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Separation and recovery of arsenic from As, Cu, and Zn rich leaching liquor using a reduction-crystallization approach

Erjun Zhang,^a Kanggen Zhou,^a Xuekai Zhang,^{ab} Changhong Peng,^a Wei Chen^{*,a} and Dewen He^{*,a}

As, Cu, and Zn rich leaching liquor is generated in the leaching process of copper dust, which contains various metals with high recovery value. Herein, an approach for the direct separation and recovery of arsenic from As, Cu, and Zn rich leaching liquor was proposed. The approach includes two steps, namely SO_2 reduction and arsenic crystallization. The factors affecting the reduction of As(v) to As(III) were investigated, including the pH, SO_2 dosage, and reduction temperature. In the crystallization stage, the impacts of sulfuric acid consumption and temperature on the crystallization of arsenic (As_2O_3) were studied. The results show that the optimal H^+ concentration, temperature, and SO_2 input for the arsenic reduction were 3.95 mol L^{-1} , 45°C , and $1.14 \text{ L g}^{-1} \text{ As(v)}$, respectively. While the optimal temperature and sulfuric acid dosage in As recovery process were 5°C and 0.1 L L^{-1} leaching liquor, respectively. Under these conditions, the As_2O_3 recovery percentage reached 96.53%, and the losses of Cu and Zn were only 3.12% and 0.75%, respectively. The precipitate contained 96.72% of As_2O_3 , 0.83% of Cu, and 0.13% Zn. Compared with the traditional technologies, this new method can improve the recovery efficiency of As_2O_3 and reduce the loss percentage of other valuable metals (Cu and Zn).

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Introduction

As_2O_3 is one of the important compounds of As, which has been widely used in the pharmaceutical, antiseptic, leather, and glass industries.^{1–4} However, it is also a toxic substance that can cause serious environmental pollution.^{5–9} Naturally, arsenic coexists with copper and zinc, and it can be enriched in the dust during the production of copper *via* pyrometallurgical process.^{10–16} The dust is usually leached by H_2SO_4 ,^{17–20} generating a large amount of As, Cu, and Zn rich leaching liquor. As, Cu and Zn have decent economic values and are widely used in various fields. Hence, recovery of these valuable metals is of great significance, not only for economic benefit but also for environmental protection.²¹

Recently, various methods have been proposed for the recovery of As from arsenic solution, including sulfide precipitation,^{22,23} calcium–arsenic coprecipitation,²⁴ iron–arsenic coprecipitation,^{25–28} ionic adsorption,^{29,30} microbe treatment methods,³¹ reduction method³² and so on.^{33,34} Among these methods, the sulfur dioxide reduction, evaporation, and crystallization methods entail to reduce As(v) to As(III), and then, evaporate and concentrate the leaching liquor to precipitate As_2O_3 crystals.^{35,36} This process results in co-precipitation of other valuable metals in

the arsenic-containing solution with As_2O_3 crystals and greatly increases the concentration of Zn, Cu, and inorganic salts in the arsenic-removal solution. The other methods for recovering As necessitate the addition of new reagents into the arsenic-containing solution to precipitate As at a certain pH. As-containing materials produced by these methods are still hazardous solid wastes and are not conducive for the sustainable ecological environment because they can only be stored or landfilled. Also, arsenic recovery by these methods can increase the concentration of impurities in the arsenic-removal solution, which causes problems in the recovery of valuable metals (such as Zn, Cu, *etc.*) from the arsenic-removal solution. Thus, a clean and effective method is urgently required to separate and recover the arsenic and valuable metals.

Herein, a new method for As_2O_3 recovery from As, Cu, and Zn rich leaching liquor was proposed. The process involves two steps, namely reduction of As(v) to As(III) by injecting SO_2 gas, and followed by direct cooling crystallization of As(III) in the form of As_2O_3 . Compared to other processes for arsenic recovery, this approach only involves in the addition of H_2SO_4 and SO_2 without introducing any impurities, which makes it easier to subsequently recover other valuable metals from the leaching liquor. The factors affecting the separation and recovery of As, including SO_2 input, $[\text{H}^+]$ concentration, and reduction temperature during the conversion of As(v) into As(III), and sulfuric acid concentration and cooling temperature during As_2O_3 crystallization, were systematically explored. This work provides a process for the recovery of arsenic from As, Cu, and Zn rich leaching liquor.

