



Selective reduction separation and recovery of tellurium and bismuth from acidic leaching solution

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Abstract: A simple and efficient method was proposed to selectively separate and recover tellurium and bismuth in an acidic leaching solution of tellurium–bismuth ore by Na_2SO_3 and Fe powder. Then, the selective reduction mechanism was investigated by SEM–EDS, XRD, XPS, ICP–OES, etc. 99.83% Te in leaching solution can be reduced by Na_2SO_3 with an excess coefficient of 16 at 80 °C for 10 min, and the grade of crude tellurium can reach 93.78%. Besides, the stirring action can accelerate the reduction of Te because the dissolution of Na_2SO_3 is promoted. Subsequently, 99.39% Bi in the reduced solution can be displaced by Fe powder with an excess coefficient of 7.5 at 60 °C for 40 min, and the grade of crude bismuth can reach 92.35%. Finally, cyclic leaching of tellurium–bismuth ore was adopted to enrich Te(IV) and Bi(III) concentrations and decrease the Fe(III) concentration in leaching solution, which can efficiently decrease the consumption of Na_2SO_3 .

Key words: selective reduction; displacement; tellurium; bismuth; leaching solution

1 Introduction

Tellurium (Te) and bismuth (Bi) are widely used in chemistry, metallurgy, solar panels, semiconductor, crystal, electronics and other modern industries [1,2]. They are always associated with other minerals, such as copper, lead, zinc, gold, silver, tungsten, and molybdenum [3,4]. Thus, at present, Te and Bi are mainly recovered from anode slime, smelting slag or smelting dusts [5,6]. In addition, some Bi can also be recovered from some Bi_2O_3 or Bi_2S_3 ores [7]. In recent years, with the increase of global demand for Te and Bi [8], more attention has been paid to recovering Te and Bi from other tellurium- or bismuth-bearing ores or

metallurgical by-products.

Tellurium–bismuth ore, found in Dashuigou, Sichuan Province, China, is an excellent raw material for producing tellurium and bismuth products [9]. The ore is characterized by extremely low grades of Te and Bi, high sulfur content, complex phase composition, etc. The traditional processes are not suitable for the treatment of the tellurium–bismuth ore [10,11]. Thus, SHAO et al [11,12] proposed an oxidic–acidic leaching method to simultaneously and efficiently enrich Te and Bi in acidic leaching solution. It avoids the problems of long process, high energy consumption, large amounts of solid waste and SO_2 pollution [8]. According to previous research [11,12], the acidic leaching solution contains many ions such as Bi^{3+} ,

Te^{4+} , Fe^{3+} , Fe^{2+} , Ca^{2+} , Mg^{2+} , Al^{3+} , Cl^- , SO_4^{2-} , and H^+ . How to efficiently recover Te and Bi from the solution is very important.

Some methods have been proposed to recover Te from solution, such as the copper displacement method [13,14], reduction method [15–17], neutralization precipitation method [18,19], and electrolysis method [20–22]. For the recovery of Bi, hydrolysis precipitation [23,24], sulfide precipitation [25], electrolysis [26], displacement method [27], and adsorption method [28] were investigated. However, the concentrations of Te, Bi and other impurity ions in the solution limit the application of neutralization precipitation, electrolysis, hydrolysis precipitation, and adsorption method. Cu_2Te or Bi_2S_3 can be obtained by the copper displacement method or sulfide precipitation for Te or Bi, rather than elemental Te or Bi [13,25]. Thus, these methods are not suitable for the recovery of Te and Bi from the complex leaching solution in this work. There is a certain difference between the potentials of Te^{4+}/Te and Bi^{3+}/Bi , indicating that they can be separated by adjusting the type and amount of reductants. Thus, SO_2 and Na_2SO_3 were selected for the reduction of Te(IV) in the leaching solution. Due to the toxicity of SO_2 , Na_2SO_3 was used in this work. Besides, Fe is usually used to recover Bi from solution in actual production. However, the complexity of the leaching solution can make the separation and recovery of Te or Bi very complicated and difficult. The simultaneous extraction of Te and Bi from the leaching solution has not been investigated and reported, and the selective reduction mechanism of Te and Bi has still been unclear. Generally, it is necessary to study the separation behaviors of Te and Bi from acidic leaching solution.

The present work aims to develop a simple and efficient method for the separation and recovery of Te and Bi from the acidic leaching solution of tellurium–bismuth ore. The method involves the selective reduction of Te in leaching solution followed by the displacement of Bi, which is controlled by Na_2SO_3 or Fe powder. This work also aims to clarify the selective reduction behaviors of Te and Bi by combining thermodynamic analysis, element migration law, and product morphology evolution. Finally, the cyclic leaching of tellurium–bismuth ore is proposed to efficiently recover Te and Bi.

2 Experimental

2.1 Materials

The tellurium–bismuth ores mainly consist of 1.52% Te, 2.99% Bi, 13.67% S, 25.77% TFe, 16.51% CaO, 8.07% MgO, 1.97% Al_2O_3 , and 3.60% SiO_2 (in mass fraction). The acidic leaching solution was acquired from tellurium–bismuth ore according to our previous research [12], whose chemical composition is listed in Table 1. The concentrations of Te and Bi are greatly low, at only 2.83 and 5.13 g/L, respectively. They exist in the leaching solution in the form of Te^{4+} , HTeO_2^+ , and Bi^{3+} [12]. Other initial materials are analytical grade chemical reagents of $\sim 100\ \mu\text{m}$ Fe powder (>98.0 wt.%) and Na_2SO_3 (>98.0 wt.%), provided by Chengdu Kelong Chemical Co., Ltd., China.

Table 1 Concentrations of main metal elements in leaching solution (g/L)

Te	Bi	Fe	Ca	Mg
2.83	5.13	69.59	1.33	6.99
Al	Cu	Mn	Ti	Co
2.21	0.04	0.79	0.01	0.001

2.2 Procedure and characterization

Firstly, Te was selectively reduced by Na_2SO_3 . A 100 mL beaker filled with 20 mL leaching solution was placed in a water bath pot. At the target temperature, a certain amount of Na_2SO_3 was added to the beaker to obtain the reduced solution and crude Te. The chemical compositions of the reduced solution were detected by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000). Subsequently, about 0.5 mL of solution was dropped on a high-purity monocrystalline silicon wafer and then dried in a vacuum drying oven. Finally, the residue was kept on the silicon wafer and determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) to obtain the valence states of Fe, Te, and Bi in the reduced solution. The phases of crude Te were detected by X-ray diffraction analyzer (XRD, RIGAKUD/MAX 2500PC) with a scanning speed of $2\ (^{\circ})/\text{min}$. The micro-morphology and element distribution of the crude Te were investigated by scanning electron microscope (SEM) coupled with energy dispersive spectrometer (EDS) (TESCAN

VEGA 3 LMH SEM). Based on the experiments above, various factors, such as reductant dosage, reduction time, reduction temperature, and stirring action, were studied systematically.

