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Physicochemical and environmental characteristics of alkali leaching residue of wolframite and process for valuable metals recovery

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Abstract: Physicochemical and mineralogical characteristics of an alkali leaching residue of wolframite were studied by XRD, SEM−EDS, chemical phase analysis, mineral liberation analyzer (MLA), and TG−DSC methods. Batch leaching tests, toxicity characteristic leaching procedure (TCLP) tests and Chinese standard leaching tests (CSLT) were conducted to determine the environmental mobility of toxic elements. The results show that, due to the high contents of W, Fe, Mn, Sn, and Nb, the residue is with high resource value, but the content of a toxic element, As, is also high. The existing minerals of the investigated elements mainly occur as monomer particles, but it is difficult to extract these valuable metals by conventional acid leaching due to their mineral properties. The release of As increases over time in acidic environment. The leaching concentration of all investigated harmful elements through TCLP is within the limiting value, while the leaching concentration of As through CSLT exceeds the limiting value by more than 4 times, so the residue is classified as hazardous solid waste based on the Chinese standard. A process for valuable metals recovery from this residue was proposed. Preliminary experimental results indicated that the main valuable metals could be extracted effectively.

Key words: alkali leaching residue; physicochemical characteristics; environmental characteristics; valuable metals recovery

1 Introduction

Tungsten is an important strategic metal that is widely used in many fields such as machinery manufacturing, chemical industry, aerospace industry and national defense industry [1,2]. The main economical tungsten mineral resources are wolframite [$(Fe,Mn)WO_4$] and scheelite ($CaWO_4$). The decomposition of tungsten minerals is one of the key processes for tungsten extraction [3]. After a long period of development, an efficient process for tungsten minerals decomposition-autoclaved alkali leaching has been proposed and has been widely applied in China [4]. However, large amount of leaching residue is inevitably generated during minerals decomposition process. According to statistics, the cumulative amount of tungsten residue has reached 1×10^6 t in China, and it increases by more than 70000 t per year [5,6]. Most of the alkali leaching residue is mainly stockpiled so far.

Generally, the alkali leaching residue contains a fair amount of valuable metals, such as W, Mo, Mn, Sn, Ta and Nb. In some cases, the contents of some metals, such as W (above 1%) and Sn (above 0.4%), are higher than that of raw ore [7]. Therefore, this type of residue can be regarded as a high valued secondary resource for some valuable metals. On the other hand, some toxic elements, such as As

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and Pb, are also enriched in the residue, which poses a potential threat to the local ecologic system [6,8]. What is worse, the alkali leaching tungsten residue has been classified as a hazardous solid waste in China according to the latest environmental law. As a result, the tungsten production industry is required to pay an environmental tax, about RMB¥1000 per ton of residue [9,10]. In recent decades, many processes have been proposed for the recovery of valuable metals and the harmless disposal of the residue: (1) beneficiation of W, Mo, Bi, and Sn by flotation and gravity separation [10−12]; (2) extraction of W, Sc, Ta, and Nb by hydrometallurgical methods [10−13]; (3) recovery of W, Mn, Fe, Ta and Nb by pyrometallurgical methods [10−12]; (4) solidification/stabilization of the toxic elements [10,14]. However, the choice of recovery and stabilization processes for the residue strongly depends on the physicochemical and mineralogical characteristics, resource value, and the potential environmental characteristics of the residue [15]. Therefore, in order to develop an efficient technology for the tungsten residue treatment, it is essential to take a systematic analysis on the characteristics of the residue. In fact, a detailed research on the characteristics of the alkali leaching residue was rarely reported, especially for the mineralogical state of valuable and toxic elements, the releasing behaviors of toxic elements, and the evaluation of environmental characteristics.

To clarify the occurrence state of valuable and harmful elements, evaluate the potential of valuable metals recovery and environmental risk of toxic elements, and select an appropriate treatment process for the residue, this study is devoted to systematically investigate the characteristics of an alkali leaching residue of wolframite, including chemical compositions, microstructure features, mineralogical characteristics of the main valuable and toxic elements, thermal properties, and releasing behaviors and environmental mobility of toxic elements. The residue was collected from an ammonium paratungstate (APT) production enterprise in Jiangxi province, China, one of the largest tungsten producers in China. Basing on the physicochemical characteristic investigation, this work also proposes a process for the comprehensive recovery of valuable metals and the harmless treatment of this residue, which provides a reference for the technology development of tungsten residue treatment.

