



Comprehensive recoveries of selenium, copper, gold, silver and lead from a copper anode slime with a clean and economical hydrometallurgical process

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HIGHLIGHTS

- A clean hydrometallurgical process for recovering valuable metals from anode slime was developed.
- The synergistic mechanism of H_2SO_4 and H_2O_2 for selenium leaching was proposed.
- Selenium and copper were recovered from the leachate by a two-step reduction process.
- Gold was selectively recovered by chloride leaching- $\text{H}_2\text{C}_2\text{O}_4$ reduction.
- Silver was efficiently recovered by Na_2SO_3 leaching- $\text{Na}_2\text{S}_2\text{O}_4$ reduction.
- Elements distribution and cost-benefit analyses for this process were performed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Anode slime
Comprehensive recovery
Hydrometallurgical process
Cleaner production
Element distribution

ABSTRACT

A clean hydrometallurgical process has been developed to efficiently and economically recover selenium, copper, gold, silver and lead from a copper anode slime. The mixture of H_2SO_4 and H_2O_2 was demonstrated to be effective for selenium leaching based on their synergistic effects, and the potential synergy mechanism was proposed. Na_2SO_3 reduction and iron powder precipitation were successively adopted to recover selenium and copper from the leaching solution. NaClO_3 - H_2SO_4 - NaCl solution was chosen to selectively leach gold, and the dissolved gold was recovered by $\text{H}_2\text{C}_2\text{O}_4$ reduction. Na_2SO_3 was used to leach silver with a sealed reactor, and the leached silver was recovered through $\text{Na}_2\text{S}_2\text{O}_4$ reduction. A lead concentrate with lead grade of 57.2% was eventually obtained after extracting selenium and copper, gold and silver. The recoveries of selenium, copper, gold, silver and lead separately achieved 92.9%, 95.8%, 99.1%, 99.4% and 99.8% under optimal conditions, and the purities of obtained products of simple substance selenium, sponge copper, metallic gold and metallic silver were 94.2%, 85.3%, 98.7% and 96.5%, respectively. The element distribution analysis indicated that the most of these valuable elements entered their products while hazardous element arsenic displayed a relatively scattered distribution. The cost-benefit analysis revealed that a revenue of 702217.8 CNY could be gained for treating one ton of anode slime using the proposed process. This process is eco-friendly and possesses high economic benefit, and thus shows good potential of industrial application.

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1. Introduction

Anode slime is an insoluble by-product produced during copper electro-refining, which has been listed as a hazardous waste due to the presence of harmful elements such as As and Cd [1]. However, it also contains appreciable amounts of Cu, Se, Au, Ag and Pb, and therefore it has been considered as an important secondary source for recovering valuable metals [2]. Currently, a large proportion of copper smelters are small and medium smelters in China and the prevalent approach to treat anode slime is pyro-metallurgy, which typically consists of sulfating roasting for selenium removal, sulfuric leaching of copper from the calcine, reduction smelting of acid leaching residue to obtain a noble lead (precious metals-lead alloy), oxidation refining of noble lead to generate a gold-silver alloy, and electrolysis of the alloy to get pure gold and silver products [3]. However, the currently pyro-metallurgical processes generally suffer from several evident disadvantages, such as high initial investment, high energy consumption and potential atmospheric pollution [4].

In order to overcome the preceding defects of pyro-metallurgical process, hydrometallurgical process has been developed. Generally, the base metals such as copper and selenium need to be pre-removed for recovering them and eliminating their negative effects on subsequent precious metals extraction. Sulfuric acid leaching assisted with a strong oxidant is a suitable choice for copper and selenium leaching. In recent studies, the effectivenesses of HNO_3 [5] and MnO_2 [6] as oxidants in H_2SO_4 solution have been demonstrated. However, in the former case, serious corrosion of equipment and possible release of hazardous NO_x gases have limited its wide industrial application. In the latter case, the foreign metal ion (Mn^{2+}) was introduced into the solution, which is unbeneficial to the subsequent copper and selenium recovery. Also, MnO_2 consumption was high for anode slime containing high content of copper [7]. In fact, selenium can also be leached in alkaline medium with oxygen as the oxidant. A two-stage leaching process, pre-leaching of copper with H_2SO_4 solution followed by selenium dissolution with NaOH solution under atmospheric conditions without using an autoclave, was employed to extract copper and selenium [8]. However, the leaching percentages of copper and selenium were unsatisfactory. Selenium leaching was considerably improved using alkaline pressure oxidative leaching due to the apparently increased oxygen solubility

under high pressure condition [9]. Nevertheless, the equipment investment is high for this process.

Recently, the predominant hydrometallurgical method for gold leaching is cyanidation [10]. However, cyanide is highly toxic and thus its use is strictly restricted [11]. Also, a high cost is needed to treat the produced cyanide-containing wastewater and tailings [12]. Thus, more attention has been paid to non-cyanide processes, among which thiourea leaching [13], thiosulfate leaching [14–16] and chloride leaching [17] have been the most extensively investigated. Nevertheless, the consumptions of thiourea and thiosulfate were high because of their serious oxidations by Fe^{3+} and $\text{Cu}(\text{NH}_3)_4^{2+}$ ions in the system. In the conventional chloride leaching, gold was leached in HCl medium in the presence of oxidants including Cl_2 [18], O_3 [19] and NaClO_3 [20]. However, some valuable elements such as lead and silver were readily dissolved, which not only complicated gold recovery but also caused a scattered distribution of these elements.

After chloride leaching of gold, silver is enriched in the residue that can be leached out with ammonia [21] or sodium sulfite [22]. However, ammonia consumption was high and its volatilization could cause a bad work condition [23]. High concentration of sodium sulfite was also needed because it could be easily oxidized by the dissolved oxygen in the pulp [24]. In addition, the dissolved silver in these two cases was usually recovered by the reduction of toxic hydrazine hydrate or formaldehyde. Sodium thiosulfate was also proposed for silver leaching [25]. Nevertheless, our previous study found that, silver leaching was difficult by direct thiosulfate leaching due to the adverse effect of associated lead element [2].

This paper presents a clean and economical hydrometallurgical process for recovering valuable elements from a copper anode slime, and the flowchart is shown in Fig. 1. First, H_2O_2 - H_2SO_4 , NaCl solution was used for dissolving selenium and copper, and they were successively recovered from leaching solution by Na_2SO_3 reduction and iron powder replacement. Then, NaClO_3 - H_2SO_4 - NaCl solution was adopted to selectively leach gold from oxidative acid leaching residue, and the leached gold was recovered by $\text{H}_2\text{C}_2\text{O}_4$ reduction. Finally, Na_2SO_3 leaching with a sealed reactor was utilized to efficiently extract silver from chloride leaching residue, and $\text{Na}_2\text{S}_2\text{O}_4$ was employed to recover the dissolved silver. A lead concentrate was acquired after the above

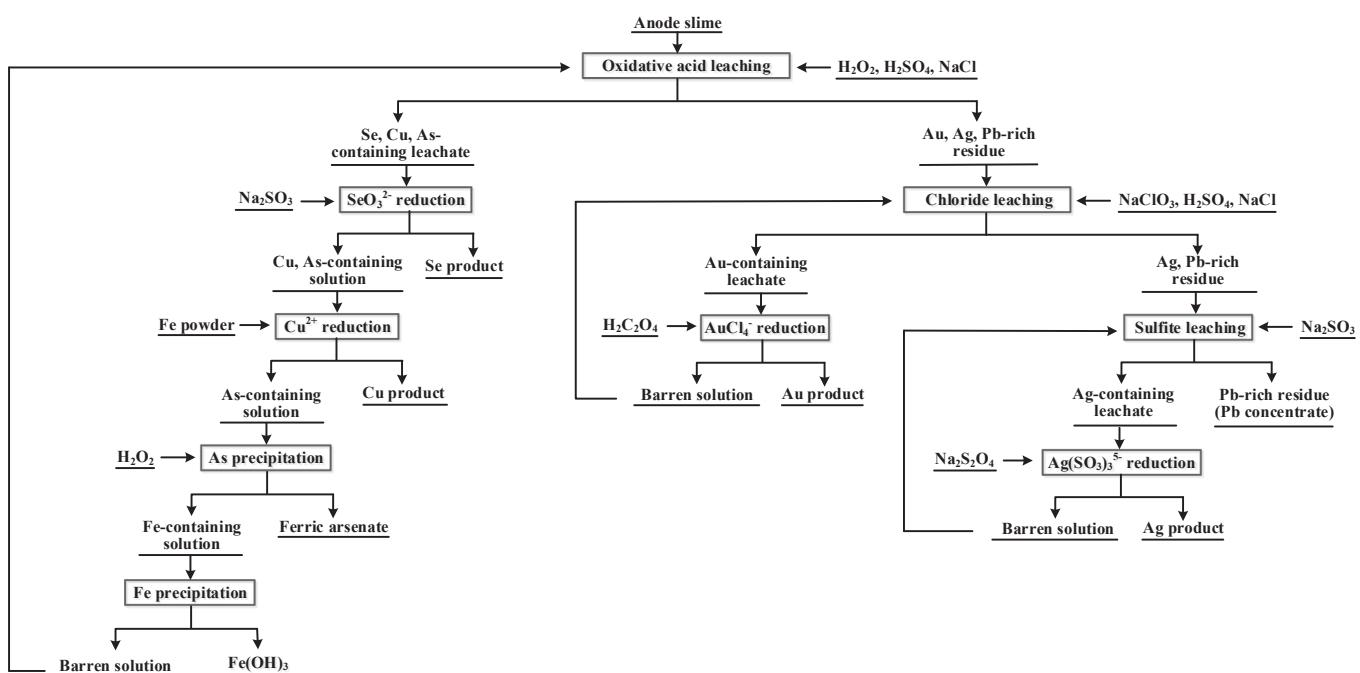


Fig. 1. The developed hydrometallurgical process for recovering Se, Cu, Au, Ag and Pb from the copper anode slime.

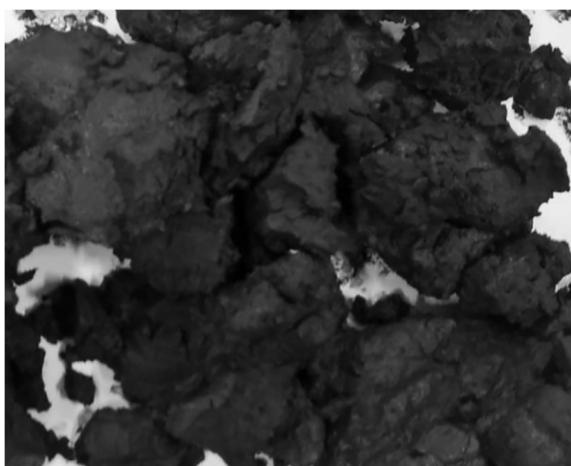


Fig. 2. Appearance of original anode slime.

processes. The element distribution analysis was conducted to indicate the general distribution of main elements in each leaching solution and residue. The cost-benefit analysis was also performed to estimate the economic feasibility of the process. The results obtained from this study are valuable for the comprehensive utilization of copper anode slime.