Bi in the reduced solution was displaced by Fe powder from reduced solution. Similarly, a 100 mL beaker filled with 20 mL reduced solution was placed in a water bath pot. At the target temperature, a certain amount of Fe powder was added to the beaker to obtain the displaced solution and crude Bi. The chemical compositions of the displaced solution were detected by ICP-OES, and the crude Bi was characterized by XRD and SEM-EDS. Thus, the effects of various influencing factors on the recovery of Bi were studied, including displacer dosage, displacement time, and displacement temperature. Under suitable conditions, crude Te and Bi can be obtained, and their compositions were further determined by ICP-OES. Finally, the effect of cyclic leaching of tellurium–bismuth ore on the recovery of Te was investigated. The leaching solution obtained by using original immersion liquid to leach the tellurium–bismuth

ore, is defined as the first leaching solution. Subsequently, the i th ($i=2, 3, 4, 5$) leaching solution was obtained by using the $(i-1)$ th leaching solution to leach the tellurium–bismuth ore, where i is the leaching cycle number of the tellurium–bismuth ore. Then, the chemical compositions of leaching solution were determined by ICP-OES. Besides, the effect of Na_2SO_3 dosage on the selective reduction of Te was further researched after cyclic leaching.

3 Results

3.1 Selective reduction of Te from leaching solution

Figure 1 presents the effects of various influencing factors on the precipitation efficiency of different elements, including reductant dosage, reduction time, reduction temperature, and stirring action. Here, the Na_2SO_3 excess coefficient (NEC) is used to express Na_2SO_3 dosage according to Reactions (1) and (2) and the reports of XU et al [29]. Notably, the valence state of Te in Te^{4+} and HTeO_2^+ is +4, so that the conversion of Te^{4+}

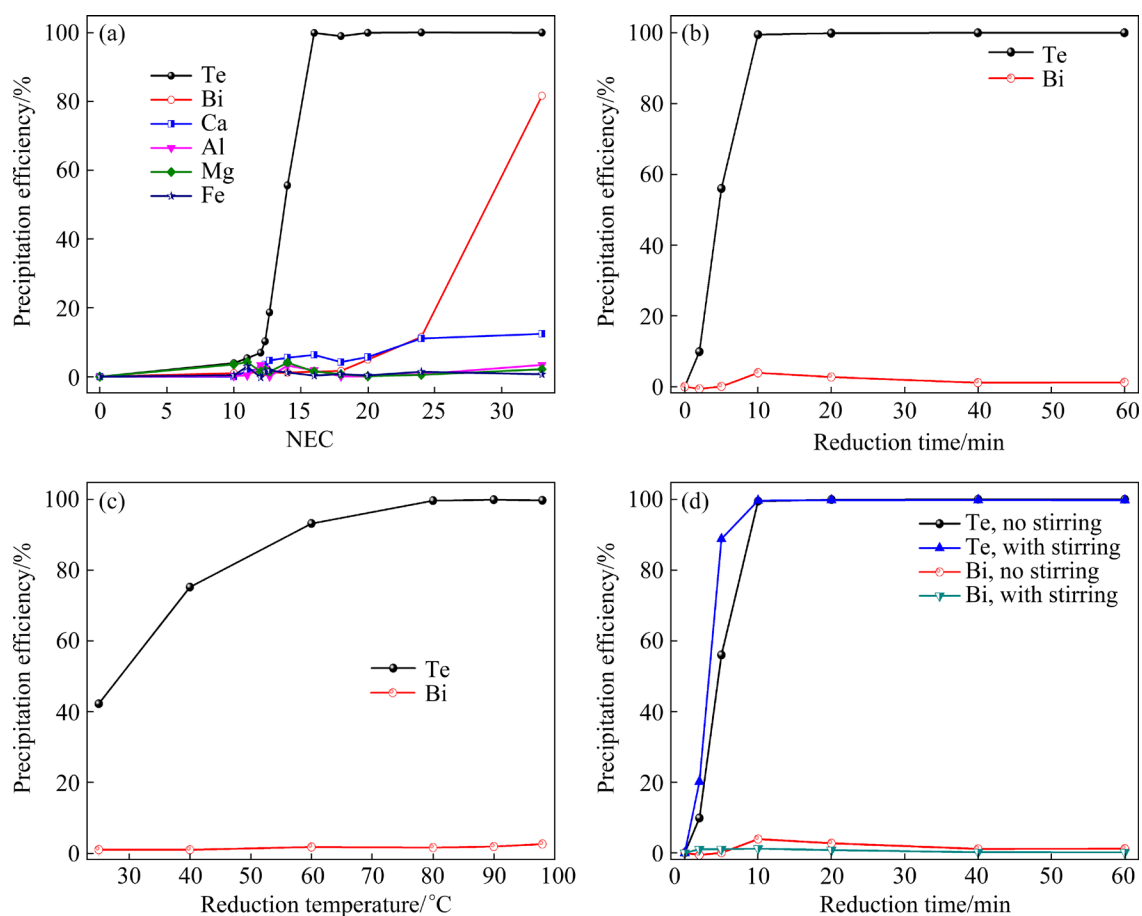
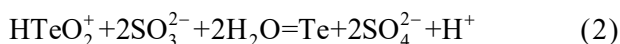
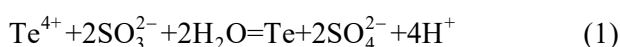


Fig. 1 Effects of various factors on precipitation efficiencies of different elements: (a) NEC; (b) Reduction time; (c) Reduction temperature; (d) Stirring action

and HTeO_2^+ to Te consumes the same amount of Na_2SO_3 . NEC has a significant influence on the reduction of Te(IV) at 90 °C for 60 min without additional stirring (Fig. 1(a)). When NEC is less than 10, Te and Bi in leaching solution cannot be reduced to metallic elements. With increasing NEC, the precipitation efficiency of Te firstly increases rapidly and then plateaus, while that of Bi first stays the same and then increases. When NEC increases to 16, the precipitation efficiency of Te can reach 99.83%, while the precipitation efficiency of Bi can only reach 1.51%. The change of Na_2SO_3 dosage has a very small impact on the precipitation efficiencies of Al, Mg, and Fe, which are always less than 2%, indicating that Al, Mg, and Fe cannot be reduced into the residue. The precipitation efficiency of Ca increases because Ca^{2+} in leaching solution can combine with SO_4^{2-} coming from the reduction of Na_2SO_3 to form slightly soluble CaSO_4 [12]. Thus, the suitable NEC is 16, which is relatively large because the leaching solution has a very low Te(IV) concentration and a high Fe(III) concentration.