^aSchool of Metallurgy and Environment, Central South University, Changsha 410083, China. E-mail: dvchen@csu.edu.cn; hedewen@csu.edu.cn

^bCollege of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China


Experimental

Materials

The As, Cu, and Zn rich leaching liquor was obtained as follows. The copper dust with high As, Cu, and Zn contents was circulating leached and filtered using sulfuric acid and hydrogen peroxide solution at the ambient temperature and pressure.³⁷ Hydrogen peroxide was used to oxidize As(III) to As(V). The copper dust was the secondary dust produced in the smelting process of copper concentrate (obtained from a copper smelting company), which contained 12.51% As, 3.02% Cu, 11.59% Zn, 0.12% Fe, 2.87% Bi, and 16.06% Pb (w/w). The XRD patterns of copper dust are shown in Fig. 1a. Since the copper dust contained negligible Fe, while Pb and Bi species were retained in the solid phase after sulfuric acid leaching due to the formation of insoluble anglesite (PbSO₄) and bismuth sulphate (Bi₂(SO₄)₃), respectively, the main constituents in the leaching liquor were As(III), As(V), Cu, and Zn, and their concentrations are listed in Table 1. All reagents were of analytical grade (>98%). Sulfuric acid was obtained from Chengdu Cologne Chemical Co., Ltd. and sulfur dioxide was provided by Hengyang Jiantao Chemical Co., Ltd.

Apparatus and procedure

The process of arsenic recovery from As, Cu, and Zn rich leaching liquor is displayed in Fig. 1b. 200 mL leaching liquor was added into a three-port conical flask (500 mL). The left interface of the conical flask was connected with a small tank of SO₂. The middle interface was connected to a separating funnel with valve and the joint was sealed with a rubber, while the right

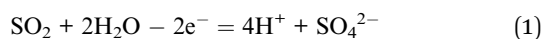
Table 1 The concentrations of the main constituents in the As, Cu, and Zn rich leaching liquor (mol L⁻¹)

| As | As(III) | As(V) | Cu | Zn |
|-------|---------|-------|-------|-------|
| 1.068 | 0.135 | 0.933 | 0.315 | 0.928 |

interface was connected to the piston. Then, the flask was fixed into a bath heater with a magnetic stirrer. Sulfuric acid was added into the separating funnel.

The initial concentration of H⁺ in the leaching liquor was 0.6 mol L⁻¹. The pH was adjusted to a certain value using sulfuric acid. SO₂ was introduced into the solution to reduce As(V) to As(III), as shown in eqn (1)–(3),³⁸ and prevent As(III) from forming Cu(AsO₂)₂ precipitates with Cu²⁺. The flow rate of SO₂ was adjusted using a switch valve.

The oxidation half-reaction:



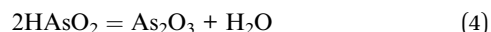
The reduction half-reaction:



Total redox reaction:



After As(V) was completely transformed into As(III), sulfuric acid was added into the leaching liquor to adjust the [H⁺] concentration. Then, ice-water bath was applied to cool the solution to crystallize As(III) in the form of As₂O₃ through eqn (4).



The recovery percentage of As₂O₃ and the precipitation percentage of Cu and Zn were calculated using eqn (5)–(7):

$$\eta_{\text{As(III)}} = (V' \times C'_{\text{As(III)}} - V \times C_{\text{As(III)}}) / (C_{\text{As}} - C_{\text{As(III)}}) \times V \times 100\% \quad (5)$$

$$\eta_{\text{As}_2\text{O}_3} = (m \times W_{\text{As}} / V \times C_{\text{As}}) \times 100\% \quad (6)$$

$$\eta_i = (C_i \times V - C'_i \times V_i) / (C_i \times V) \times 100\% \quad (7)$$

where $\eta_{\text{As(III)}}$ is the conversion efficiency of As(III), $\eta_{\text{As}_2\text{O}_3}$ is the recovery percentage of As₂O₃, η_i is the precipitation rate of Cu and Zn, V is the initial volume of the leaching liquor, V' is the solution volume of As(V) deoxidizing As(III), V_i is the volume of filtration solution after the precipitation of As₂O₃. C_{As} and $C_{\text{As(III)}}$ are the initial concentrations of As and As(III), respectively, while $C'_{\text{As(III)}}$ is the concentration of As(III) in the transformed solution. C_i is the concentration of Cu and Zn in the precipitation and filtration solution of As₂O₃, m is the weight of As₂O₃, and W_{As} is the content of As in As₂O₃.