2 Experimental

2.1 Material

A tungsten residue, which was generated from autoclaved alkali leaching process of wolframite under the conditions of 160 °C reaction temperature, (6.06−7.07) MPa reaction pressure, and NaOH solution as leaching agent, was chosen as material in the tests, since wolframite has been used as the main raw material in tungsten industry for a long time and autoclaved alkali leaching process is widely used for wolframite decomposition in China. The agents used in this work are analytically pure.

2.2 Determination of physicochemical characteristics

The contents of the main elements such as W, Mo, Mn, Fe, Sn, Pb, Nb, and As in the residue and the phase composition of some elements were determined by Changsha Research Institute of Mining and Metallurgy, China.

The microtopography features of the residue were observed by a scanning electron microscope (SEM−EDS, JSM−7900F, JEOL, Japan).

The crystallographic composition was analyzed by X-ray diffraction (XRD, TTR III, with Cu K_α radiation, Rigaku, Japan), and the analysis was operated with a 2θ range from 10° to 80°, a step size of 0.02°, and a scanning speed of 2 (°)/min. The XRD data were analyzed by Jade 6.5 software. The occurrence states of the main valuable metals and toxic elements were analyzed by mineral liberation analyzer (MLA) (MLA 650, configured with a scanning electron microscope FEI Quanta 650, an energy spectrometer Bruker Quantax 200 with Dual XFlash 5010, and a software MLA 3.1 for automatic analysis of mineral parameters).

Thermal stability of the residue was tested by TG−DSC test (Model: NETZSCH STA 449 F3) under flowing air with a flow velocity of 50 mL/min at a heating rate of 10 °C/min.

2.3 Determination of environmental mobility of toxic elements

The toxic metals releasing behaviors of the residue were determined through batch leaching experiments. The effects of leaching time in the range of 2 to 24 h and initial pH in the range of 2 to 12 on the releasing behaviors of toxic metals were investigated. In each run, moisture content of the residue ($w(H_2O)$, %), was determined firstly. A sample with a dry mass of 10 g (the mass of the sample was calculated by the formula of $10/(100\%-w(H_2O))$), was transferred to a 250 mL Erlenmeyer flask, and leaching agent with specified pH was then added into the flask (pH was adjusted by diluted mixture of sulfuric acid and nitric acid with a mass ratio of 2:1). The flask was shaken at the vibrational frequency of 150 r/min using a shaker for specified time during leaching experiments. The leaching solution was acidified and analyzed.

The leaching toxicity was evaluated through the toxicity characteristic leaching procedure (TCLP) [16,17] and Chinese standard leaching test (CSLT) [15,18]. In the TCLP, a sample with a dry mass of 50 g was transferred to a 2 L extraction bottle, then the acetic acid solution with a pH of 2.88±0.05 was added into the bottle as leaching agent under a liquid to solid ratio of 20:1. The leaching test was conducted in a flip oscillator running at (30±2) r/min and was maintained for 24 h. The leachate was separated by a pressure filter using a filter membrane with 0.45 μm aperture.

The CSLT was conducted according to the standard method (GB 5085.3—2007 and HJ/T 299—2007) of China. The leaching agent was the diluted mixture of sulfuric acid and nitric acid with a mass ratio of 2:1, the pH was adjusted to 3.20±0.05, and the liquid to solid ratio was 10:1. The leaching experiment was maintained for 18 h in a flip oscillator. The leachate was separated by a pressure filter using a filter membrane with 0.45 μm aperture.

The concentrations of metals in the leachate obtained from the above experiments were determined by ICP-OES (Avio−500, PerkinElmer) and ICP-MS (iCAP-RQ, Thermo Scientific). The calibration standards used for ICP analysis were purchased from the National Nonferrous Metal and Electronic Material Analysis and Testing Center of China. The concentration of fluorine was determined by fluorinion selective electrode (PHSJ−4F). The experiments and tests were conducted three times, and the average was taken as the final result.