As the reduction time and reduction temperature increase with a NEC of 16 without additional stirring (Figs. 1(b) and (c)), the precipitation efficiency of Te firstly rises and then plateaus, while the precipitation efficiency of Bi remains basically unchanged and is less than 2% because of the limited Na_2SO_3 dosage. During the reduction process, the average reduction speed of Te(IV) in 0–2 min is lower than that in 2–10 min, because Na_2SO_3 particles take time to dissolve into leaching solution without external stirring. The reduction temperature has a significant effect on the precipitation efficiency of Te. With the increase of reduction temperature from 25 to 80 °C, the precipitation efficiency of Te also increases from 42.21% to 99.74%. This indicates that higher reduction temperature is beneficial to the reduction and separation of Te(IV) in leaching solution. Therefore, 10 min and 80 °C were selected as the suitable reduction time and reduction temperature for the selective reduction of Te(IV), respectively.

Under a stirring speed of 300 r/min controlled by magnetic stirring, the reduction speed of Te in the leaching solution increases significantly

(Fig. 1(d)). After reducing for 2 min, the precipitation efficiency of Te can reach 20.19% with stirring action, while 9.87% without stirring action. After reducing for 5 min, the precipitation efficiency of Te can reach 88.78% with stirring action, which is 1.58 times as much as that without stirring action. After 10 min, the precipitation efficiency of Te achieves its peak value regardless of stirring. Therefore, stirring action can accelerate the dissolution of Na_2SO_3 and further promote the reduction of Te(IV).

In summary, 99.83% of Te in leaching solution can be reduced to crude Te under suitable conditions: NEC of 16, 10 min, and 80 °C. As shown in Table 2, the grade of Te in crude Te can reach 93.78%, and the remaining metal impurities mainly include Ca, Mg, Fe, and Bi.

Table 2 Composition of crude tellurium (wt.%)

Te	Bi	Fe	Ca	Mg	Al	Cu	Mn	Others
93.78	0.39	0.79	1.23	1.18	0.05	0.06	0.18	Bal.

3.2 Displacement of Bi from reduced solution

Figure 2 shows the effects of various factors on the precipitation efficiencies of different elements, including displacer dosage, displacement time, and displacement temperature. Similarly, the Fe powder excess coefficient (FEC) was used to express the Fe powder dosage according to Reaction (3). As FEC, displacement time, and displacement temperature increase, the precipitation efficiency of Bi firstly increases slowly and then plateaus, while the precipitation efficiencies of Ca, Mg, and Al are always less than 2%, which indicates that the impurity metal ions have little effect on the displacement of Bi. Excessive Fe powder will lead to a surplus and further affect the grade of crude Bi, while insufficient Fe powder cannot reduce Bi in the reduced solution as much as possible. The precipitation efficiency of Bi can reach 99.5% at 80 °C for 60 min when FEC is 7.5 (Fig. 2(a)). It is worth noting that FEC is relatively high because the reaction with H^+ will increase the consumption of Fe powder and the low Bi(III) concentration in the reduced solution will also increase FEC. The displacement speed is the largest within the initial 0–5 min, and the precipitation efficiency of Bi can reach 99.40% after 40 min (Fig. 2(b)). The precipitation efficiency of Bi increases slowly and then plateaus with increasing

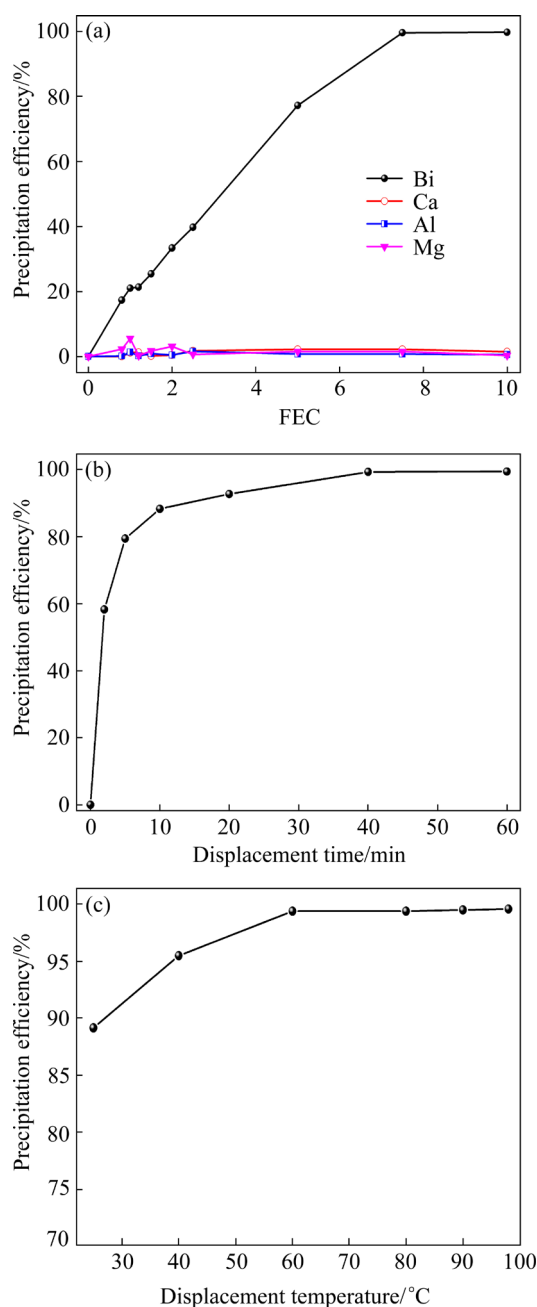


Fig. 2 Effects of various factors on precipitation efficiencies of different elements in reduced solution: (a) FEC; (b) Displacement time; (c) Displacement temperature

temperature, and it can reach 89.15% at 25 °C, 95.49% at 40 °C, and 99.39% at 60 °C (Fig. 2(c)). Based on the results above, FEC of 7.5, 40 min, and 60 °C can be regarded as the suitable conditions for the displacement of Bi(III). 99.39% of Bi in the reduced solution can be displaced by Fe powder, the grade of Bi in crude Bi can reach 92.35%, and the remaining metal impurities mainly include Fe, Ca, Mg, Al, etc (listed in Table 3).