Analytical methods

The concentrations of Cu, Zn, and As in the leaching liquor were determined *via* inductively coupled plasma-optical emission

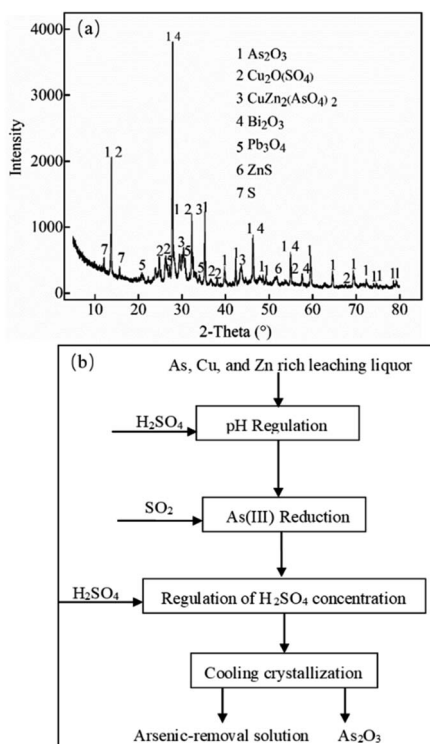


Fig. 1 (a) XRD patterns of the copper dust. (b) The process of arsenic recovery from As, Cu, and Zn rich leaching liquor.



spectroscopy (ICP-OES). The $[H^+]$ was measured *via* acid–base titration. The solid sample was dissolved by HNO_3 and HCl , and then the elemental contents were determined by ICP-OES. The phase compositions of the residues were obtained *via* X-ray diffraction (XRD, D/max 2500v/pc, Cu $K\alpha$ radiation). The particle size of the precipitates was determined by the laser particle size analyzer (Malvern Instruments, MS200). Before particle size measurement, the precipitates were ultrasonically dispersed. The content of As(III) was determined with the cerous sulfate–potassium bromate titration, while that of As(V) was obtained by subtracting the As(III) from total As concentration.

Results and discussion

Thermodynamics studies

The thermodynamic Gibbs free energies of the main reactions in the system are listed in Table 2. The relationship between potential and pH for each chemical reactions can be expressed as follows:³⁹

$$aOx + nH^+ + ze = bRed \quad (8)$$

$$E = -\frac{\Delta_r G^\theta}{zF} - \frac{0.0591}{z} \lg \frac{[Red]^b}{[Ox]^a} - \frac{0.0591n}{z} pH \quad (9)$$

where Ox and Red are the oxidized and reduced states of species, a , b , n , and z are the number of oxidized species, hydrogen ions, electrons, and reduced species participated in the equation, respectively, and F is the Faraday constant.

The Eh–pH diagrams of Cu–As–S–O–H₂O system at different temperatures are displayed in Fig. 2. Under different pH and Eh values, As(III) had different forms in the solution. At 25 °C (see Fig. 2a), when pH was in the range of -0.5 – 2 and Eh lower than 0.45 V, As and Cu in the leaching liquor co-precipitated in the form of $Cu(AsO_2)_2$ or Cu_3As . When Eh < 0.5 V, $HAsO_3$ transformed into $HAsO_2$ as the Eh value decreased continuously.