2.4 Experiments on valuable metals recovery

Carbothermal reduction experiments were conducted in a box type furnace (SQFL−1700C, Shanghai Jujing Precision Instrument Manufacturing Co., LTD, China) with the atmosphere of nitrogen. In each run, 200 g of dried alkali leaching residue was mixed with a certain amount of carbon (reductant) in a crucible, then the crucible was placed in the furnace and nitrogen was injected. After 0.5 h, the system was heated up to the designed temperature and maintained for a certain period of time. The multicomponent alloy obtained from carbothermal reduction experiments was crushed to <74 μm.

The alkaline smelting of multicomponent alloy was conducted in a box type furnace (SQFL−1700C, Shanghai Jujing Precision Instrument Manufacturing Co., LTD, China) with argon atmosphere. In each run, 5 g of multicomponent alloy powder was mixed with a certain amount of alkali medium in a crucible, and the crucible was then placed in the furnace. After that, argon flow was injected, and the system was heated up to the designed temperature and smelted for 90 min.

The alkaline slag obtained from alkaline smelting was leached for 90 min in hot water of 60 °C with a stirrer, and the leachate and leaching residue were separated by a pressure filter. The leachate was then transferred to a beaker and stirred with a magnetic stirrer, and the pH of the leachate was adjusted to 8 under stirring. After pH adjustment, the system was kept stirring for 30 min, and then the precipitate was separated from the solution using a pressure filter.

3 Results and discussion

3.1 Chemical composition of residue

The main elemental composition of the alkali leaching residue is presented in Table 1. The residue contains W (1.22%), Fe (18.24%), Mn (17.25%), Ca (4.74%), and Si (7.03%) as the major elemental compositions, some other valuable metals including Sn (0.74%), Ta (0.16%), Nb (0.61%), Mo (0.27%), and Bi (0.54%) also exist in the residue, which contribute to a high resource value of the residue.

With the continued exploitation of high-grade mineral resources around the world, the raw ore grades of many metals have become extremely low.

It was reported that the grades of WO_3, Sn, and Nb_2O_5 in the raw ore of mineral processing industry were as low as 0.30%, 0.17%, and 0.12%, respectively [19,20,21]. Obviously, the content of W, Sn, and Nb in this residue is higher than that of corresponding raw ore. Therefore, this residue can be considered as a high value secondary resource. Besides, the main toxic elements in the residue are Pb (0.32%), As (0.75%), and trace amount of Cr (0.019%). The As content is fairly high, so the occurrence state and releasing behavior of As should be the main concern regarding the environmental characteristics of the residue.

Table 1 Main elemental composition of alkali leaching residue (wt.%)

W	Mn	Fe	Sn	Nb	Ta	Mo
1.22	17.25	18.24	0.74	0.61	0.16	0.27
Bi	Pb	As	Al	Ca	Si	Cr
0.54	0.32	0.75	1.96	4.74	7.03	0.019
Sc	Na	Ti	S	C	F	Others
0.03	3.68	0.23	1.84	1.09	0.20	39.08

3.2 Occurrence state of main valuable and toxic elements

The microtopography of the residue was observed with a scanning electron microscope, as microtopography features of a solid waste play an important role in the environmental characteristics and the selection of treatment process. Figure 1(a) clearly shows that, the residue consists of irregular particles with different sizes, in which the majority of these particles are ultra-fine, even smaller than 10 μm. There are many cracks on the surface of relatively large particles, which may be due to the grinding pretreatment before tungsten extraction. Some large particles are covered with many fine particles. The fine particles and cracks on the large particles may cause the release of toxic elements when the residue is exposed to natural environment. Table 2 shows the EDS analysis results of large particles (Area 1) and fine particles (Area 2). The results reveal that, the large particles (Area 1) contain high content of Fe and relatively low content of Mn, while the fine particles (Area 2) contain high content of Mn and relatively low content of Fe. Besides, Bi and Sn are not detected on the surface of fine particles (Area 2), and the content of Pb and As on the surface of large particles is higher than that on fine particles.