Table 3 Composition of crude bismuth (wt.%)

Bi	Te	Fe	Ca	Mg	Al	Cu	Mn	Ti	Others
92.35	0.26	3.14	0.69	0.16	0.02	0.06	0.02	0.02	2.10

4 Discussion

4.1 Mechanism of selective reduction and separation of Te and Bi

From Fig. 1(a), the reduction of Te(IV) can be divided into three parts: (1) Te(IV) cannot be reduced to Te when NEC is less than 10; (2) Te(IV) in leaching solution can be separated by controlling NEC in the range of 10–16; (3) Bi can also be reduced to crude Te when NEC increases to about 18, and much Bi can be reduced to crude Te after nearly 25. This implies that there is competitive reduction during the selective reduction process. The competitive relationship was firstly revealed by the transformation of the ionic valence state in leaching solution during the reduction process. As shown in Fig. 3, when NEC increases from 0 to 10, the peak of Fe(III) shifts to the peak of Fe(II), while the peaks of Te(IV) and Bi(III) have no significant change. Fe^{3+} cannot be completely transformed into Fe^{2+} because of the reduction limitation of Fe(III) and the oxidation of Fe(II) during the preparation of the sample. This indicates that Fe^{3+} in leaching solution can be preferentially reduced to Fe^{2+} . With NEC increasing from 10 to 16, the peak of Te(IV) gradually disappears, while the peak of Bi(III) has no change. This implies that Te(IV) can be reduced to metallic element when NEC is in the range of 10–16.

The selective reduction sequence of ions in the leaching solution is usually controlled by thermodynamic conditions. Thus, this process was analyzed by combining Gibbs free energy changes, Pourbaix diagrams and potentials. When Na_2SO_3 or Fe powder is added directly into leaching solution, some corresponding reactions may occur. Table 4 shows their Gibbs free energy changes and equilibrium constants at 298.15 K [30,31]. Te(IV) and Bi(III) in leaching solution can be reduced to metallic elements, and Fe^{3+} can only be reduced to Fe^{2+} rather than Fe. According to the Pourbaix diagrams of Te–H₂O and Bi–H₂O [12,32] and Reactions (9) and (10), the elemental Te and Bi

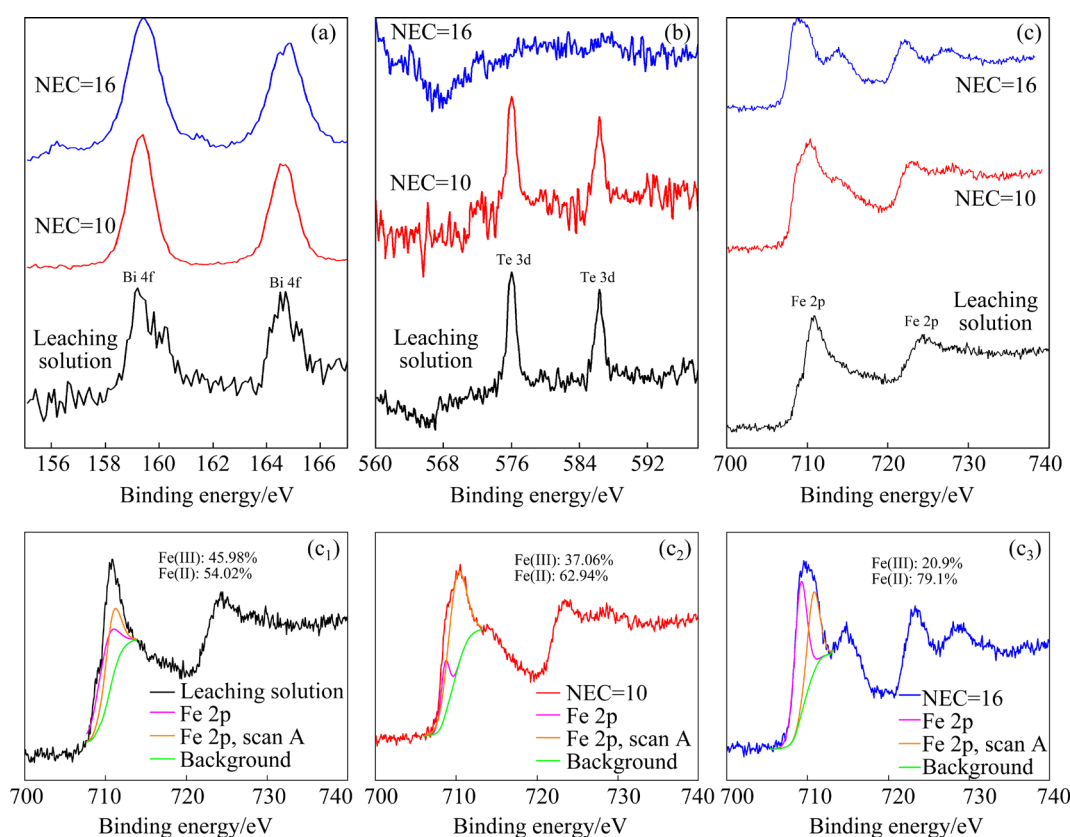


Fig. 3 XPS peaks of Bi, Te, and Fe in leaching solution and solution after selective reduction with NEC values of 10 and 16: (a) Bi; (b) Te; (c) Fe; (c₁–c₃) XPS peaks of Fe in different solutions

Table 4 Possible reactions, their Gibbs free energy changes and equilibrium constants at 298.15 K