2. Experimental work

2.1. Material and reagents

The copper anode slime used in this study was provided by Qinghai Copper Industry Co., Ltd in Xining city, China, and the appearance of which is shown in Fig. 2. The original anode slime was a grayish black solid that contained large quantity of water, and thus it was dried at 100 °C for 48 h to remove its free moisture. Then, the sample was dry-milled in a planetary ball mill to certain particle size for subsequent experiments. Reagents, such as H₂O₂, H₂SO₄, NaClO₃, Na₂SO₃, H₂C₂O₄, Na₂S₂O₃, NaCl and iron powder were analytically grade. Distilled water was utilized throughout all experiments.

2.2. Experimental methods

For each leaching experiment, a pyrex 250 mL PVC reactor equipped with a mechanical stirrer was used as the reactor, which was placed in a thermostatically controlled water bath to maintain the required temperature. At the beginning of the test, distilled water, reagents and anode slime were sequentially added into the reactor to form the pulp whose density was 20%. Then, it was immediately agitated at a constant speed of 300 rpm. When the reaction was completed, the pulp was filtrated by a vacuum filter. The obtained solution sample was subjected to the concentration analysis of concerned elements to calculate their leaching percentages, and the residue was washed and dried for subsequent detection and leaching experiment.

For each test of valuable element recovery from leaching solution, 50 mL of the solution was introduced into the PVC reactor and the temperature was elevated to the pre-set value. Then, a predetermined amount of reductant was added, and the stirrer was turned on. At the end of the experiment, the solution was filtered. The recovery percentage of valuable elements was calculated based on the analysis of solution samples. The solid product was dried and packed in vacuum bags for further analysis.

2.3. Analytical methods

Particle size distribution of anode slime presented in Table 1 was detected by the vibrating screen. Semi-quantitative chemical

Table 1
Particle size distribution of anode slime.

Size (um)	+74	-74 to +44	-44 to +37	+37
Mass (%)	1.68	9.15	88.35	0.82

Table 2
XRF analysis result of the anode slime.

Element	Pb	O	Cu	Se	Ag	Au
Content (wt.%)	27.02	23.2	12.54	4.17	5.73	0.13
S	Bi	Sb	As	Ba	Ni	Sn
9.36	4.61	2.62	2.39	2.34	1.39	1.31

Table 3
Quantitative chemical assay results of main elements in the anode slime.

Element	Cu	Se	Ag	Au	Pb	As
Content (wt.%)	11.4	4.08	5.00	0.15	28.5	2.12

composition of anode slime indicated in Table 2 was determined by X-ray fluorescence (XRF, S4 Pioneer, Bruker) analysis using a Panalytical Axios-Max spectrometer. Quantitative chemical assay of main elements in the anode slime displayed in Table 3 was performed by acid digestion followed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PS-6, Baird). Mineralogical compositions of the samples were identified by an X-ray diffractometer (XRD, D/Max 2500, Rigaku) with a scanning angle from 5° to 80°. Scanning electron microscope (SEM, MIA3, TESCAN) coupled with energy dispersive spectrometer (EDS, Oxford) was used to study the surface morphology and composition of the anode slime. The percentage of each phase of an element in the anode slime was determined with chemical phase analysis whose procedure has been stated in our previous study [26].

3. Results and discussion

3.1. Characterization of anode slime

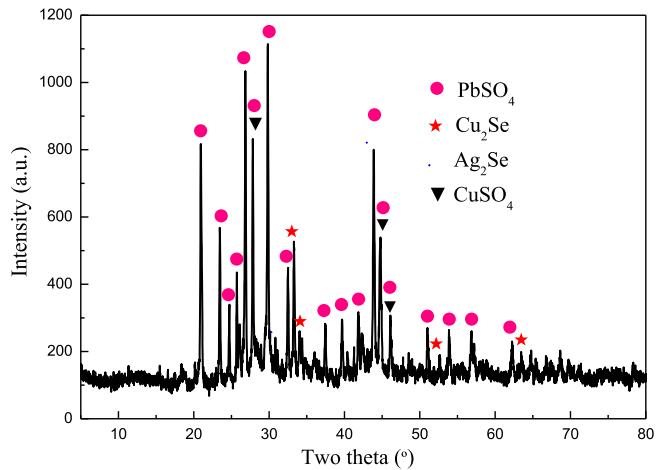
The particle size distribution of anode slime is shown in Table 1. 98.32% of the particles were found to be smaller than 74 um, and furthermore 89.17% of them were lower than 44 um. The results of chemical composition analyses displayed in Tables 2 and 3 indicate that the contents of Cu, Se, Au, Ag and Pb were separately 11.4%, 4.08%, 0.15%, 5.0% and 28.5%, and these five elements occupied the major economic value of anode slime based on the content and market price of each metal/metalloid. The content of hazardous element arsenic also reached 2.12%. The chemical phase analysis shown in Table 4 indicates that the main Cu, Se and As phases were copper sulfate, silver selenide and arsenate, respectively.

The XRD spectrogram of anode slime is shown in Fig. 3, where the main phases were PbSO₄, Cu₂Se, AgSe and CuSO₄. Gold phase was not identified because of its relatively low content. The SEM-EDS analysis result of anode slime is indicated in Fig. 4. A few particles were dispersed, and the others gathered together. The element distribution maps of EDS analysis indicate that Pb and S distributions were consistent, and O was also densely distributed at their areas, demonstrating the presence of PbSO₄. A basically coincident distribution of Cu and S was also observed, and O also occurred at their regions, which implied the existence of CuSO₄. Similarly, the distribution areas of Cu, Se and Ag were also highly consistent, suggesting the occurrences of Ag₂Se and Cu₂Se.

Table 4

Chemical phase analysis results of Cu, Se and As in the anode slime.

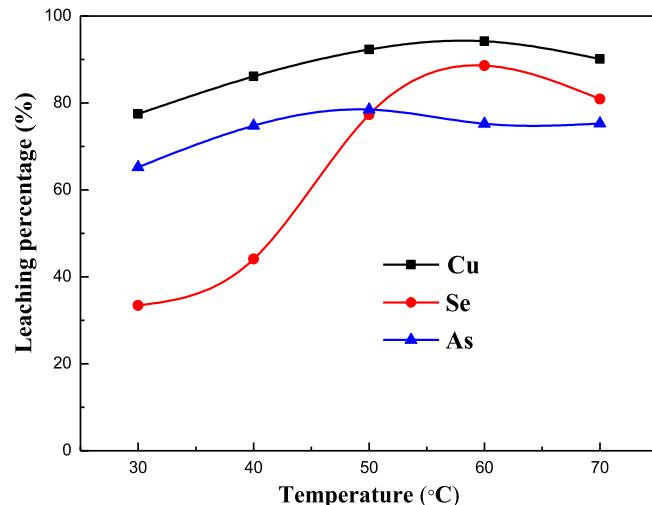
Copper phase	Simple substance copper	Copper oxides	Copper sulfides	Copper sulfate	Cuprous selenide	Total
Content	2.48	0.2	1.98	5.88	0.86	11.4
Distribution	21.7	2.8	12.2	56.4	6.9	100
Selenium phase	Simple substance selenium	Cuprous selenide		Silver selenide	Others	Total
Content	0.62	1.85		1.32	0.29	4.08
Distribution	6.4	24.1		62.4	7.1	100
Arsenic phase	Arsenic oxides	Arsenic sulfides		Arsenate	Others	Total
Content	0.57	0.10		1.15	0.3	2.12
Distribution	4.9	26.7		54.3	14.1	100

**Fig. 3.** XRD pattern of the anode slime.

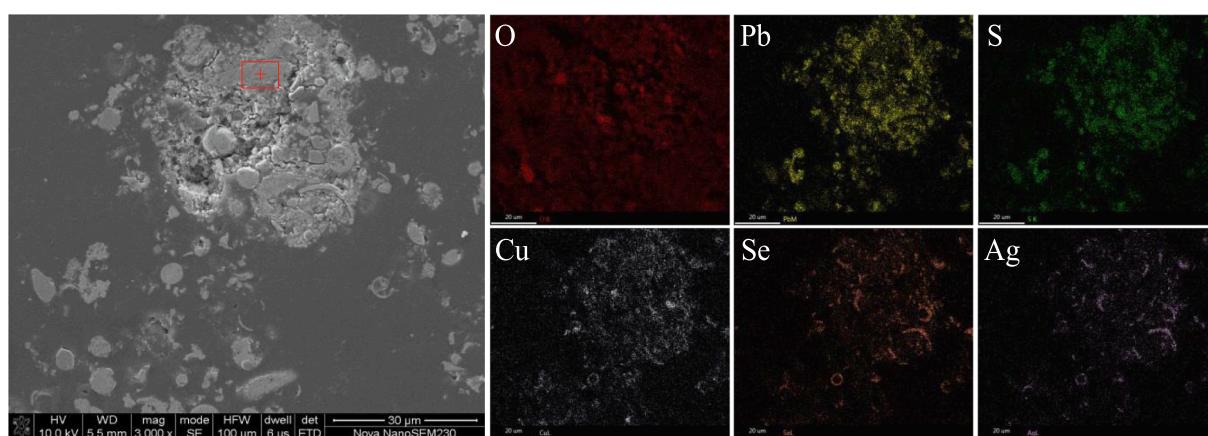
3.2. Copper and selenium extraction

3.2.1. Oxidative acid leaching of copper and selenium

3.2.1.1. Effect of temperature. In this investigation, copper and selenium leaching was performed in H_2SO_4 medium- H_2O_2 was selected as the oxidant because it has strong oxidation ability ($E_0 = 1.77 \text{ V vs SHE}$) and is also a green reagent [27–29]. The purpose of adding NaCl is to hinder silver dissolution from the anode slime as much as possible. It should be noted that arsenic was dissolved under this condition, and thus its leaching was also studied. The effect of temperature on the leachings of copper, selenium and arsenic is shown in Fig. 5. Copper leaching percentage attained 77.5% at 30 °C because most of the copper (i.e. 78.1%) in the anode slime existed in the forms of copper sulfate and simple substance copper that could be easily leached at low temperatures [6]. There was a gradual increase in copper leaching percentage as temperature increased from 30 °C to

**Fig. 5.** Effect of temperature on copper, selenium and arsenic leachings. Conditions: H_2SO_4 150 g/L, H_2O_2 1.5 M, NaCl 6 g/L and time 2 h.