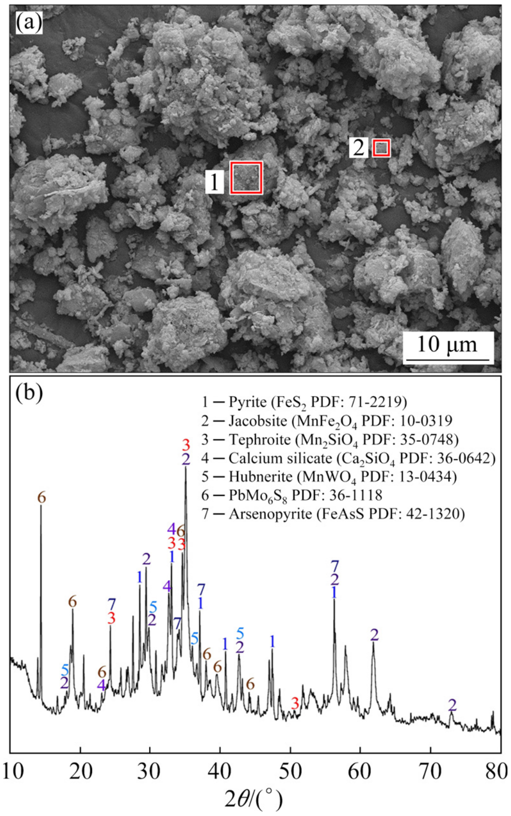

Fig. 1 SEM image (a) and XRD pattern (b) of residue

Table 2 EDS analysis results of large (Area 1 in Fig. 1(a)) and fine (Area 2 in Fig. 1(a)) particles (wt.%)

Area	Fe	Mn	W	Si	Al	Ca	Mo
1	37.67	7.77	7.38	18.88	2.26	4.35	1.95
2	27.05	26.33	3.68	15.29	3.90	6.33	1.59
Area	Bi	Pb	Sn	As	Cr	Na	
1	3.28	3.57	0.52	1.19	0.15	8.65	
2	0.00	0.81	0.00	0.50	0.00	12.60	

The XRD pattern (Fig. 1(b)) obtained by slow scanning shows that, the main crystalline phases in the residue are fairly complicated. Pyrite, jacobsite, silicate of manganese and calcium are the main phases in the XRD pattern. Meanwhile, lead molybdenum sulfide, hubnerite (one of the sources of wolframite), and arsenopyrite are also detected. The phases of some other elements, such as Bi and Nb, are not detected, which may be due to their low content or low crystallinity.

The elemental composition results show that, tungsten is a main valuable metal with relatively high content, while arsenic is a toxic element with high content. The phase compositions of tungsten and arsenic were analyzed through chemical analysis method. Table 3 indicates that, the main phases of tungsten are scheelite and wolframite, and the mass fractions of scheelite and wolframite are 44.31% and 37.97%. A small amount of tungsten exists in the form of tungstite (17.72%). For the phase composition of arsenic (Table 4), the mass fractions of arsenate, arsenic sulfide, and arsenic oxides are 41.33%, 8.13%, and 1.47%, respectively. The other 49.07% of arsenic exists in insoluble arsenic compound. It is inferred that this part of insoluble compound may be arsenopyrite. Although the arsenic oxides account for a very small proportion, the oxides cannot be ignored as their impacts on environment are critical [15].

Table 3 Phase composition of tungsten in residue (wt.%)

Wolframite	Scheelite	Tungstite	Total
37.97	44.31	17.72	100.00

Table 4 Phase composition of arsenic in residue (wt.%)

Arsenic oxides	Arsenate	Arsenic sulfide	Insoluble arsenic compound	Total
1.47	41.33	8.13	49.07	100.00

To further understand the occurrence states of various valuable metals and toxic elements, mineralogical characteristics analysis was conducted by MLA. Figure 2 shows the SEM images of the minerals of the main valuable and toxic elements. The occurrence of these elements is summarized as follows.

(1) The detected tungsten minerals are scheelite and wolframite, and these two minerals mainly exist in the form of monomer particles (Figs. 2(a) and (c)); a small portion of scheelite is associated with iron manganese oxide colloid (Fig. 2(b)); some wolframite is associated with calcium-rich iron manganese oxide colloid (Fig. 2(d)).

(2) The detected iron minerals are pyrite, hematite and oxide colloids, and both the pyrite and hematite exist in the form of monomer particles (Figs. 2(e) and (f)); some Fe forms oxide colloids with Mn, Si, and Ca, and is associated with various minerals of W, Nb Mo, Bi, and As.

(3) The detected manganese minerals are vernadite and oxide colloids, and the vernadite mainly exists in the form of monomer particles (Fig. 2(g)); the majority of Mn forms oxide colloids with Fe, Si, and Ca.