No.	Chemical reaction	$\Delta G^\ominus/(\text{kJ}\cdot\text{mol}^{-1})$	$\lg K$
1	$\text{Te}^{4+} + 2\text{SO}_3^{2-} + 2\text{H}_2\text{O} = \text{Te} + 2\text{SO}_4^{2-} + 4\text{H}^+$	-261.510	45.832
2	$\text{HTeO}_2^+ + 2\text{SO}_3^{2-} + 2\text{H}_2\text{O} = \text{Te} + 2\text{SO}_4^{2-} + \text{H}^+$	-255.172	44.721
3	$2\text{Bi}^{3+} + 3\text{Fe} = 3\text{Fe}^{2+} + 2\text{Bi}$	-400.417	70.177
4	$\text{HTeO}_2^+ + 3\text{H}^+ = \text{Te}^{4+} + 2\text{H}_2\text{O}$	6.338	-1.111
5	$2\text{Fe}^{3+} + \text{SO}_3^{2-} + \text{H}_2\text{O} = 2\text{Fe}^{2+} + \text{SO}_4^{2-} + 2\text{H}^+$	-169.761	29.752
6	$\text{Fe}^{2+} + \text{SO}_3^{2-} + \text{H}_2\text{O} = \text{Fe} + \text{SO}_4^{2-} + 2\text{H}^+$	57.735	-10.119
7	$2\text{Bi}^{3+} + 3\text{SO}_3^{2-} + 3\text{H}_2\text{O} = 2\text{Bi} + 3\text{SO}_4^{2-} + 6\text{H}^+$	-247.091	43.305
8	$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4$	-12.207	2.139
9	$\text{Te} + 4\text{H}^+ = \text{Te}^{4+} + 2\text{H}_2$	219.254	-38.426
10	$2\text{Bi} + 6\text{H}^+ = 2\text{Bi}^{3+} + 3\text{H}_2$	183.572	-32.173
11	$\text{Te}^{4+} + 2\text{Fe} = \text{Te} + 2\text{Fe}^{2+}$	-409.620	71.790
12	$\text{HTeO}_2^+ + 2\text{Fe} + 3\text{H}^+ = \text{Te} + 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$	-403.282	70.679
13	$\text{Fe} + 2\text{H}^+ = \text{Fe}^{2+} + \text{H}_2$	-72.282	12.668
14	$2\text{Fe}^{3+} + \text{Fe} = 3\text{Fe}^{2+}$	-220.870	38.709
15	$2\text{Te}^{4+} + 2\text{Bi}^{3+} + 7\text{Fe} = 2\text{BiTe} + 7\text{Fe}^{2+}$	-378.222	66.287
16	$3\text{Te}^{4+} + 2\text{Bi}^{3+} + 9\text{Fe} = \text{Bi}_2\text{Te}_3 + 9\text{Fe}^{2+}$	-1219.872	213.793
17	$2\text{Te}^{4+} + 2\text{Bi}^{3+} + 7\text{SO}_3^{2-} + 7\text{H}_2\text{O} = 2\text{BiTe} + 7\text{SO}_4^{2-} + 14\text{H}^+$	243.552	-42.663
18	$3\text{Te}^{4+} + 2\text{Bi}^{3+} + 9\text{SO}_3^{2-} + 18\text{H}_2\text{O} = \text{Bi}_2\text{Te}_3 + 9\text{SO}_4^{2-} + 36\text{H}^+$	2027.638	-355.182

present stably in the solution and can be further separated by filtration. Notably, when Fe powder firstly is added into the leaching solution, Te(IV) and Bi(III) can be reduced to BiTe or Bi₂Te₃ based on Reactions (15) and (16). Thus, Fe powder cannot be firstly added into the leaching solution to reduce Te(IV) and Bi(III).

Because the Gibbs free energy changes can only reveal the possibility of reaction, the reaction sequence is usually controlled by the corresponding electrode potential during the selective reduction process. Thus, the electrode potential was considered by taking the reaction of metal ions (Mⁿ⁺) with Fe as an example.



The Gibbs free energy change of Reaction (19) can be expressed as follows [33]:

$$\Delta_r G_m = -2nFE \quad (20)$$

where R is the molar gas constant, 8.314 J/(mol·K); n is the number of transferred electrons; F is the charge of 1 mol electron; E denotes the electrode potential of Reaction (19), which can be calculated by Eq. (21):

$$E = \varphi \left(\frac{M^{n+}}{M} \right) - \varphi \left(\frac{Fe^{2+}}{Fe} \right) \quad (21)$$

where φ is the electrode potential between the metal ion and the corresponding metal.

If a reaction can happen spontaneously, the following equations should be satisfied because E needs to be more than 0 and $\Delta_r G_m$ needs to be less than 0:

$$\varphi(M^{n+}/M) > \varphi(Fe^{2+}/Fe) \quad (22)$$

Similarly, metal ions (Mⁿ⁺) can be reduced spontaneously by Na₂SO₃ powder, and Eq. (23) can be obtained:

$$\varphi(M^{n+}/M) > \varphi(SO_3^{2-}/SO_4^{2-}) \quad (23)$$

The electrode potential relationship between metal ions and their corresponding products is shown in Fig. 4 [34,35]. The potential of Fe³⁺/Fe²⁺ is the highest and greater than that of Te⁴⁺/Te and SO₄²⁻/SO₃²⁻. However, the potential of Fe²⁺/Fe is lower than that of SO₄²⁻/SO₃²⁻. It implies that Fe³⁺ can be preferentially reduced to Fe²⁺ but cannot be further reduced to Fe. There is a certain difference between the potentials of Te⁴⁺/Te and Bi³⁺/Bi, which indicates that they can be separated by adjusting the

type and amount of reductant. Impurity metal ions, such as Ca²⁺, Mg²⁺, and Al³⁺, cannot be reduced into the residue, because their corresponding potentials are relatively negative. These results are consistent with Fig. 1(a).

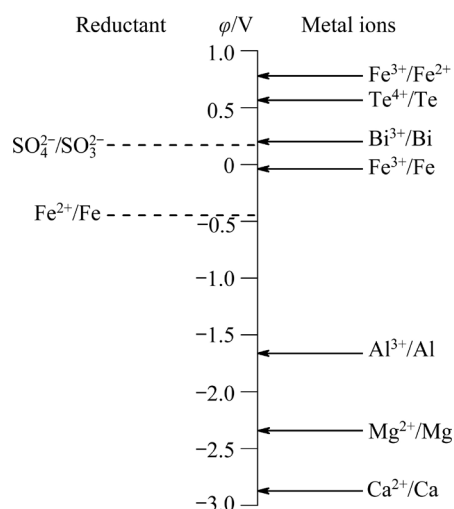


Fig. 4 Standard electrode potentials of various metal ions and their corresponding products

In addition to element migration and thermodynamic conditions, the selective reduction mechanism was further clarified by the phase evolution and microscopic morphology evolution. Based on Figs. 1(a) and 3, Fig. 5 presents the effect of NEC on the microscopic morphology of crude Te at 90 °C for 60 min. When NEC is less than 13, there are no corresponding SEM images because of the extremely low precipitation efficiency of Te and few Te products. As NEC increases, the crude Te particles grow gradually and then reach a peak when NEC increases to 16. At the same time, some needle-like crystals mainly including Ca, S, and O appear on the surface of crude Te. Based on the detection results, the needle-like or rod-shaped crystals are mainly calcium sulfate. Ca²⁺ and SO₄²⁻ in the leaching solution are saturated [12]. However, their saturation state can be broken because of the formation of some SO₄²⁻ after the reduction of Na₂SO₃, further resulting in the precipitation of calcium sulfate. More Na₂SO₃ can bring about more SO₄²⁻, further promoting the growth and coarsening of calcium sulfate. Therefore, the Na₂SO₃ dosage should be as low as possible to prevent the formation of calcium sulfate when Te(IV) in the leaching solution is reduced into crude tellurium as much as possible.