60 °C, which is probably because copper sulfides, one of the copper phases in the slime, dissolved at higher temperatures. In comparison, the increase of temperature in the range of 30–60 °C more evidently promoted selenium dissolution, and the leaching percentage reached 86.2% at 60 °C. The result of thermodynamic analysis displayed in Fig. 6(a, b) can account for this. According to the Eh-pH diagram of Se-Ag-H₂O system, a wide stability region of Se exists between Ag_2Se and H_2SeO_3 , showing that an intermediate product of simple substance selenium may be generated during the oxidation of selenide to selenite. The area of the stable region of Se at 60 °C is smaller than that at 30 °C, which indicates that increasing temperature is beneficial to decrease the stability of Se. In addition, the pulp pH is around −0.5 under the experimental condition of 150 g/L H_2SO_4 . At this pH value, the lowest

**Fig. 4.** SEM-EDS analysis of the anode slime.

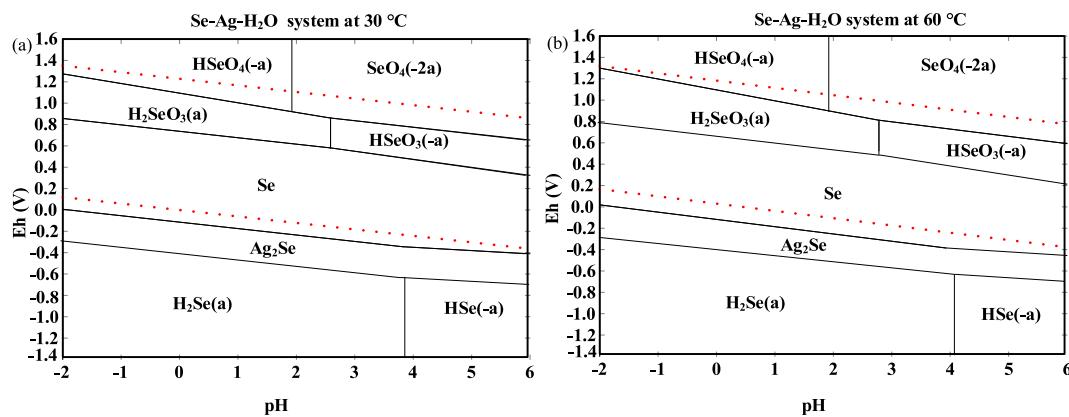


Fig. 6. Eh-pH diagrams of Se-Ag-H₂O system plotted at (a) 30 °C and (b) 60 °C under the conditions of 1.0 M Se and 101 kPa.

potentials for the oxidation of Se to H₂SeO₃ at 30 °C and 60 °C are 0.76 V and 0.74 V, respectively. The potential at 60 °C is obviously lower, revealing that Se oxidation becomes easier at a higher temperature. So, the oxidation of Ag₂Se, the primary selenium phase in the anode slime, was promoted effectively by the increase of temperature.

However, copper and selenium leaching percentages dropped when the temperature continuously increased from 60 °C to 70 °C. This can be attributed to the apparently increased decomposition of H₂O₂ with temperature beyond 60 °C, through Eq. (1) [30]. In our experiment, a large number of bubbles were observed in the pulp at 70 °C, also supporting the decomposition of H₂O₂. Therefore, the actual H₂O₂ concentration for copper and selenium leaching descended, resulting in the decrease of their leaching percentages. Arsenic leaching percentage increased with increasing temperature until 50 °C. Afterwards, it slightly declined at 60 °C and then tended to be stable. From the above, the optimal temperature was chosen as 60 °C that was used for subsequent tests.

The apparent activation energies for copper and selenium leaching were determined on the basis of the Arrhenius equation. The curves of the variation of ln r as a function of 1000/T were plotted and r is the average growth rate of leaching percentage within 2 h, and this method is accordance with the method adopted in our previous studies [10,11]. The apparent activation energies calculated based on the slopes of the two straight lines in the figures were separately 3.22 kJ/mol and 23.54 kJ/mol, which are the typical values for diffusion and mix controlled reactions, respectively [12].



3.2.1.2. Effect of leaching time. The effect of time on copper, selenium and arsenic leachings is displayed in Fig. 7. Apparently, copper leaching kinetics was very fast, and 82.8% of the copper was leached within 30 min. Then, the leaching percentage slightly increased and arrived at 93.7% at 2 h. In comparison, selenium leaching was slower, and the leaching percentage was only 35.9% in 30 min. The potential reason is that in the anode slime the main copper phases are copper sulfate and simple substance copper, and the primary selenium phases are cuprous selenide and silver selenide. Copper sulfate is easily dissolved in water and the oxidation potential of simple substance copper is lower than those of cuprous selenide and silver selenide. Thus, the oxidation dissolution of copper phases is easier than that of selenide phases, resulting in the quicker leaching kinetics of copper [5]. However, it increased to 89.9% with the increase of time to 2 h. When leaching time was beyond 2 h, increasing the time did not result in any significant change in the dissolutions of copper and selenium. Temperature had little effect on arsenic dissolution compared with the situations of copper and selenium, and its leaching percentage basically kept at about 75%. So, the optimal leaching time was chosen to be 2 h.

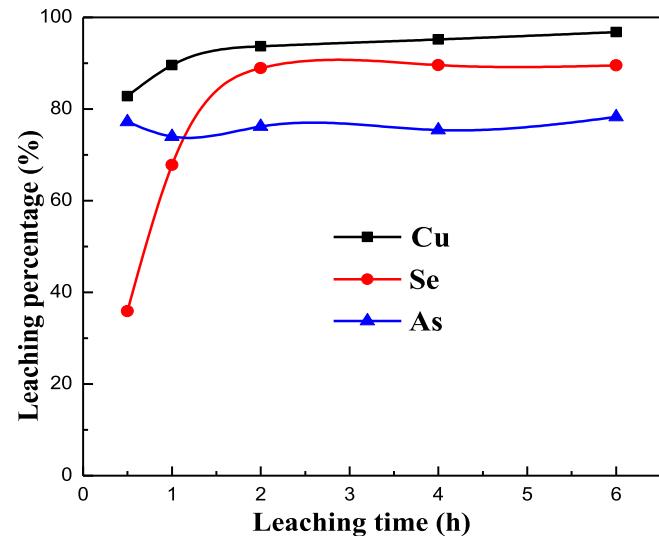


Fig. 7. Effect of time on copper, selenium and arsenic leachings. Conditions: H₂SO₄ 150 g/L, H₂O₂ 1.5 M, NaCl 6 g/L and temperature 60 °C.

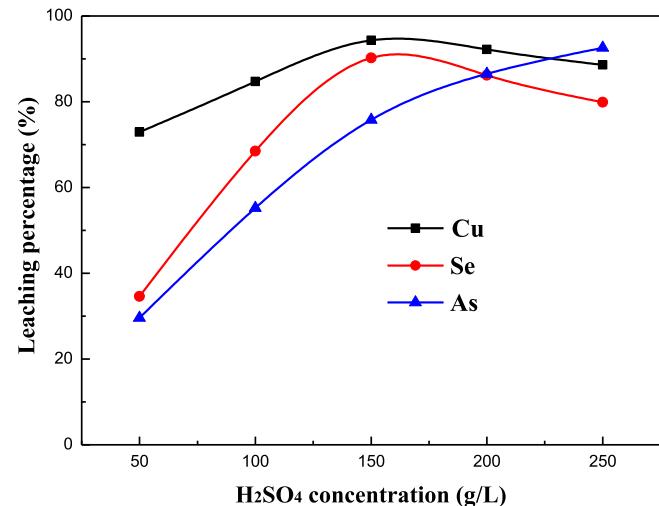


Fig. 8. Effect of H₂SO₄ concentration on copper, selenium and arsenic leachings. Conditions: H₂O₂ 1.5 M, NaCl 6 g/L, temperature 60 °C and time 2 h.

3.2.1.3. Effect of H₂SO₄ concentration. The effect of H₂SO₄ concentration on copper, selenium and arsenic leachings is shown in Fig. 8. Increasing acid concentration brought about obvious increase in the leaching percentages of copper, selenium and arsenic in the initial

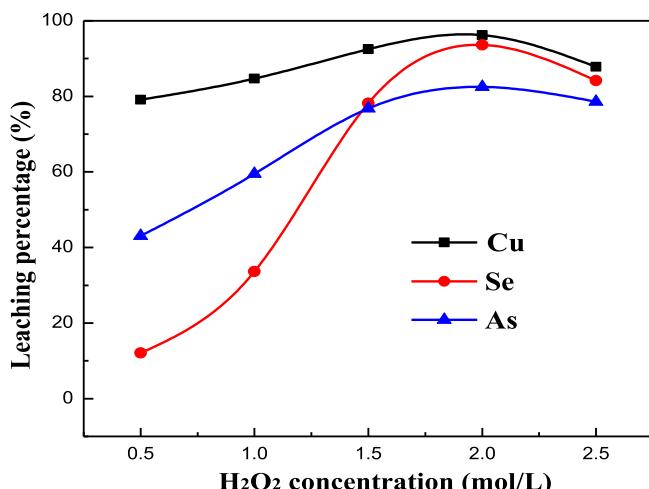


Fig. 9. Effect of H₂O₂ concentration on copper, selenium and arsenic leachings.
Fig. 10. Selenium leaching with different reagents: (a) 150 g/L H₂SO₄, (b) 2 M H₂O₂, (c) 150 g/L H₂SO₄ + 0.5 M H₂O₂, (d) 150 g/L H₂SO₄ + 1 M H₂O₂ and (e) 150 g/L H₂SO₄ + 2 M H₂O₂.

H₂SO₄ concentration range of 50–150 g/L. The potential reason is that increasing hydrogen ion concentration raised the reactant concentration, therefore boosting copper, selenium and arsenic dissolutions. When H₂SO₄ concentration was beyond 150 g/L, arsenic leaching percentage increased continuously while both the copper and selenium leaching percentages declined, which could be ascribed to the formation of passivation species during the leaching. Under the condition of high H₂SO₄ concentration, large quantities of arsenic dissolved in the form of arsenate anion which reacted with cupric cation in the pulp to form insoluble cupric arsenate precipitate (solubility product K_{sp} = 7.6 × 10⁻³⁶) on the surfaces of copper and selenium phases. This caused the passivation of copper and selenium leaching, therefore resulting in the decrease of their leaching percentages [31]. From the above, 150 g/L was selected as the optimal acid concentration.

3.2.1.4. Effect of H₂O₂ concentration. The effect of H₂O₂ concentration on copper, selenium and arsenic leachings is indicated in Fig. 9. Copper and arsenic leaching percentages gradually increased with the increase of H₂O₂ concentration in the initial range of 0.5–2 M, and reached their separate maximums of 96.2% and 82.5% at 2 M H₂O₂. Compared with the situation of copper and arsenic, increasing H₂O₂ concentration more markedly promoted selenium leaching and the leaching percentage increased from 12.1% at 0.5 M H₂O₂ to 93.6% at 2 M H₂O₂. The increased leaching percentages of these three elements resulting from the increase of H₂O₂ concentration can be ascribed to the increased oxidation potential (i.e. oxidation ability) of the pulp. During the leaching, H₂O₂ can decompose into the hydroxyl anion (OH⁻) and active species of hydroxyl radical (HO^{*}) (Eq. (2)) [32]. The HO^{*} has a higher redox potential (2.8 eV) than that of H₂O₂ (1.8 eV) [33,34] which can efficiently oxidize copper and selenium phases in the anode slime. However, H₂O₂ exerted negative effects on copper, selenium and arsenic leachings when its concentration exceeded 2 M. This may be due to the fact that the reactive HO^{*} radical was consumed by excessive H₂O₂, leading to the formation of less reactive HO₂^{*} radical (Eq. (3)) [35]. As a result, the oxidation ability of H₂O₂ was reduced, resulting in the decrease of the leaching percentages of copper and selenium. According to Eq. (2), when H₂O₂ decomposed, equal molar quantities of HO^{*} and OH⁻ are generated, i.e., the concentration change trend of HO^{*} is consistent with that of OH⁻ in a specific range of H₂O₂ concentration when side reaction shown in Eq. (3) does not occur. Also, the OH⁻ concentration can be expressed by the pulp pH because of their relationship of [OH⁻] = 10^{pH-14}. According to our experimental

record, the pulp pH at 0.5, 1, 1.5, 2, 2.5 M H₂O₂ were separately −0.51, −0.47, −0.43, −0.38, −0.37. This indicated that the pH initially increased with the increased H₂O₂ concentration and reached the maximum at 2 M H₂O₂, i.e., HO^{*} concentration also increased in the range of 0.5–2 M H₂O₂. When H₂O₂ concentration exceeded 2 M, the pH basically kept steady, which means that increased H₂O₂ concentration did not promote the reaction in Eq. (2). The excess H₂O₂ likely reacted with HO^{*}, as displayed in Eq. (3). As a result of this, part of the generated HO^{*} was consumed. The above analysis can explain the decrease of leaching percentages of copper, selenium and arsenic when H₂O₂ concentration was higher than 2 M. Based on the above, the pulp pH recorded can be used to support our explanation on the effect of H₂O₂ concentration.



