11. Che, J.; Zhang, W.; Ma, B.; Chen, Y.; Wang, L.; Wang, C. A shortcut approach for cooperative disposal of flue dust and waste acid from copper smelting: Decontamination of arsenic-bearing waste and recovery of metals. *Sci. Total Environ.* **2022**, *843*, 157063. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Gao, W.; Xu, B.; Yang, J.; Yang, Y.; Li, Q.; Zhang, B.; Liu, G.; Ma, Y.; Jiang, T. Recovery of valuable metals from copper smelting open-circuit dust and its arsenic safe disposal. *Resour. Conserv. Recy.* **2022**, *179*, 106067. [\[CrossRef\]](#)
13. Zhang, W.; Che, J.; Xia, L.; Wen, P.; Chen, J.; Ma, B.; Wang, C. Efficient removal and recovery of arsenic from copper smelting flue dust by a roasting method: Process optimization, phase transformation and mechanism investigation. *J. Hazard. Mater.* **2021**, *412*, 125232. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Khalid, M.K.; Hamuyuni, J.; Agarwal, V.; Pihlasalo, J.; Haapalainen, M.; Lundström, M. Sulfuric acid leaching for capturing value from copper rich converter slag. *J. Clean. Prod.* **2019**, *215*, 1005–1013. [\[CrossRef\]](#)
15. Vestola, E.A.; Kuusenaho, M.K.; Närhi, H.M.; Tuovinen, O.H.; Puhakka, J.A.; Plumb, J.J.; Kaksonen, A.H. Acid bioleaching of solid waste materials from copper, steel and recycling industries. *Hydrometallurgy* **2010**, *103*, 74–79. [\[CrossRef\]](#)
16. Liu, Y.; Huang, Z.; Qin, Q. Study on Recovering Copper and Zinc from Slag by Process of Acid Leaching and Solvent Extraction. *Min. Metall. Eng.* **2012**, *32*, 76–79.
17. Zhang, Y.; Feng, X.; Qian, L.; Luan, J.; Jin, B. Separation of arsenic and extraction of zinc and copper from high-arsenic copper smelting dusts by alkali leaching followed by sulfuric acid leaching. *J. Environ. Chem. Eng.* **2021**, *9*, 105997. [\[CrossRef\]](#)

18. Yao, W.; Min, X.; Li, Q.; Li, K.; Wang, Y.; Wang, Q.; Liu, H.; Qu, S.; Dong, Z.; Qu, C.; et al. Formation of arsenic–copper-containing particles and their sulfation decomposition mechanism in copper smelting flue gas. *T. Nonferr. Metal. Soc.* **2021**, *31*, 2153–2164. [\[CrossRef\]](#)
19. Shahrashoub, M.; Bakhtiari, S. The efficiency of activated carbon/magnetite nanoparticles composites in copper removal: Industrial waste recovery, green synthesis, characterization, and adsorption-desorption studies. *Microporous Mesoporous Mater.* **2021**, *311*, 110692. [\[CrossRef\]](#)
20. Li, H.; Zhang, H.; Long, J.; Zhang, P.; Chen, Y. Combined Fenton process and sulfide precipitation for removal of heavy metals from industrial wastewater: Bench and pilot scale studies focusing on in-depth thallium removal. *Front. Environ. Sci. Eng.* **2019**, *13*, 49. [\[CrossRef\]](#)
21. Nidheesh, P.V.; Singh, T.A. Arsenic removal by electrocoagulation process: Recent trends and removal mechanism. *Chemosphere* **2017**, *181*, 418–432. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Zhang, W.; Che, J.; Wen, P.; Xia, L.; Ma, B.; Chen, J.; Wang, C. Co-treatment of copper smelting flue dust and arsenic sulfide residue by a pyrometallurgical approach for simultaneous removal and recovery of arsenic. *J. Hazard. Mater.* **2021**, *416*, 126149. [\[CrossRef\]](#)
23. Zhang, X.; Tian, J.; Hu, Y.; Han, H.; Luo, X.; Sun, W.; Yue, T.; Wang, L.; Cao, X.; Zhou, H. Selective sulfide precipitation of copper ions from arsenic wastewater using monoclinic pyrrhotite. *Sci. Total Environ.* **2020**, *705*, 135816. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Jiang, G.; Peng, B.; Chai, L.; Wang, Q.; Shi, M.; Wang, Y.; Liu, H. Cascade sulfidation and separation of copper and arsenic from acidic wastewater via gas-liquid reaction. *T. Nonferr. Metal. Soc.* **2017**, *27*, 925–931. [\[CrossRef\]](#)
25. Zhang, X.; Yuan, J.; Tian, J.; Han, H.; Sun, W.; Yue, T.; Yang, Y.; Wang, L.; Cao, X.; Lu, C. Ultrasonic-enhanced selective sulfide precipitation of copper ions from copper smelting dust using monoclinic pyrrhotite. *T. Nonferr. Metal Soc.* **2022**, *32*, 682–695. [\[CrossRef\]](#)
26. Jarošíková, A.; Ettler, V.; Mihaljevič, M.; Drahot, P.; Culka, A.; Racek, M. Characterization and pH-dependent environmental stability of arsenic trioxide-containing copper smelter flue dust. *J. Environ. Manage.* **2018**, *209*, 71–80. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Yue, T.; Niu, Z.; Hu, Y.; Han, H.; Sun, W.; Tian, J.; Xu, Z.; Wang, L.; Yang, Y. Arsenic (V) adsorption on ferric oxyhydroxide gel at high alkalinity for securely recycling of arsenic-bearing copper slag. *Appl. Surf. Sci.* **2019**, *478*, 213–220. [\[CrossRef\]](#)
28. Fan, C.; Li, K.; He, Y.; Wang, Y.; Qian, X.; Jia, J. Evaluation of magnetic chitosan beads for adsorption of heavy metal ions. *Sci. Total Environ.* **2018**, *627*, 1396–1403. [\[CrossRef\]](#)
29. Li, Y.; Zhu, X.; Qi, X.; Shu, B.; Zhang, X.; Li, K.; Wei, Y.; Wang, H. Removal and Immobilization of Arsenic from Copper Smelting Wastewater using Copper Slag by in Situ Encapsulation with Silica Gel. *Chem. Eng. J.* **2020**, *394*, 124833. [\[CrossRef\]](#)
30. Ding, W.; Tong, H.; Zhao, D.; Zheng, H.; Liu, C.; Li, J.; Wu, F. A novel removal strategy for copper and arsenic by photooxidation coupled with coprecipitation: Performance and mechanism. *Chem. Eng. J.* **2020**, *401*, 126102. [\[CrossRef\]](#)
31. Wang, A.; Zhou, K.; Zhang, X.; Zhou, D.; Peng, C.; Chen, W. Reductive removal of arsenic from waste acid containing high-acidity and arsenic levels through iodide and copper powder synergy. *Chem. Eng. J.* **2019**, *373*, 23–30. [\[CrossRef\]](#)
32. Liu, Z.; Sheng, M.; He, Y.; Zhou, H.; Huang, J.; Luo, X.; Zhang, Y. Coordination mechanism of aluminum with oxalate and fluoride in aluminum crystallization from vanadium extraction wastewater. *J. M. Liq.* **2022**, *347*, 117992. [\[CrossRef\]](#)
33. Cao, H.; Fu, J.; Liu, Y.; Chen, S. Facile design of superhydrophobic and superoleophilic copper mesh assisted by candle soot for oil water separation. *Colloids Surf. A* **2018**, *537*, 294–302. [\[CrossRef\]](#)