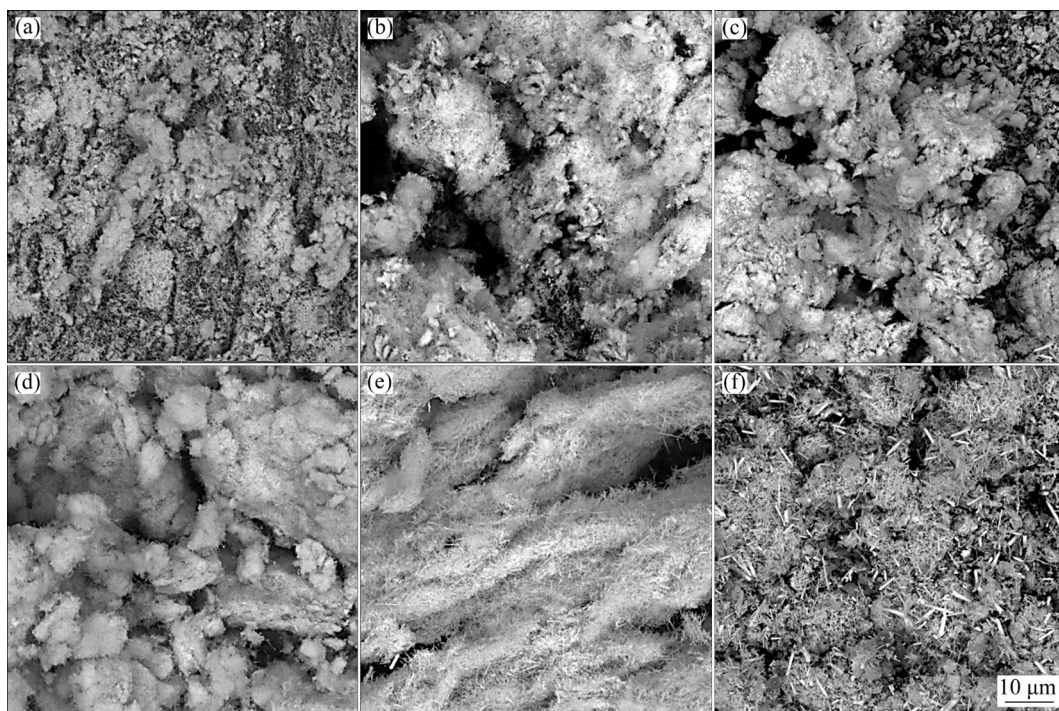


Fig. 5 SEM images of crude tellurium after selective reduction of leaching solution with different NEC values: (a) 13; (b) 16; (c) 18; (d) 20; (e) 24; (f) 32

After selective reduction of Te(IV), Bi in the reduced solution is further separated and recovered by Fe powder. Based on Fig. 2(b), the effect of displacement time on the phase evolution of crude Bi with FEC of 7.5 at 80 °C is presented in Fig. 6. After displacement for 2 min, the peak of crude Bi can be detected. With increasing displacement time, the peak of Fe gradually weakens until it disappears, and the peak intensity of elemental Bi gradually increases. It indicates that Fe powder is gradually displaced by Bi. Figure 7 and Table 5 further reveal the microscopic morphology evolution and EDS results of Bi, respectively. After displacement for 2 min, white particles are visible on the surface of the Fe powder (Fig. 7(a)), indicating that Fe powder begins to be displaced by Bi, and Bi particles attach to the surface of Fe powder. As the displacement time increases, the elemental Bi gradually covers the entire surface of the Fe powder. When the displacement time increases to 40 min, there are no black particles in the crude Bi (Fig. 7(e)), which indicates that Fe powder has been displaced by Bi as much as possible. Notably, many small crude Bi particles can form around the crude Bi particles. Fine Bi particles form large free surface energy to facilitate agglomeration according to the free surface energy theory [36].

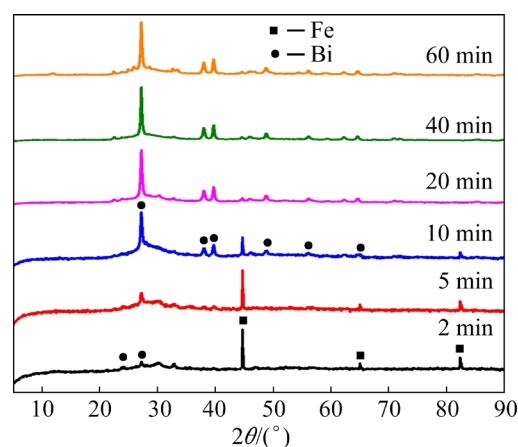


Fig. 6 XRD patterns of residue after Fe displacement from solution after selective reduction of leaching solution

In summary, the selective reduction and separation mechanisms of Te and Bi are shown in Fig. 8. Te(IV) and Bi(III) can be separated and recovered by controlling the dosage and addition sequence of Na_2SO_3 and Fe powder. As the selective reduction process goes, the color of the solution gradually transforms from tawny to green, because Fe^{3+} in the leaching solution is gradually reduced to Fe^{2+} and Fe^{3+} can be preferentially reduced to Fe^{2+} , which is consistent with Figs. 1(a) and 3. The crude Te is gray-black granular and the