From Figs. 8 and 9, H₂SO₄ and H₂O₂ both exerted an important effect on selenium leaching. In order to further investigate their roles, a series of comparative experiments were conducted, and the results are shown in Fig. 10. As can be seen, only 0.4% and 5.8% of the selenium were leached using single 150 g/L H₂SO₄ or 2 M H₂O₂, and thus both of them were ineffective for selenium leaching. However, when the two components were adopted simultaneously, the selenium leaching percentage reached 93.6% which was much higher than those obtained with single reagent. This indicates that the combination of H₂SO₄ and H₂O₂ displayed an evident synergistic effect on selenium dissolution.

Based on the above thermodynamic analysis and experiment results, a possible synergistic effect mechanism of H₂SO₄ and H₂O₂ was proposed as follows: Selenides such as Ag₂Se and Cu₂Se were firstly oxidized in H₂SO₄ medium by O₂ into intermediate product of simple substance selenium, as described in Eqs. (4) and (5); Then, the generated simple substance selenium was further oxidized by H₂O₂ into selenite, as shown in Eq. (6). The overall oxidizing reactions of selenides are listed as Eqs. (7) and (8).

XRD analyses of the residues obtained with different leaching reagents were performed, as displayed in Fig. 11. No peak of simple substance selenium occurred with single 150 g/L H₂SO₄ (a). Several weak peaks were observed with single 2 M H₂O₂ (b), which means that a small quantity of selenides in the anode slime was oxidized into simple substance selenium. Compared with the situations of single reagent, the peak intensities evidently increased with 150 g/L H₂SO₄ + 0.5 M H₂O₂ (c), indicating the more complete transformation of selenides to simple substance selenium. The peak intensities were

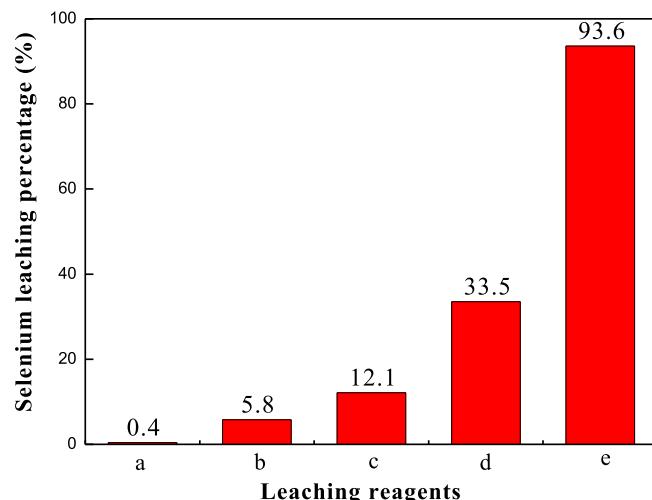


Fig. 10. Selenium leaching with different reagents: (a) 150 g/L H₂SO₄, (b) 2 M H₂O₂, (c) 150 g/L H₂SO₄ + 0.5 M H₂O₂, (d) 150 g/L H₂SO₄ + 1 M H₂O₂ and (e) 150 g/L H₂SO₄ + 2 M H₂O₂.

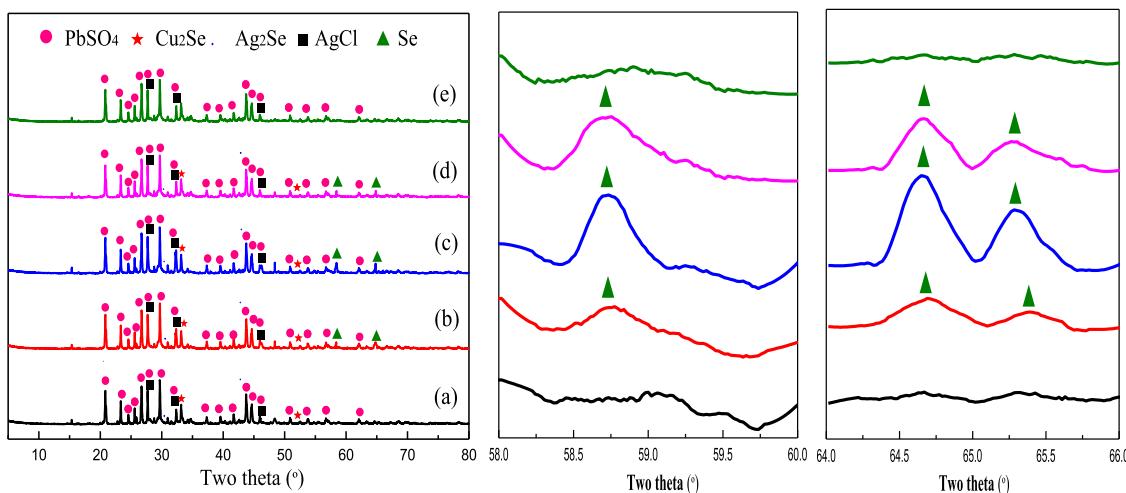
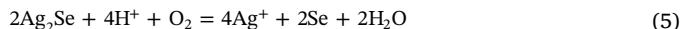
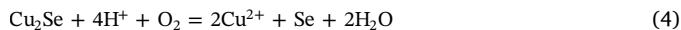


Fig. 11. XRD patterns of the leach residues obtained with different reagents: (a) 150 g/L H₂SO₄, (b) 2 M H₂O₂, (c) 150 g/L H₂SO₄ + 0.5 M H₂O₂, (d) 150 g/L H₂SO₄ + 1 M H₂O₂ and (e) 150 g/L H₂SO₄ + 2 M H₂O₂.

reduced with 150 g/L H₂SO₄ + 1 M H₂O₂ (d), and the reason is that part of simple substance selenium was further oxidized into soluble SeO₃²⁻ and entered into the solution. The peaks disappeared with 150 g/L H₂SO₄ + 2 M H₂O₂ (e), showing that all the simple substance selenium was oxidized under this condition. From the above, intermediate product simple substance selenium could be formed during oxidative acid leaching, which supports the aforesaid mechanism.



Conditions: H₂SO₄ 150 g/L, NaCl 6 g/L, temperature 60 °C and time 2 h.

3.2.2. Recovery of selenium and copper

3.2.2.1. Selenium recovery by sodium sulfite reduction. The chemical compositions analysis of oxidative acid leaching solution indicates that it contained 21933.6 mg/L copper and 7637.8 mg/L selenium. The oxidation-reduction potential of SeO₃²⁻/Se (E₀ = +0.74 V) is higher than that of Cu²⁺/Cu (E₀ = +0.34 V), and thus SeO₃²⁻ is easier to be reduced than Cu²⁺ under the same conditions. So, a two-step reduction process was adopted to recover selenium and copper successively. Na₂SO₃ was used to reduce selenium, and the results of effects of reaction conditions on selenium recovery are indicated in Fig. 12(a–c).

As shown in Fig. 12(a), only 35.6% of selenium was recovered when the SO₃²⁻/SeO₃²⁻ molar ratio was 2:1 (i.e. theoretical dosage). The recovery percentage dramatically increased with the ratio increased, and achieved the maximum of 99.3% at molar ratio 4:1. Further increase of the ratio did not promote selenium reduction. However, copper precipitation percentage rose as the molar ratio increased in the entire abscissa range.

As presented in Fig. 12(b), the impact trend of temperature was analogous with that of SO₃²⁻/SeO₃²⁻ molar ratio for selenium recovery. Selenium recovery percentage arrived at its highest point at 60 °C. On the contrary, copper precipitation percentage gradually declined as the temperature was elevated, which can be ascribed to the enhanced dissolution of newly-generated copper precipitate at higher temperatures 34.

As Fig. 12(c) indicated, the rate of selenium reduction was very quick, and 97.6% of the selenium was reduced in 5 min. The recovery percentage increased to 99.3% at 10 min, and then it basically leveled off. Only 1.1% of copper was reduced within 5 min, and the copper precipitation percentage slowly increased in the time range studied.

Based on the above results, the optimal conditions for selenium recovery were established as follows: Na₂SO₃/SeO₃²⁻ molar ratio 4:1, temperature 60 °C and time 10 min. Fig. 13(a) displays the appearance of obtained product of simple substance selenium under the conditions. The product was black and comprised of uniform spherical particles, and its XRD pattern shown in Fig. 13(b) demonstrates that selenium was the only phase. SEM image displayed in Fig. 13(c) manifests that some spherical particles clustered together. As can be seen from EDS spectrum presented in Fig. 13(d), there was a high peak of selenium, and a copper peak and an arsenic peak were also observed in the spectrum but they were very weak. This indicates that the major element in the product was selenium, and only a small quantity of copper and arsenic existed. The chemical composition analysis shows that the selenium content was 94.2%. From the above, quick and selective selenium reduction could be realized with Na₂SO₃ as the reductant, and a high grade product of simple substance selenium could be obtained.

3.2.2.2. Copper recovery by iron powder replacement. The arsenic concentration in the leaching solution before and after selenium recovery were separately 3498.2 mg/L and 3345.6 mg/L, and thus 3.6% of the arsenic in the anode slime entered into the simple substance selenium. The copper concentration only slightly decreased to 21692.3 mg/L, and iron powder was used to replace copper on the basis of the evident difference between the electrode potentials of the two metals (Fe²⁺/Fe = -0.44 V, Cu²⁺/Cu = +0.34 V). Optimal replacement parameters that were established by conditional tests were Fe/Cu molar ratio 1.4, temperature 25 °C, stirring speed 200 rpm and time 5 min, under which 99.6% of the copper was replaced.

Fig. 14(a) indicates the morphology of sponge copper product gained under the optimum conditions, and it was made up of black flake-shaped solids. Fig. 14(b) shows the XRD pattern, the main detected phases were Cu and Cu₂O. The reason for the occurrence of Cu₂O may be that the precipitated copper particles were partially oxidized as the replacement reaction occurred in an open reactor [36].