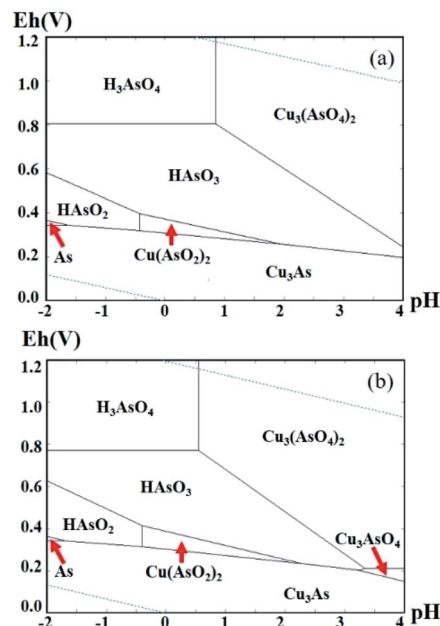


Fig. 2 Eh–pH diagrams of the Cu–As–S–O–H₂O system at (a) 25 °C and (b) 65 °C. Figures were drawn by the HSC Chemistry Software (Version 6.0, Outokumpu Research Oy, Finland). The initial concentrations were $C_{As} = 1.068 \text{ mol L}^{-1}$, $C_S = 3.218 \text{ mol L}^{-1}$, $C_{Cu} = 0.315 \text{ mol L}^{-1}$, and $C_{Zn} = 0.928 \text{ mol L}^{-1}$.

When Eh < 0.35 V, As and Cu also co-precipitated in the form of Cu_3As . Therefore, for the reduction of As(V) to As(III), the solution pH value should be lower than -0.5 , and Eh should be strictly controlled so that it is not too low to cause co-precipitation of As and Cu in the form of Cu_3As .

Comparing Fig. 2a with 2b, the Eh–pH region for $Cu(AsO_2)_2$ formation varied at different temperatures, which was enlarged at a higher temperature. This indicates that the temperature may have a significant influence on the reduction of As(V) to As(III).

Factors on As(v) to As(III) conversion and Cu/Zn precipitation

To explore the feasibility and effectiveness of arsenic recovery from the As, Cu, and Zn rich leaching liquor by the reduction–cooling crystallization approach, the effects of SO_2 input, H^+ concentration, and temperature on the conversion of As(V) to As(III) and Cu/Zn precipitation were studied.

Effect of SO_2 input. As presented in Fig. 3, under different SO_2 dosages and initial acidities, the conversion percentage of As(V) to As(III) and precipitation percentages of Cu and Zn were quite different. As shown in Fig. 3a, both the SO_2 injection and initial H^+ concentration had significant impact on the As(V) to As(III) conversion percentage. Under the same initial concentration of H^+ , as the SO_2 injection volume increased gradually, the conversion percentage of As(V) to As(III) increased. Addition of SO_2 resulted in a decrease in the redox potential in the liquor, which was beneficial for the reduction of As(V) to As(III).³⁵ Moreover, when the SO_2 injection volume was fixed, with a gradual rise in initial H^+ concentration, the solubility of $Cu(AsO_2)_2$ increased. Thus, the As(V) to As(III) conversion percentage increased.

Table 2 The Gibbs free energies ($\Delta_r G^\theta$) of main chemical reactions

| Equilibrium reaction | $\Delta_r G^\theta$ (kJ mol ⁻¹) | |
|---|---|---------|
| | 25 °C | 65 °C |
| $H_2AsO_4^- + H^+ = H_3AsO_4$ | –12.79 | –15.82 |
| $HAsO_4^{2-} + H^+ = H_2AsO_4^-$ | –38.63 | –43.84 |
| $H_3AsO_4 + 2H^+ + 2e = H_3AsO_3 + H_2O$ | –110.78 | –108.64 |
| $H_2AsO_4^- + 3H^+ + 2e = H_3AsO_3 + H_2O$ | –123.66 | –124.46 |
| $HAsO_4^{2-} + 4H^+ + 2e = H_3AsO_3 + H_2O$ | –162.29 | –168.31 |
| $HAsO_4^{2-} + 3H^+ + 2e = H_2AsO_3^- + H_2O$ | –109.60 | –112.22 |
| $H_3AsO_3 = HAsO_2 + H_2O$ | –0.32 | –0.60 |
| $AsO_4^{3-} + 4H^+ + 2e = H_2AsO_3^- + H_2O$ | –175.81 | –185.53 |
| $AsO_4^{3-} + 8H^+ + 5e = As + 4H_2O$ | –300.34 | –308.18 |
| $H_3AsO_3 + 3H^+ + 3e = As + 3H_2O$ | –71.85 | –66.56 |
| $H_2AsO_3^- + 4H^+ + 3e = As + 3H_2O$ | –124.54 | –122.65 |
| $As + 3H^+ + 3e = AsH_3$ | 60.71 | 64.13 |
| $SO_2 + H_2O = H_2SO_3$ | –0.64 | 3.10 |
| $H_2SO_3 + H_2O - 2e = HSO_4^- + 3H^+$ | 19.68 | 21.33 |
| $HSO_4^- = H^+ + SO_4^{2-}$ | 10.93 | 16.11 |
| $3Cu^{2+} + 2HAsO_4^- = Cu_3(AsO_4)_2 + 2H^+$ | –82.18 | –107.62 |
| $Cu^{2+} + 2HAsO_2 = Cu(AsO_2)_2 + 2H^+$ | –7.38 | –8.00 |