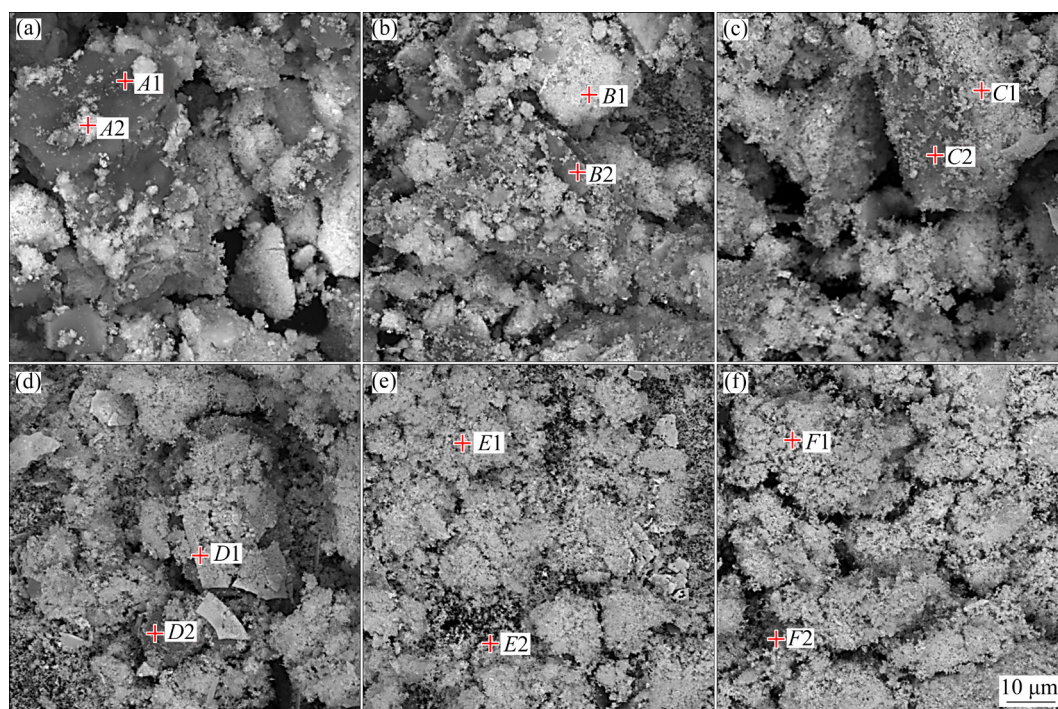


Fig. 7 SEM images of crude bismuth at different displacement time: (a) 2 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 40 min; (f) 60 min

Table 5 EDS results for crude bismuth in Fig. 7 (wt.%)

Point	Fe	Bi	Point	Fe	Bi
A1	96.23	3.77	D1	2.17	97.83
A2	10.65	89.35	D2	88.58	11.42
B1	5.49	94.51	E1	0.01	99.99
B2	80.51	19.49	E2	0.02	99.98
C1	20.12	79.88	F1	–	100.00
C2	46.51	53.49	F2	–	100.00

crude Bi black granular, whose XRD patterns are presented in Fig. 9. The XRD patterns of the products have only the diffraction peak of elemental Te or Bi, indicating that Te and Bi in the leaching solution can be efficiently separated and reduced to elemental Te and Bi. Te^{4+} or HTeO_2^+ can transform to elemental Te by Na_2SO_3 , and Bi^{3+} can be displaced to elemental Bi by Fe powder. After selective reduction of Te(IV) and Bi(III) in the leaching solution, Fe^{2+} in the tail liquid can be oxidized to Fe^{3+} by chlorination or oxidation, which can render the tail liquid recycled to leach the tellurium–bismuth ore.

4.2 Improvement of selective reduction and separation of Te and Bi

In this work, to decrease the consumption of

Na_2SO_3 dosage, cyclic leaching [37] of tellurium–bismuth ore was proposed to enrich the Te(IV) concentration and decrease the Fe(III) concentration in leaching solution.

Figure 10 shows the effect of the leaching cycle number on the leaching efficiency and the concentrations of Te and Bi from the tellurium–bismuth ore with a liquid/solid ratio of 6:1 mL/g at 90 °C for 40 min, according to previous research [12,38]. As the leaching cycle number increases, the concentrations of Te and Bi in the leaching solution gradually increase, while the leaching efficiencies of Te and Bi gradually decrease, similar to the result reported by HU et al [39]. As the leaching cycle number increases to 3, the concentrations of Te and Bi in leaching solution increase to 7.73 and 14.50 g/L, respectively, which are nearly three times as high as those of the first leaching solution (Fig. 10(a)). However, the leaching efficiencies of Te and Bi decrease to 71.76% and 82.13%, respectively (Fig. 10(b)). With a further increase of the leaching cycle number, the leaching efficiencies of Te and Bi are less than 25% and 50%, respectively. The effective concentrations of Fe^{3+} and Fe^{2+} decrease and increase, respectively, which results in a decrease of the potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and inhibits the leaching of Te and Bi in the tellurium–bismuth ore [12,40,41].

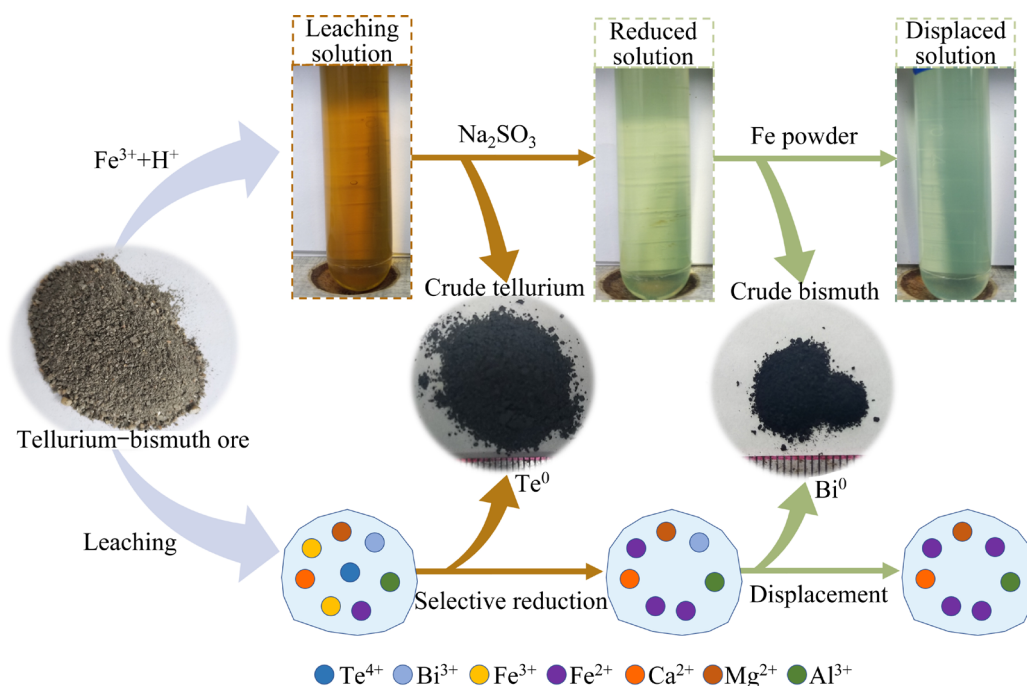


Fig. 8 Schematic diagram showing mechanisms of selective reduction and separation of Te and Bi