SEM-EDS analysis results of the sponge copper are given in Fig. 14(c, d). It can be seen in Fig. 14(c) that the plate-like large particles overlapped with each other, and some fine particles were embedded in the flaky grains. As EDS spectrum in Fig. 14(d) shows, two evident copper peaks were observed, and the peaks of impurity elements

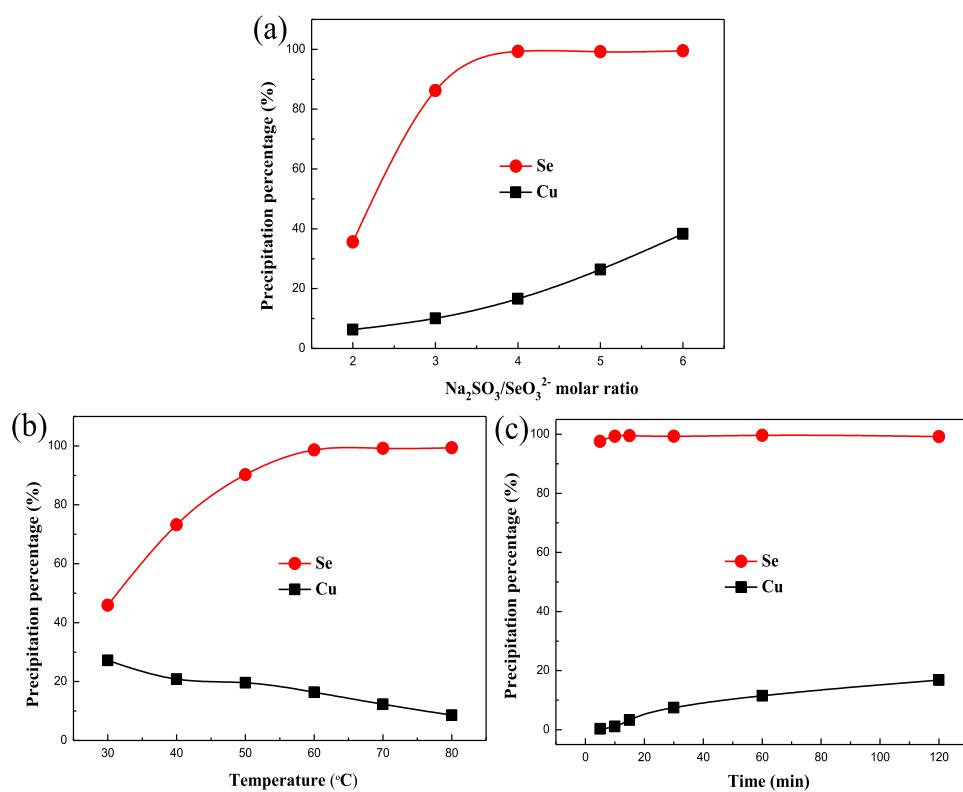


Fig. 12. Effects of reaction conditions on selenium recovery. (a) Effect of Na₂SO₃/SeO₃²⁻ molar ratio under the conditions: temperature 60 °C and time 2 h; (b) effect of temperature under the conditions: Na₂SO₃/SeO₃²⁻ molar ratio 4:1 and time 2 h; (c) effect of time under the conditions: Na₂SO₃/SeO₃²⁻ molar ratio 4:1 and temperature 60 °C.

sulfur, arsenic, iron and oxygen also occurred in the product. The chemical composition analysis performed with acid digestion and ICP-OES indicates that the copper content was 85.3%, and the element oxygen was probably the main remaining component. The existence of oxygen is due to the oxidation of precipitated copper by dissolved oxygen, which supported the XRD result.

After copper recovery, the arsenic concentration in the leaching solution decreased to 2823.1 mg/L, and thus only 12.4% of the arsenic entered the sponge copper and most of the arsenic was still remained in the solution. The element iron was introduced into the copper-containing barren solution and its concentration attained 25935.3 mg/L. For this solution, iron can be utilized to remove arsenic by generating

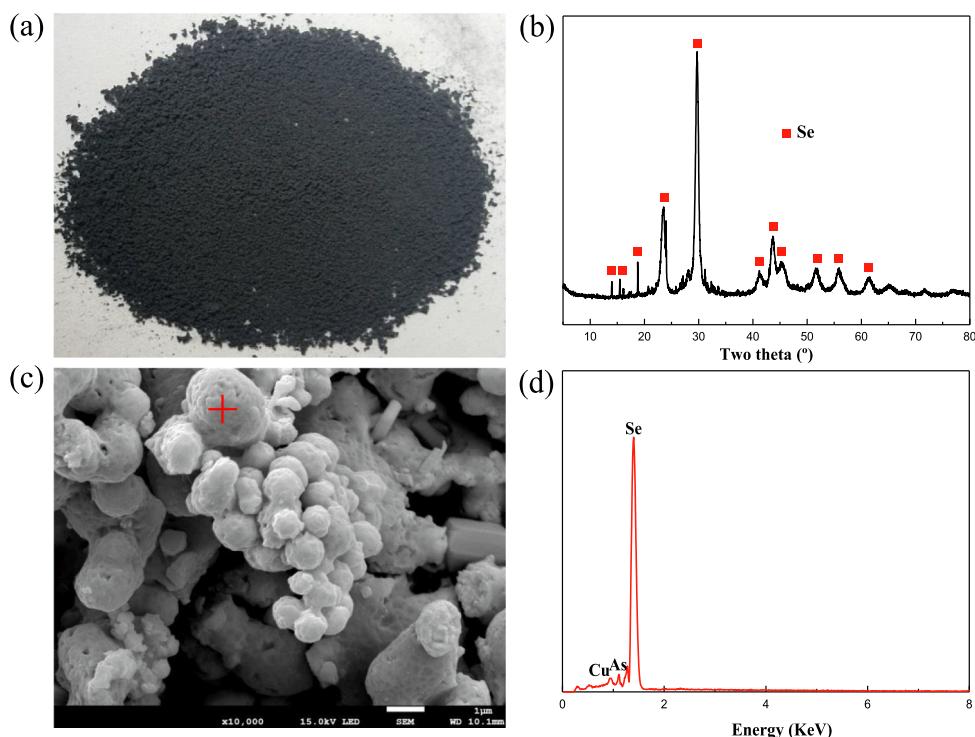


Fig. 13. (a) morphology, (b) XRD pattern, (c) SEM image and (d) EDS spectrum of simple substance selenium product.

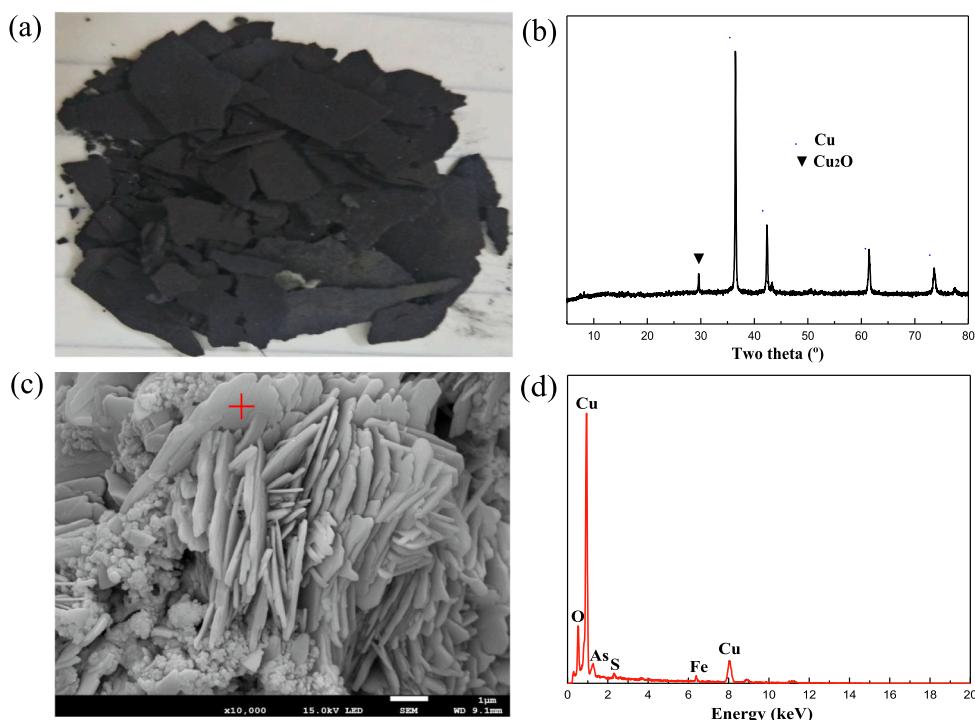


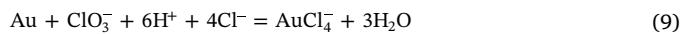
Fig. 14. (a) morphology, (b) XRD pattern, (c) SEM image and (d) EDS spectrum of sponge copper product.

thermodynamically stable phase ferric arsenate ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). This method has the advantages of high arsenic removal percentage and high stability of arsenic precipitate [37]. However, iron content in the solution was excess because the theoretical Fe:As molar ratio was 1:1 for ferric arsenate. After arsenic precipitation, the residual iron could be removed in the form of ferric hydroxide by adjusting the solution pH [38]. Final solution could be recycled back to copper and selenium leaching, as shown in Fig. 1.

3.3. Gold extraction

3.3.1. Chloride leaching of gold

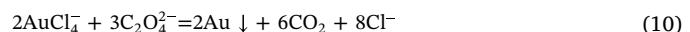
From Fig. 15(a), the acid leaching residue was grayish black, and the XRD pattern in Fig. 15(d) shows that Cu_2Se , AgSe and CuSO_4 which were the main phases in the anode slime disappeared and a new AgCl phase occurred. Simple substance gold is the primary existence form of Au in copper anode slime [17] and its grade increased after oxidative acid leaching based on the result of chemical composition of the leaching residue presented in Fig. 16. $\text{NaClO}_3\text{-H}_2\text{SO}_4\text{-NaCl}$ solution was selected to leach gold, and the reaction is expressed by Eq. (9). One important purpose of using H_2SO_4 and NaCl is to hinder silver and lead dissolutions from the residue by generating PbSO_4 and AgCl precipitates. The optimum leaching parameters established by conditional tests were as follows: NaClO_3 32 g/L, H_2SO_4 150 g/L, NaCl 7.2 g/L, temperature 70 °C and time 4 h, under which 99.3% of the gold was leached. As displayed in Fig. 16, the concentrations of silver and lead in the leaching solution were separately 0.41 mg/L and 15.8 mg/L, and the corresponding leaching percentages were only 0.003% and 0.02%, respectively. This will simplify the composition of leaching solution and facilitate subsequent gold recovery from the solution



3.3.2. Gold recovery

Gold was recovered from the leaching solution by $\text{H}_2\text{C}_2\text{O}_4$ reduction, as indicated in Eq. (10). The optimal reduction parameters established by conditional tests were as follows: $\text{H}_2\text{C}_2\text{O}_4$ 10.5 g/L, pH 1.5,

temperature 70 °C and time 160 min, under which 99.8% of gold was reduced. The morphology of the recovered product is presented in Fig. 17(a). It can be observed that the product had a bright golden color. The SEM images displayed in Fig. 17(b, c) indicate that gold mainly took the shape of thin slice with high transparency, and there were also a small quantity of fine particles. The result of EDS analysis in Fig. 17(d) shows that only a very weak copper peak existed in the spectrum, and the others were gold peaks. The chemical composition analysis indicates that the gold content attained 98.7%. Thus, the purity of product was high and its impurity could be controlled at a low level under the given reduction condition.