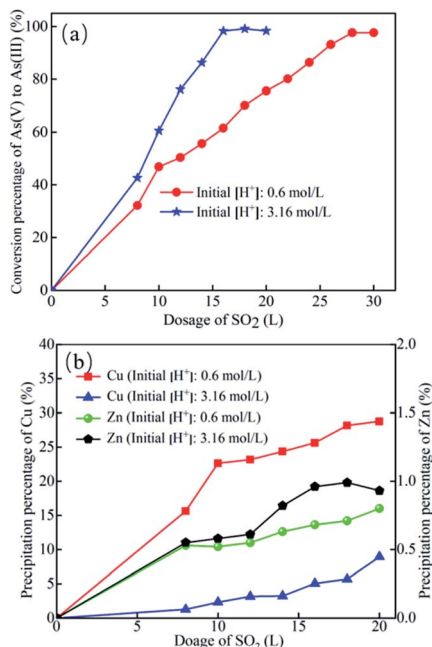


Fig. 3 Effect of SO₂ injection on (a) As(v) to As(III) conversion percentage and (b) the precipitation percentages of Cu and Zn (Temperature: 40 °C; SO₂ input speed: 50 mL min⁻¹).

With the injection of SO₂, the final concentration of H⁺ in the liquor increased naturally (eqn (3)), which led to a rise in the solubility product of Cu(AsO₂)₂ and CuAs₃ and a gradual decrease in Cu²⁺ precipitation percentage. When SO₂ injection reached a certain volume, the final [H⁺] and solubility of Cu(AsO₂)₂ and Cu₃As increased. Therefore, the Cu precipitation percentage decreased. Since Zn ions would not bind with Cu and As ions to form precipitate, SO₂ injection had no effect on the precipitation of Zn(II) ion. Thus, Zn ions were precipitated *via* physical entrainment of a small amount of Zn ions into the As₂O₃, Cu(AsO₂)₂, and Cu₃As precipitates.

As shown in Fig. 3a and b, when the initial concentration of H⁺ was 0.6 mol L⁻¹ and SO₂ injection volume was 28 L, the conversion rate of As(III) reached 97.62% while the precipitation percentage of Cu ion was higher than 25%. This result suggests that the Cu(II) ions in the leaching liquor suffered a considerable loss. When H⁺ concentration was 3.16 mol L⁻¹ and SO₂ input was 16 L, the conversion percentage of As(III) was 98.32%, while the precipitation percentages of Cu and Zn were 5.06% and 0.96%, respectively. Considering the cost, As₂O₃ quality, and loss of Cu and Zn ions, the optimal SO₂ input for As(III) conversion was 16 L/14 g (1.14 L g⁻¹ As(v)).