(4) The detected tin mineral is cassiterite which exists in the form of monomer particles (Fig. 2(h)).

(5) The detected niobium mineral is pyrochlore which mainly exists in the form of ultrafine particles associated with calcium-rich iron manganese oxide colloid (Fig. 2(i)).

(6) The detected bismuth minerals are metal Bi and bismuthinite, some Bi is associated with bismuthinite which grows on the edges of Bi particles (Fig. 2(j)), and some Bi is associated with iron manganese calcium silicon oxide colloid (Fig. 2(l)); a part of bismuthinite is associated with ultrafine pyrite (Fig. 2(k)) except the interlocked particles with Bi.

(7) The detected molybdenum mineral is molybdenite, the majority of molybdenite exists in the form of needle-like monomer particles (Fig. 2(m)), and some molybdenite is associated with iron manganese calcium silicon oxide colloid (Fig. 2(n)).

(8) The detected lead mineral is galena which exists in the form of monomer particles (Fig. 2(o)).

(9) The detected arsenic mineral is arsenopyrite, the majority of arsenopyrite exists in the form of monomer particles (Fig. 2(p)), and some arsenopyrite is associated with iron manganese oxide colloid (Fig. 2(q)).

(10) The detected chromium mineral is chromite which mainly exists in the form of fine monomer particles (Fig. 2(r)).

The MLA analysis results reveal that, the detected minerals are mainly monomer particles, which is the result of sufficient liberation of most minerals in wolframite concentrate caused by grinding pretreatment before leaching. The tungstite, arsenic oxides, and arsenate detected in chemical phase analysis are not found by MLA, which may be due to the low crystallinity degree of these minerals or that the ultra fine particles are wrapped by oxide clays. The lead molybdenum sulfide ($PbMo_6S_8$) detected by XRD may be the interlocked particles of undeveloped molybdenite and galena. Based on the presented mineral properties of the main valuable metals, it can be concluded that, it is difficult to extract these valuable metals from the