3.4. Silver extraction

3.4.1. Sulfite leaching of silver

The gold-leaching residue was pale yellow and AgCl and PbSO_4 were the main phases, as indicated in Fig. 15(b) and (e). Na_2SO_3 is a clean and effective reagent and can be used to leach AgCl through the coordination reaction between SO_3^{2-} and Ag^+ [22], as described in Eqs. (11)-(12). Fig. 18(a) is the silver speciation diagram for $\text{Ag}^+\text{-Cl}^-$ - SO_3^{2-} system under different Na_2SO_3 concentrations. As can be seen, $\text{Ag}(\text{SO}_3)_2^{3-}$ was the main species in the range of 0–0.5 mol/L Na_2SO_3 , and beyond this range $\text{Ag}(\text{SO}_3)_3^{5-}$ became the predominant species.

The test results of effects of reaction conditions on silver leaching are shown in Fig. 19(a-d). It has been reported that the high sodium sulfite consumption was mainly originated from its oxidation by the dissolved oxygen in the pulp [25]. So, a comparative leaching test was carried out to investigate the differences of silver leaching with open and closed reactors. As indicated in Fig. 19(a), both of the silver leachings were unsatisfying at 50 g/L Na_2SO_3 , but the leaching percentage was evidently lower when an open reactor was used, and the likely reason is that Na_2SO_3 in the reactor was quickly consumed by the dissolved oxygen, resulting in the more serious lack of coordination agent to leach silver. Silver leaching percentage increased quickly and reached 86.3% at 250 g/L Na_2SO_3 with the use of an open reactor.

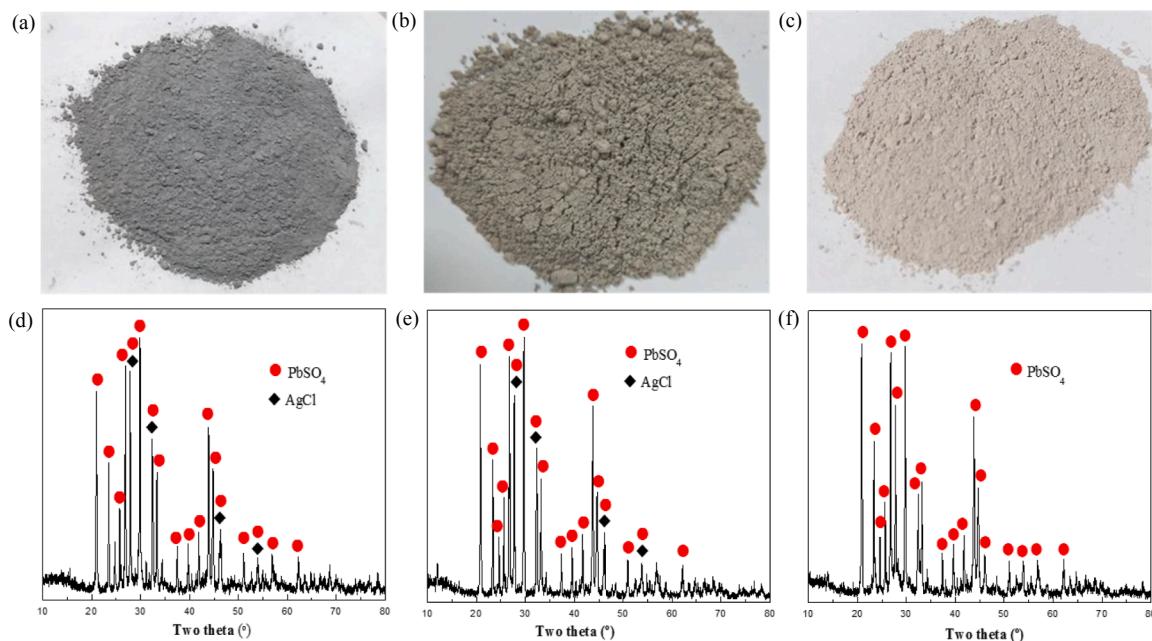


Fig. 15. Morphologies of residues from (a) oxidative acid leaching, (b) chloride leaching and (c) sulfite leaching and their corresponding XRD patterns (d–f).

However, further increase of Na_2SO_3 concentration led to the decrease of leaching percentage. The potential reason is that when Na_2SO_3 concentration was beyond 250 g/L, more sulfite was oxidized into sulfate that reacted with silver sulfite complexes to form silver sulfate precipitate, as depicted by Eqs. (13) to (15). In comparison, silver leaching percentage reached 90.8% at 150 g/L Na_2SO_3 with the use of a closed reactor. Afterwards, it only slightly increased with the increase of concentration until 300 g/L Na_2SO_3 . However, sulfite is more readily crystallized out from solution at higher concentrations, and therefore resulting in the pipe blockage. From the above, it can be concluded that

a satisfactory silver leaching percentage could be obtained with relatively lower concentration of Na_2SO_3 using a sealed reactor. Thus, the following experiments in Fig. 19(b–d) were conducted with sealed reactors, where the Na_2SO_3 concentration was 150 g/L.

As Fig. 19(b) showed, silver leaching percentage increased with increased pH in the initial range of 8–10. This can be explained by the increased stability of sulfite which acts as the leach reagent of silver in this range, as seen in Fig. 18(b). The main species were H_2SO_3 and HSO_3^- under acid conditions in this figure, and SO_3^{2-} didn't occur until the pH increased to 5. After that, the fraction of SO_3^{2-} increased

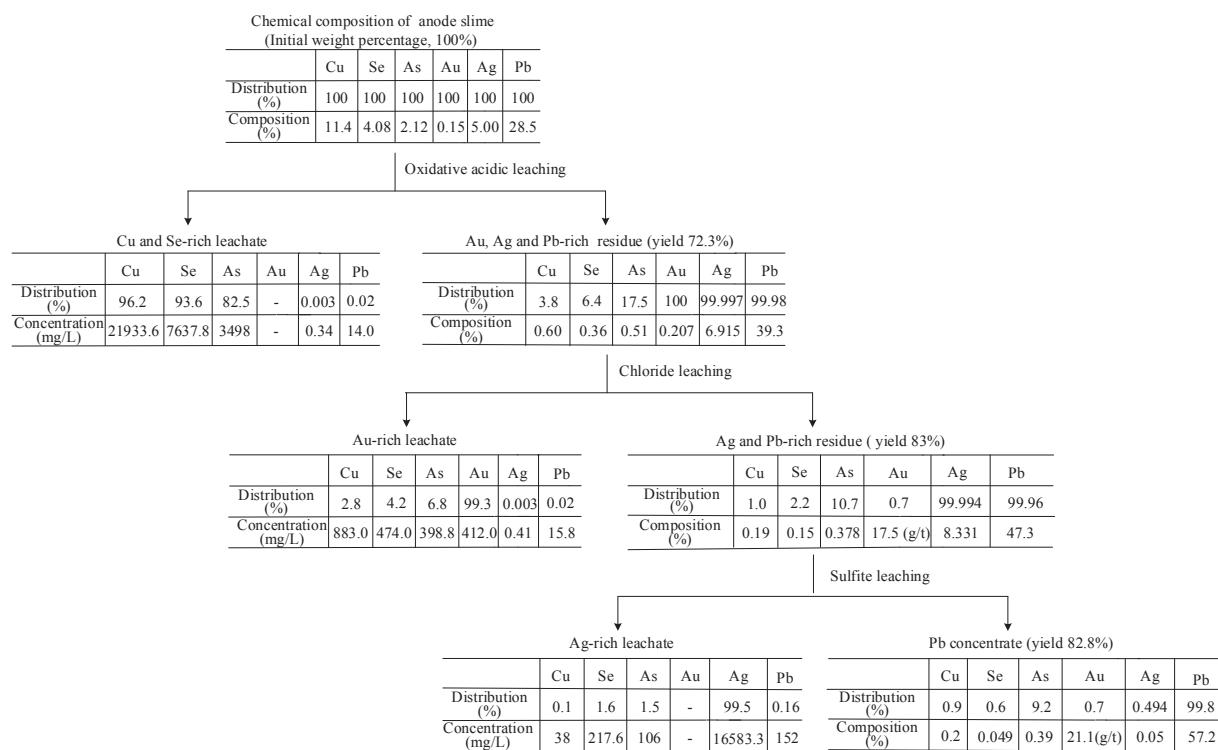


Fig. 16. Distributions of main elements in each leaching in the developed hydrometallurgical process.

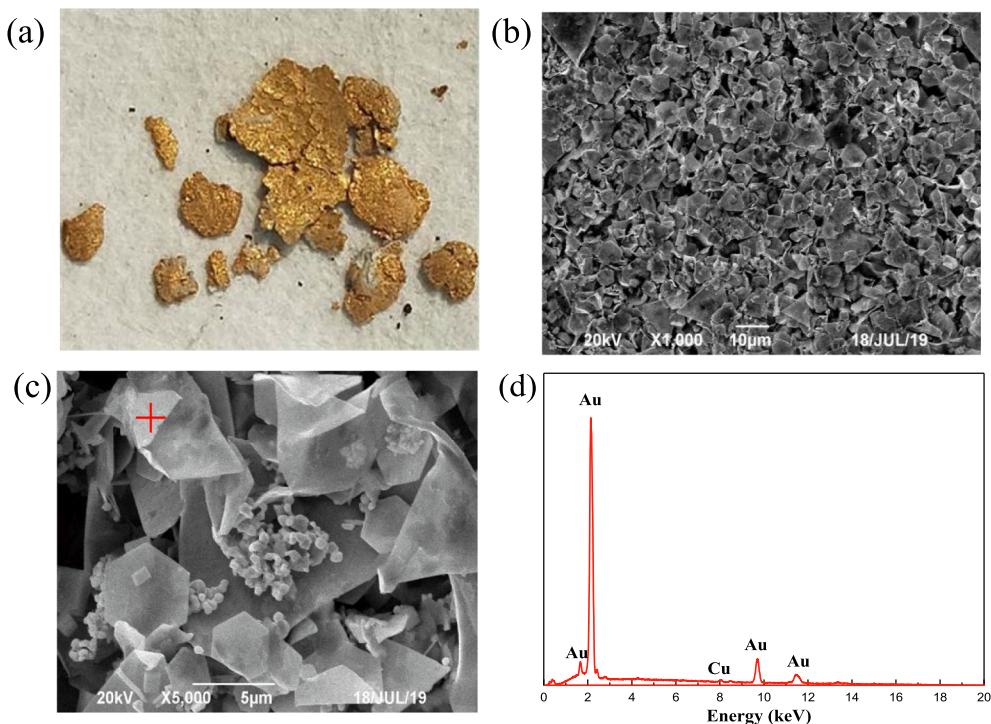


Fig. 17. (a) morphology, (b, c) SEM images and (d) EDS spectrum of metallic gold product.

rapidly and attained its highest point at pH 10. Nevertheless, silver could be precipitated as Ag_2O at a higher pH than 10 [9], leading to the decrease of its leaching percentage in Fig. 19(b).