Effect of H⁺ concentration. As shown in Fig. 4a, H⁺ concentration had a significant impact on the conversion of As(v) to As(III). When H⁺ concentration was 0.6 mol L⁻¹, the conversion percentage was only 65.13%, while the precipitation percentage of Cu ions reached 30.61%. This indicates that the sole addition of SO₂ was not enough to decrease the redox potential of the liquor for As(v) reduction. Moreover, under such low [H⁺], As(III) species easily co-precipitated with Cu²⁺ to form Cu(AsO₂)₂, as evidenced by the XRD result of the Cu–As co-precipitation in Fig. 4b. So, increasing the H⁺ concentration is advantageous for

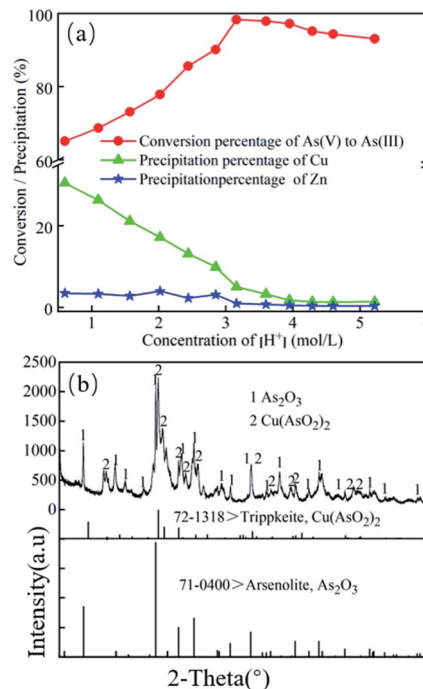


Fig. 4 (a) Effect of H⁺ concentration on the conversion percentage of As(v) to As(III) and the precipitation percentage of Cu and Zn. (b) XRD result of the precipitate. Experimental condition: temperature 40 °C, SO₂ input 16 L, SO₂ input speed 50 mL min⁻¹.

avoiding the precipitation of Cu(AsO₂)₂. When H⁺ concentration was 3.16 mol L⁻¹, the conversion rate of As(III) increased to 98.32%, while the precipitation percentage of Cu ion dropped to 5.06%. When H⁺ concentration increased to 3.95 mol L⁻¹, the precipitation percentage of Cu ion continuously decreased to 2.77%, while that of As tended to reach an equilibrium. In comparison, the precipitation percentage of Zn was negligible, which was mainly attributed to the entrainment of precipitates. Thus, the optimal concentration of H⁺ was 3.95 mol L⁻¹.

Effect of temperature. As shown in Fig. 5, the conversion percentage of As(v) to As(III) increased from 92% to 98.99% when the temperature increased from 15 °C to 45 °C. At this stage, the increase of temperature can promote the reduction of

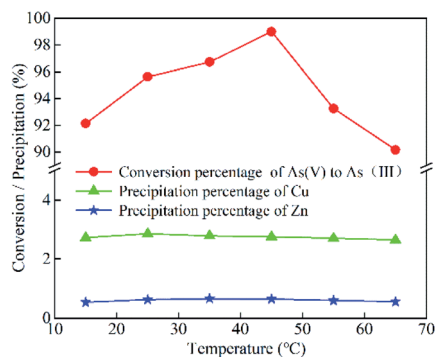


Fig. 5 Effect of temperature on the conversion of As(v) to As(III) and Cu/Zn precipitation (the initial [H]: 3.95 mol L; SO₂ input: 16 L; SO₂ input speed: 50 mL min⁻¹).



As(v) to As(III). However, it is not conducive to the dissolution of SO₂ at high temperatures.⁴⁰ Therefore, further increasing the temperature from 45 °C to 60 °C resulted in a decrease in the conversion percentage of As(v) to As(III) due to the decrease of SO₂ solubility. In comparison, the temperature had a slight effect on the precipitation of Cu and Zn ions in the leaching liquor in the range of 15–65 °C; thus, the precipitation percentage changed slightly. These results suggested that the optimum temperature of As(v) to As(III) conversion was 45 °C.

Under the optimal condition (3.95 mol L⁻¹ [H⁺], temperature of 45 °C, and SO₂ input of 1.14 L g⁻¹ As(v)), the conversion efficiency of As(v) to As(III) can reach up to about 98.99%, while the precipitation of Cu and Zn were kept below 2.77% and 0.64%, respectively. Therefore, the losses of Cu and Zn were well controlled, which laid the foundation for the follow up recovery of Cu and Zn.