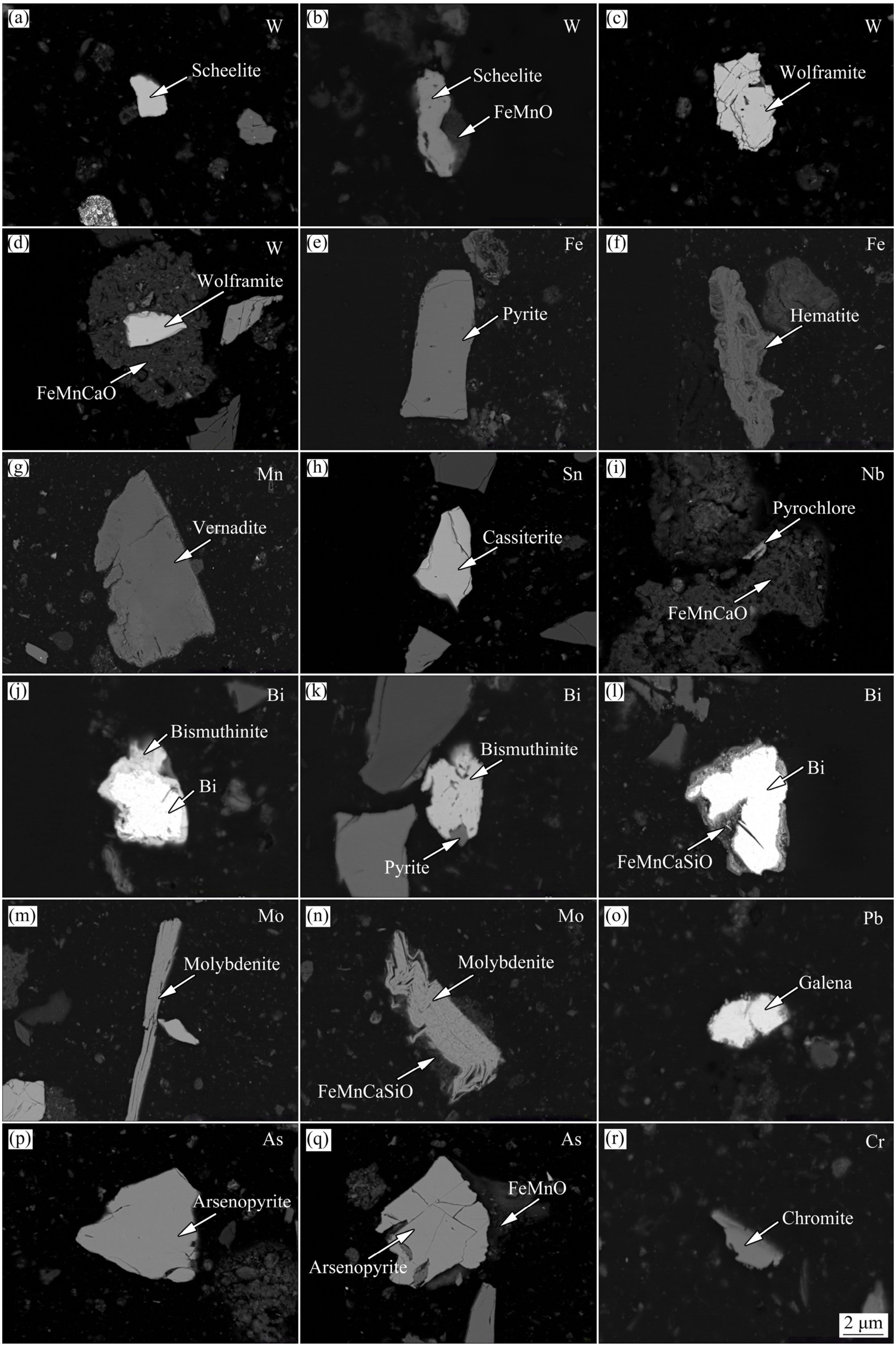

Fig. 2 Occurrence state of various main valuable and toxic elements

existing minerals, such as pyrite, cassiterite, and pyrochlore, by conventional acid leaching. Pretreatment (for example, high-temperature roasting) is necessary for decomposing the minerals of valuable metals into leachable compounds.

3.3 Thermal characteristics of residue

TG−DSC test was conducted to evaluate the thermal stability of the residue. Figure 3 shows the TG−DSC curves of the residue. As presented in Fig. 3, two mass loss stages and a mass gain stage are observed. A mass loss of 5.55% is observed from room temperature to 469.9 °C, which is due to the volatilization of adsorbed and bonded water. The result also illustrates that the residue has a good thermal stability when temperature is lower than 469.9 °C. It is worth noting that, an abnormal phenomenon during the test is that a slight mass gain of 1.45% occurs from 469.9 to 557.6 °C, and a strong exothermic peak is observed on the DSC curve. Considering that a certain amount of pyrite exists in the residue according to the XRD pattern (Fig. 1) and MLA analysis (Fig. 2(e)), it can be concluded that, the mass increase may be attributed to the oxidation of pyrite (an exothermic reaction) and the formation of sulfate under air flow and high temperature. HU et al [22] have reported that, during the oxidation process of pyrite, sulfates including ferrous sulfate ($FeSO_4$) and ferric sulfate [$Fe_2(SO_4)_3$] can be formed as minor products from 803 to 873 K (530 to 600 °C, which is similar to the temperature range in this work) and will result in mass gain. WANG et al [23] also stated that, for the oxidation of pyrite, Fe—S—O was first formed under certain conditions, which might cause mass gain. The additional mass loss above 557.6 °C is mainly caused by the decomposition of sulfides and arsenic compounds. In this temperature range, the molybdenite and bismuthinite contained in the residue (see Fig. 2) can be oxidized into MoO_3 and Bi_2O_3 [24−26]. Besides, some residual arsenopyrite may ultimately convert to As_2O_3 at about 650 °C [27].