As indicated in Fig. 19(c), silver leaching percentage increased with an increase of temperature until it reached maximum at 35 °C, and then it dropped gradually. The likely reason for the decrease of leaching percentage is that the solubility of Na_2SO_3 decreased at higher temperatures, leading to the lack of silver ligand (i.e. SO_3^{2-}) in the pulp. As a result of this, the generated silver sulfite complexes were unstable and easily decomposed into silver oxide/hydroxide precipitate. As presented in Fig. 19(d), the increase of time promoted silver leaching, and 99.5% of the silver was leached after leaching for 6 h. After that, silver leaching percentage basically kept steady.

From the above results, the optimal leaching conditions were as follows: Na_2SO_3 150 g/L, temperature 35 °C, pH 10 and time 6 h, under which 99.5% of silver in the gold-leaching residue was leached. The apparent activation energy for silver leaching was also determined by using the same method in Section 3.2.1. The curve of the variation of $\ln r$ as a function of $1000/T$ was and r is the average growth rate of silver

leaching percentage within 3 h. The slope of the straight line in the figure was -1.37849 , and thus the apparent activation energy was determined to be 11.46 kJ/mol, which is the typical value for diffusion controlled reactions [12].

The morphology displayed in Fig. 15(c) indicates the residue is gray, and its XRD pattern in Fig. 15(f) shows that PbSO_4 was the only existed phase. The main chemical composition of residue is shown in Fig. 16, and the lead content reached 57.2%. Therefore, it can be used as feed to lead smelters.

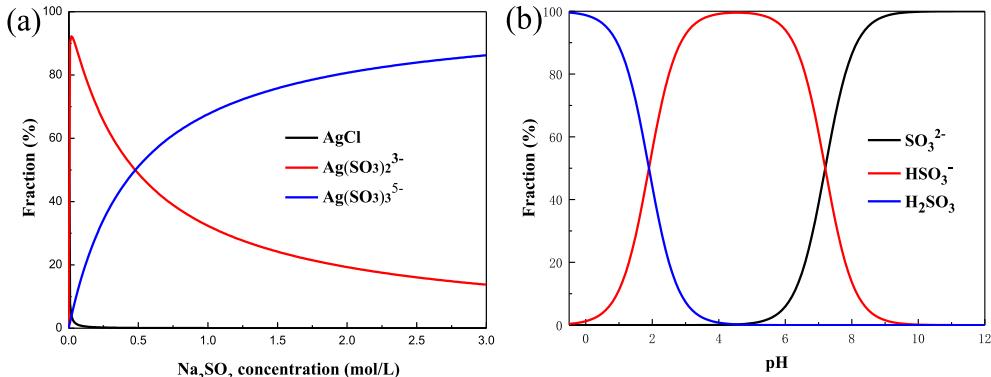
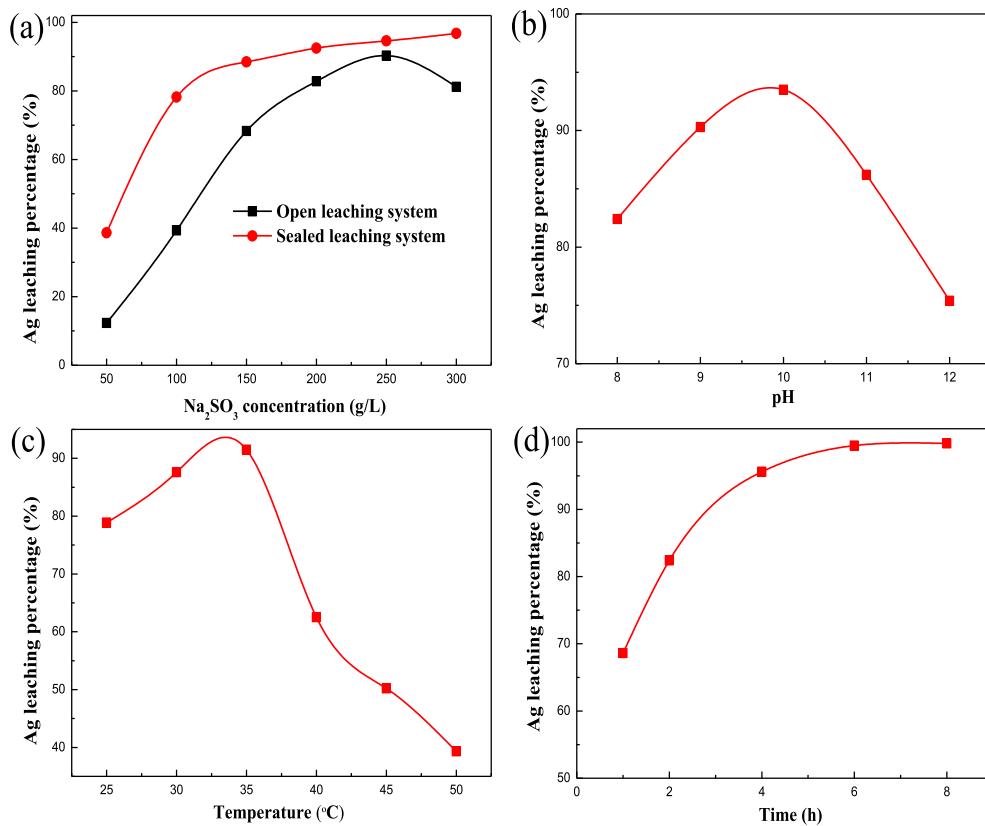


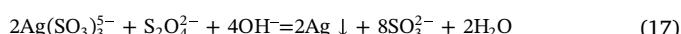
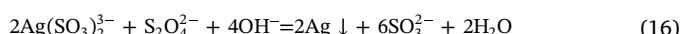
Fig. 18. (a) silver speciation diagram for $\text{Ag}-\text{Cl}-\text{SO}_3^{2-}$ system at different Na_2SO_3 concentrations, and (b) sulfur speciation diagram for $\text{SO}_3^{2-}-\text{H}_2\text{O}$ system at different pH.



3.4.2. Silver recovery

After sulfite leaching, $\text{Na}_2\text{S}_2\text{O}_4$, a green and efficient reductant, was adopted to recover silver from the leaching solution, as displayed in Eqs. (16) and (17). An evident advantage of this recovery method is that the reductant itself is eventually transformed into sulfite, and thus the obtained barren solution can be returned to leaching stage after silver recovery, resulting in the decrease of leaching agent cost. The optimal operating parameters established by conditional tests were as follows: $\text{Na}_2\text{S}_2\text{O}_4$ 16 g/L, pH 10, temperature 25 $^{\circ}\text{C}$ and time 20 min, under which 99.7% of silver was recovered.

The morphology, XRD pattern, SEM-EDS results of obtained silver product are presented in Fig. 20(a–d). Fig. 20(a) shows that the product was consisted of ash black fine particles. Fig. 20(b) indicates that there was only a single phase of metallic silver in the pattern. The SEM imagine shown in Fig. 20(c) manifests that the rounded particles with different sizes stacked mutually. EDS spectrum presented in Fig. 20(d) indicates that an obvious silver peak was detected and a small sulfur peak also occurred, and the chemical composition analysis shows that the silver content achieved 96.5%.



3.5. Element distribution and cost-benefit analyses

3.5.1. Element distribution analysis

Fig. 16 shows the general distribution of main elements in each leaching solution and residue produced by the proposed hydro-metallurgical process in this study. The detailed chemical compositions of the residues after being extracted valuable elements are shown as Table 5.

93.6% of selenium in the anode slime was dissolved by H_2SO_4 leaching assisted with H_2O_2 , and then 99.3% of the dissolved selenium was reduced by Na_2SO_3 . Thus, 92.9% of selenium in the slime went into

Fig. 19. Effects of reaction conditions on silver leaching. (a) effect of Na_2SO_3 concentration with open and sealed reactor under the conditions: pH 9, temperature 25 $^{\circ}\text{C}$ and time 3 h; (b) effect of pH under the conditions: Na_2SO_3 150 g/L, temperature 25 $^{\circ}\text{C}$ and time 3 h; (c) effect of temperature under the conditions: Na_2SO_3 150 g/L, pH 10 and time 3 h; (d) effect of time under the conditions: Na_2SO_3 150 g/L, temperature 35 $^{\circ}\text{C}$ and pH 10.

the simple substance selenium product. The rest of the selenium in the residue was mainly leached into the pregnant solution of chloride leaching of gold. After gold reduction, the dissolved selenium was remained in the barren solution.

As with selenium, the majority of copper (96.2%) in the slime was leached during oxidative acid leaching. After iron powder precipitation, 99.6% of the leached copper was recovered. Therefore, 95.8% of copper in the slime entered the sponge copper product. Similarly, the residual copper in the residue was mainly dissolved into the gold-containing pregnant solution, and a small portion of dissolved copper entered the metallic gold product and the rest was kept in the barren solution after gold reduction.

Gold was stable and undissolved during selenium and copper leaching, and enriched in the oxidative acid leaching residue. 99.3% of gold in the residue was oxidized and went into the solution through chloride leaching, and 99.8% of dissolved gold was recovered by $\text{H}_2\text{C}_2\text{O}_4$ reduction. Thus, 99.1% of gold in the slime entered the metallic gold product. The unleached gold went into the final residue/lead concentrate, and the gold content attained 21.1 g/t. When selling this lead concentrate product, the benefit of gold is included because its content has achieved the level of price calculation.

Silver was almost not leached during oxidative acid leaching and chloride leaching, and enriched in the residue. Afterwards, 99.5% of silver was extracted by sulfite leaching in a sealed reactor, and 99.7% of dissolved silver was reduced by $\text{Na}_2\text{S}_2\text{O}_4$. Therefore, 99.4% of silver in the slime went into the metallic silver product. Similar to the situation of gold, the unextracted silver also entered the lead concentrate.

As the most abundant element in the slime, lead was nearly insoluble during oxidative acid leaching, chloride leaching and sulfite leaching. As a result, lead was efficiently enriched after the leachings of selenium and copper, gold and silver, and 99.8% of element lead went into the lead concentrate.