Factors affecting As₂O₃ crystallization

As the concentration of sulfuric acid and temperature may affect the solubility of As₂O₃ crystallization, their effects on the As₂O₃ crystallization percentage were further investigated.

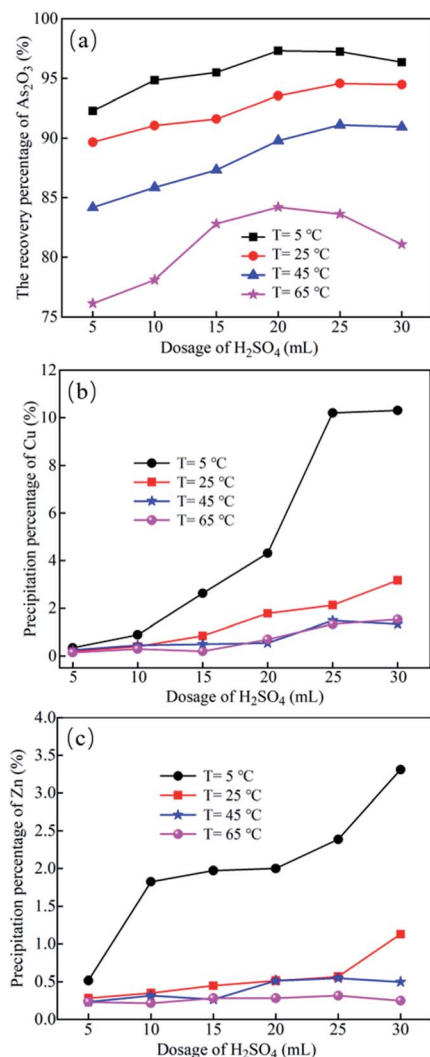


Fig. 6 Effects of sulfuric acid dosage on the recovery of As₂O₃ (a) and the precipitation of Cu (b) and Zn (c). Volume of the leaching liquor: 200 mL.

Table 3 The main component analysis of As₂O₃ crystal products (w/w, %)

| Elements | As | Cu | Zn | S |
|----------|-------|------|------|------|
| Content | 73.94 | 0.83 | 0.13 | 0.92 |

As shown in Fig. 6a, when solution temperature decreased from 65 °C to 5 °C, the crystallization (recovery) percentage of As increased significantly. The crystallization of As₂O₃ is an exothermic process, and the degree of supersaturation is the main driver of crystallization.³ When sulfuric acid concentration is determined, the solubility of As₂O₃ decreases when lowering the temperature, which is beneficial for As₂O₃ crystallization. When temperature was fixed, the recovery percentage of As₂O₃ increased with the dosage of sulfuric acid increasing from 5 to 20 mL/200 mL, and then displayed a gradual decrease with further increase in sulfuric acid concentration. Generally, the solubility of As₂O₃ decreases with the increasing acidity, but excess [H⁺] may result in reverse dissolution of As₂O₃.⁴¹ Therefore, the recovery percentage of As₂O₃ showed an initial increase and then gradually decreased with elevated sulfuric acid dosage.

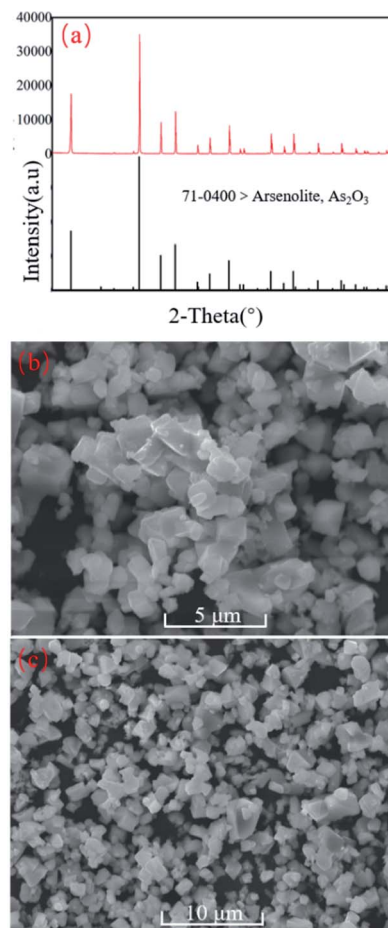


Fig. 7 XRD (a) and SEM images (b and c) of As₂O₃ crystal products. Experimental condition: temperature 5 °C and sulfuric acid dosage 0.1 L L⁻¹ leaching liquor.