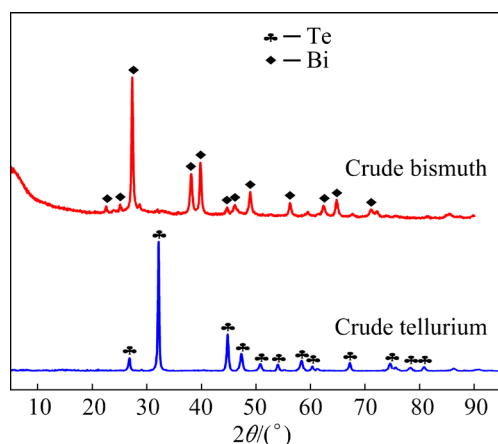


Fig. 9 XRD patterns of crude tellurium and bismuth

Figure 11 shows the effect of NEC on the precipitation efficiency of Te and Bi in the third leaching solution at 80 °C for 10 min by varying the Na_2SO_3 dosage. As NEC increases, the precipitation efficiency of Te firstly remains the same, then rises sharply and finally plateaus, while the precipitation efficiency of Bi is always less than 1%. When NEC is less than 1, Te and Bi in the leaching solution cannot be reduced. At this stage, Na_2SO_3 is mainly used to reduce the excessive Fe^{3+} to Fe^{2+} , which is consistent with Figs. 1(a) and 3. When NEC increases from 1 to 5, the precipitation efficiency of Te also increases from 0.67% to 99.55%, respectively. With a further increase of NEC, the

precipitation efficiencies of Te and Bi have no obvious changes.

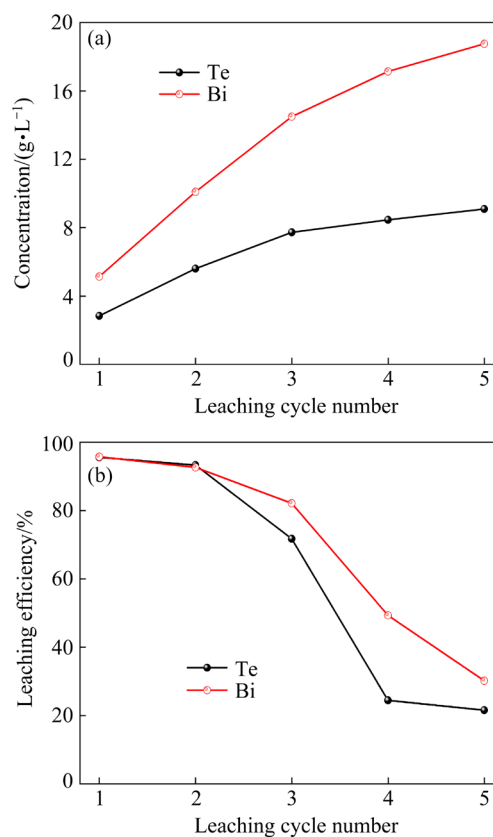


Fig. 10 Effect of leaching cycle number on leaching of Te and Bi: (a) Concentrations of Te and Bi in leaching solution; (b) Leaching efficiencies of Te and Bi

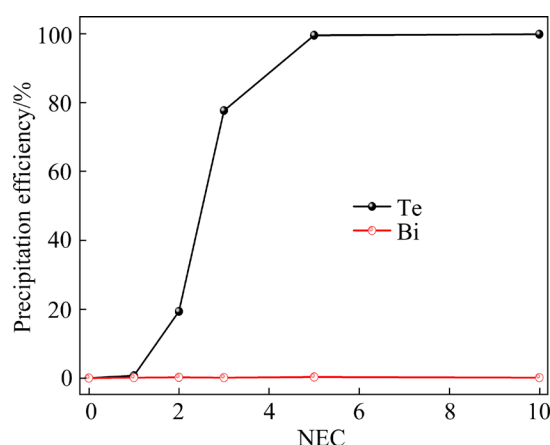


Fig. 11 Effect of NEC on precipitation efficiencies of Te and Bi in the third leaching solution

5 Conclusions

(1) As the selective reduction process goes, Fe^{3+} in the leaching solution is gradually reduced to Fe^{2+} . Te^{4+} or HTeO_2^+ can transform to gray-black granular elemental Te by Na_2SO_3 , and Bi^{3+} can be displaced to black granular elemental bismuth by Fe powder.

(2) 99.83% Te in leaching solution can be reduced by Na_2SO_3 with an excess coefficient of 16 at 80 °C for 10 min, and the grade of crude tellurium can reach 93.78%. The stirring action can promote the dissolution of Na_2SO_3 particles and further accelerate the reduction of Te. As the Na_2SO_3 dosage increases, the crude Te particles can gradually grow and coarsen and some needle-like or rod-shaped CaSO_4 crystals appear on the surface of the crude Te.

(3) 99.39% Bi in the reduced solution can be displaced by Fe powder with an excess coefficient of 7.5 at 60 °C for 40 min, and the grade of crude bismuth can reach 92.35%.

(4) Cyclic leaching of tellurium–bismuth ore is used to enrich Te(IV) and Bi(III) concentrations and decrease the Fe(III) concentration in leaching solution. Three cycles can be regarded as a suitable leaching cycle, and the Na_2SO_3 excess coefficient can be decreased to 5 with the precipitation efficiency of Te being 99.55%.

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选择性还原分离和回收酸性浸出液中的碲和铋

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摘 要: 提出一种用 Na_2SO_3 和 Fe 粉选择性分离和回收碲铋矿酸性浸出液中碲、铋的简单、高效方法。采用 SEM-EDS、XRD、XPS 和 ICP-OES 等手段研究碲、铋的选择性还原机理。过剩系数为 16 的 Na_2SO_3 在 80 °C 和 10 min 条件下可还原 99.83% 的 Te, 粗碲品位达 93.78%。此外, 搅拌促进 Na_2SO_3 溶解, 从而加速 Te 还原。过剩系数为 7.5 的 Fe 在 60 °C 和 40 min 条件下可置换 99.39% 的 Bi, 粗铋品位达 92.35%。采用循环浸出碲铋矿的方法可提高浸出液中 Te(IV) 和 Bi(III) 的浓度并降低 Fe(III) 的浓度, 减少 Na_2SO_3 的消耗。

关键词: 选择性还原; 置换; 碲; 铋; 浸出液

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