Compared with the preceding valuable elements, the distribution of hazardous element arsenic is relatively scattered. 82.5% of the arsenic

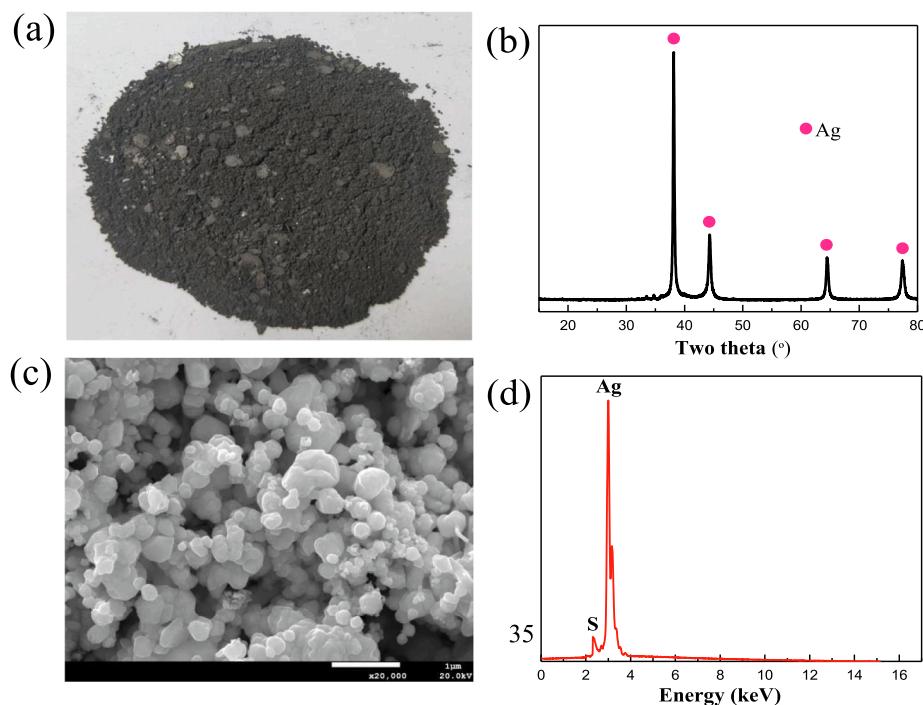


Fig. 20. (a) Morphology, (b) XRD pattern, (c) SEM image and (d) EDS spectrum of metallic silver product.

was dissolved during oxidative acid leaching. After selenium and copper recoveries, 3.6% and 12.4% of the arsenic went into the products of simple substance selenium and sponge copper, and the rest of dissolved arsenic was remained in the copper-containing barren solution. 6.8% and 1.5% of the arsenic were separately leached at the stages of chloride leaching and sulfite leaching, and then they were kept in the gold-containing and silver-containing barren solutions. The remaining 9.2% of arsenic entered the lead concentrate.

It is well-known that arsenic is a poisonous and hazardous impurity element whose contents separately reached 0.15%, 0.27% and 0.39% in the simple substance selenium, sponge copper and lead concentrate. As a result of this, the price calculation coefficients of these products will be reduced slightly, leading to their a little decreased economic values. To eliminate/weaken the adverse effects of arsenic on the recovery of valuable elements, the solution potential should be closely monitored to make it remained at a suitable level for the purpose of minimizing the co-precipitation of arsenic with selenium and copper during their recoveries from the leaching solution. In addition, oxidative alkaline leaching pretreatment can be performed to leach the remaining arsenic in the oxidative acid leaching residue before gold leaching, and sodium arsenate hydrate product is obtained after evaporation and cooling crystallization of the leaching solution. This will be beneficial to decrease the arsenic content in the lead concentrate [39].

According to Fig. 1, three kinds of barren solutions will be produced after recovering selenium and copper, gold and silver from their leaching solutions. When these solutions are recycled, the impurity components may gradually accumulate with the increased recycling times. This may exert an unbeneficial effect on the leaching of valuable elements. To solve this potential problem, a certain proportion of these

solutions can be regularly open-circuited to remove the accumulated impurity components with the purification technologies of neutralization precipitation, sulfide precipitation, membrane separation, etc. After the purification treatment, the solutions can be returned to the leaching stage.

3.5.1.1. Cost-benefit analysis. A preliminary analysis of cost and benefit for treating one ton of anode slime was conducted to evaluate the economic feasibility of the developed hydrometallurgical process. For the calculation of total cost, electric power, water, workers' wage and reagent were considered [40]. The total benefit involves the obtained products of selenium, copper, gold, silver and lead. The price of each metal/metalloid was its spot price from the website of Shanghai Metals Market (<https://www.smm.cn/>, visiting date 2019-10-21). The prices of used chemical reagents, industrial electric power, water, and workers' wage and price calculation coefficient of each metal/metalloid for the products were provided by Qinghai Copper Industry Co., Ltd. The calculation results are given in Table 6.

As can be seen, the costs of electric power, water, workers' wage and reagent were 487.9, 34.8, 4500 and 4838.3 CNY, respectively. Therefore, the total cost was 9861 CNY. 41.7 kg simple substance selenium, 129.6 kg sponge copper, 1.4865 kg metallic gold, 52.2 kg metallic silver and 496.9 kg lead concentrate were gained, and their total value was 712078.8 CNY. Based on the above calculation results, a revenue of 702217.8 CNY is obtained. So, the developed hydrometallurgical process in the study possesses good economic benefit.

A preliminary comparison of the developed process with previously reported hydrometallurgical processes was also made. First of all, the mixture of H_2SO_4 and H_2O_2 was used for selenium and copper leaching.

Table 5

The chemical compositions of the residues after being extracted useful elements (wt.%).

Leach residue	Cu	Se	Ag	Au	Pb	As	O	S	Bi	Sb	Ba	Sn	Ni
Oxidative acid leaching	0.6	0.36	6.915	0.15	39.3	0.51	17.8	7.50	6.25	3.95	3.63	1.87	1.71
Chloride leaching	0.19	0.15	8.331	17.5	47.3	0.378	23.6	6.25	5.06	3.86	3.86	1.72	1.65
sulfite leaching	0.2	0.049	0.05	21.1	57.2	0.39	22.8	8.26	4.6	4.63	4.88	1.46	1.58

Table 6

Estimated cost and benefit for treating one ton of anode slime by the developed process.

Stage	Process	Electric consumption (kW·h)	Cost (CNY) ^a
Selenium and copper recovery	Oxidative acid leaching	44	57.2
	Filtering	20	26
	Selenium reduction	3.6	4.6
	Filtering	20	26
	Copper reduction	1.8	2.3
	Filtering	20	26
Gold recovery	Chloride leaching	66	85.8
	Filtering	20	26
	Reduction	44	57.2
	Filtering	20	26
Silver recovery	Sulfite leaching	72	93.6
	Filtering	20	26
	Reduction	4	5.2
	Filtering	20	26
Total Water	Price (CNY/ton)	3	487.9
Workers' wage	Wage (CNY/person-day)	250	34.8
Reagent	Price (CNY/kg)	Dosage (kg)	Cost (CNY)
98% H ₂ SO ₄	0.4	1293	556
30% H ₂ O ₂	1	1135	1135
Fe powder	2	130.6	261.2
NaClO ₃	4.2	120	504
H ₂ C ₂ O ₄	2.9	41.2	119.5
Na ₂ SO ₃	2	978	1956
Na ₂ S ₂ O ₄	6	48.3	289.8
NaCl	0.3	56	16.8
Total Products	Price (metal/metalloid price, CNY/kg × calculation coefficient)		4838.3
Selenium	110 × 0.95	41.7	4357.7
Copper	47 × 0.83	129.6	5055.7
Gold	340000 × 0.98	1.4865	495301.8
Silver	4260 × 0.90	52.2	200134.8
Lead concentrate	16.9 × 0.50	496.9	4198.8
Total	340000 × 0.85	496.9 × 21.1 g/t	3030
			712078.8

^aThe price of industrial electric power is 1.3 CNY/kW·h.

Compared with the previous one-step processes of HNO₃ + H₂SO₄ and MnO₂ + H₂SO₄, the oxidant H₂O₂ is better than HNO₃ and MnO₂ because it avoids the formation of harmful gas (NO_x) and introduction of foreign ions (Mn²⁺). In comparison with the two-step processes of H₂SO₄ leaching of copper followed by alkaline leaching of selenium under atmospheric or high pressure conditions, higher leaching percentages of copper and selenium could be obtained with lower cost.

Then, the combination of NaClO₃, H₂SO₄ and NaCl was adopted for gold leaching. Compared with previously reported cyanide leaching, thiourea leaching and thiosulfate leaching, the leaching reagents are nontoxic/low-toxic, and furthermore gold could be selectively leached without the dissolutions of silver and lead.

In addition, silver was leached with Na₂SO₃ under a sealed reactor and then recovered from the leaching solution by Na₂S₂O₄ reduction. In comparison with previous ammonia leaching, Na₂SO₃ is an eco-friendly reagent. Compared with previous sulfite leaching under an open condition, the adoption of a sealed condition effectively decreases the sodium sulfite consumption deriving from its oxidation by dissolved oxygen in the pulp. More importantly, in comparison with previous silver recovery from the leaching solution by hydrazine hydrate or

formaldehyde reduction, Na₂S₂O₄ is very environmentally friendly. In addition, the oxidation reaction product of Na₂S₂O₄ is Na₂SO₃, i.e. the silver leaching reagent. Thus, the return of this barren leaching solution to leaching stage will be favorable to decline the reagent dosage and furthermore reduce the cost of silver extraction.

4. Conclusions

In this work, a clean and economical hydrometallurgical process was developed to recover Cu, Se, Au, Ag and Pb from a copper anode slime. The combination of H₂SO₄ and H₂O₂ showed a synergistic effect on selenium leaching, and H₂O₂ promoted the oxidation of the intermediate product simple substance selenium to selenite in H₂SO₄ medium. 93.6% of selenium and 96.2% of copper were leached by the oxidative acid leaching, 99.3% of selenium and 99.6% of copper in the leaching solution were successively recovered by Na₂SO₃ reduction and iron powder replacement. 99.3% of gold was selectively leached from the acid leaching residue with NaClO₃-H₂SO₄-NaCl solution and then 99.8% of the dissolved gold was recovered using H₂C₂O₄ reduction. 99.5% of silver in the chloride leaching residue was dissolved using Na₂SO₃ in a sealed reactor and 99.6% of the leached silver was recovered by Na₂S₂O₄ reduction. The products of simple substance selenium, sponge copper, metallic gold and metallic silver were obtained whose purities separately achieved 94.2%, 85.3%, 98.7% and 96.5%. A lead concentrate containing 57.2% of lead was also gained. The element distribution analysis indicates that 92.9% of selenium, 95.8% of copper, 99.1% of gold, 99.4% of silver and 99.8% of lead in the anode slime entered their separate products, but the distribution of element arsenic was relatively scattered. The cost-benefit analysis manifests that a revenue of 702217.8 CNY can be gained for treating one ton of the copper anode slime by the proposed hydrometallurgical process, which shows good economic benefit and industrial application prospect.

Declaration of Competing 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.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 51504293), Qinghai Provincial Major Scientific and Technological Special Project of China (No. 2018-GX-A7), Hunan Provincial Natural Science Foundation of China (No. 2018JJ4038) and Fundamental Research Funds for the Central Universities of Central South University (No. 150110003) for their financial supports of this research. The authors also expressed their thanks to Qinghai Copper Industry Co., Ltd for providing anode slime sample.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.124762>.

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