Table 4 The elemental analysis of Cu–Zn-containing solution (mol L^{−1})

| Elements | As | Cu | Zn | [H ⁺] |
|----------|-------|-------|-------|-------------------|
| Content | 0.034 | 0.305 | 0.926 | 7.05 |

The impacts of H₂SO₄ concentration and temperature on Cu and Zn precipitation were also studied for comparison. As shown in Fig. 6b and c, as the dosage of sulfuric acid increased at a certain temperature, the precipitation percentage of CuSO₄ and ZnSO₄ increased slightly. As the temperature decreased at a certain dosage of sulfuric acid, the precipitation percentage of Cu and Zn ions gradually increased.

In combination with the results in Fig. 6b and c, the optimum dosage of sulfuric acid for As₂O₃ crystallization was 20 mL/200 mL (0.1 L L^{−1}) leaching liquor, while the suitable temperature was 5 °C.

Under the optimal condition, *i.e.*, temperature of 5 °C and sulfuric acid dosage 0.1 L L^{−1} leaching liquor, most arsenic were crystallized in the form of As₂O₃ from the liquor with an recovery efficiency of 96.72%, while the losses of Cu and Zn in the system were only 0.83% and 0.13%, respectively. Conventional evaporation crystallization process inevitably results in co-precipitation of copper and zinc with arsenic under such high concentrations.⁴⁰ Through precisely controlling the sulfuric acid concentration and temperature, the co-precipitation of copper and zinc can be avoided. Therefore, high purity As₂O₃ crystals can be obtained for arsenic recovery through this approach, and the As-removed liquor can be further processed to recover Cu and Zn resources.

Characterization of leaching residues

The crystallization composition is listed in Table 3. The XRD pattern is presented in Fig. 7a, while SEM images are presented in Fig. 7b and c. From Table 3 and Fig. 7, the constituents of precipitates were Cu, Zn, and S elements apart from the As₂O₃ phase, among which the content of As₂O₃ was 96.72%. The particle size of As₂O₃ precipitates was about 100 nm. The as-crystallized As₂O₃ can be used as the raw material for the extraction of arsenic metal. The solution after As₂O₃ crystallization and filtration contained some valuable elements, including Cu and Zn. The constituent analysis result of the solution is presented in Table 4. The As-removed liquor can be used for the subsequent recovery of Cu and Zn ions.

Conclusions

In this work, a reduction-cooling crystallization approach was proposed for the separation and recovery of arsenic from As, Cu, and Zn rich leaching liquor. In the reduction step, 98.99% of As(v) was successfully converted to As(III), while the precipitation of Cu and Zn were kept low (2.77% and 0.64%) under the condition of 3.95 mol L^{−1} [H⁺], temperature of 45 °C, and SO₂ input of 1.14 L g^{−1} As(v). In the cooling crystallization step, As(III) was separated and recovered in the form of As₂O₃ from the leaching liquor, and the highest recovery efficiency (96.53%) can be obtained under the optimal condition: temperature of

5 °C and sulfuric acid dosage 0.1 L L^{−1} leaching liquor. In the whole process, only sulfuric acid and SO₂ were used without introducing any impurities, and most Cu and Zn were retained in the leaching liquor, which simplified the subsequent recovery of valuable metals (Cu and Zn). This work may offer a new insight in the separation and recovery of the valuable arsenic elements from As, Cu, and Zn rich leaching liquor, and provide a prerequisite for the recovery of Cu and Zn in the subsequent process.

Author contributions

Erjun Zhang: conceptualization, data curation, validation, writing – review & editing, Kanggen Zhou: conceptualization, writing – original draft, supervision, Xuekai Zhang: investigation, data curation, Changhong Peng: supervision, resources, methodology, Wei Chen: conceptualization, writing – review & editing, funding acquisition, Dewen He: supervision, resources.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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