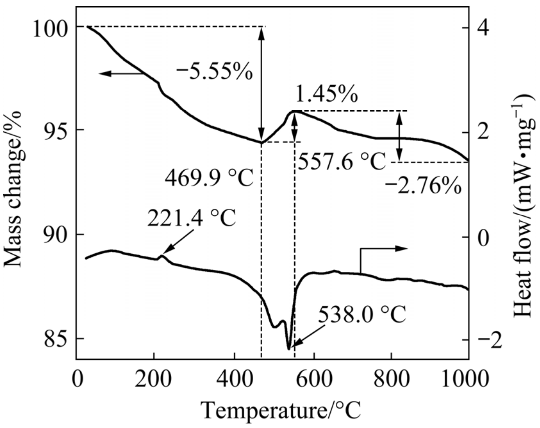

Fig. 3 TG−DSC curves of residue

3.4 Environmental characteristics of residue

3.4.1 Leaching behaviors of toxic elements

The release of toxic elements in the residue can be affected by natural conditions when the residue is disposed in a segregated landfill. The effects of contacting time and pH value of solution on the dissolution of As and Pb were investigated. The results are shown in Fig. 4. Figure 4(a) indicates that, under the initial pH of 3.00±0.05 and liquid to solid ratio of 10:1, the leaching concentration of As increases over time within 12 h and remains stable over 12 h, while the leaching concentration of Pb is fairly low (<1 mg/L). Figure 4(b) shows that, under the liquid to solid

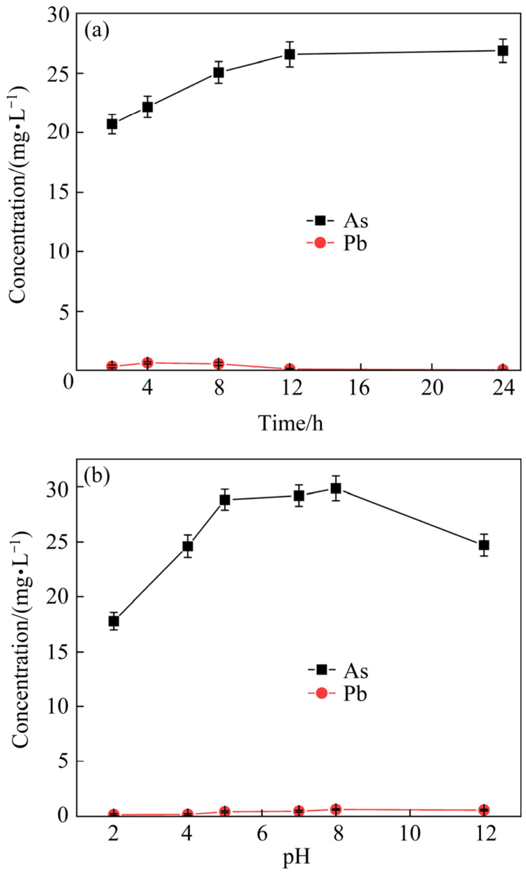

Fig. 4 Effects of leaching time under initial pH of 3.00±0.05 and liquid to solid ratio of 10:1 (a), and initial pH under liquid to solid ratio of 10:1 and leaching time of 20 h (b) on leaching concentrations of As and Pb

ratio of 10:1 and leaching time of 20 h, the leaching concentration of As increases with the increase of initial pH from 2 to 8 and then decreases. The result is similar to the releasing behavior of As in a sludge from copper and lead−zinc smelter reported by YAO et al [15]. Some researchers stated that, under alkaline condition, the formation of iron-oxyhydroxide phases and arsenic oxide passivation films on the arsenopyrite surface (which was the main arsenic mineral in this residue) reduced the diffusion of dissolved oxygen in the solution and the oxidation dissolution of arsenopyrite [28]. The leaching concentration of Pb is fairly low in the whole investigated pH range. Therefore, there is a high risk of As release during the disposal of the leaching residue even in the neutral environment.

3.4.2 Leaching toxicity assessment

To determine the mobility of harmful elements and assess the potential risk of the residue when disposed in a segregated landfill, TCLP and CSLT were conducted on the residue.

Environmental risk coefficient is put forward to assess the environmental risk caused by the harmful elements leached from the residue. The coefficient γ is defined as Eq. (1):

$$\gamma=c_i/C_i \tag{1}$$

where c_i is the concentration of an element in leachate, and C_i is the standard limiting concentration. The higher the coefficient, the greater the environmental risk, and vice versa.

Table 5 lists the leaching concentrations and corresponding environmental risk coefficients of the main harmful elements. As can be seen in Table 5, the leaching concentrations of all the investigated elements obtained by TCLP do not exceed the limiting values of US Environmental Protection Agency (EPA) [15], and the coefficients of these elements are fairly low. However, for the results obtained by CSLT, the leaching concentration of As exceeds the limiting value of GB 5085.3—2007 of China [29], the environmental risk coefficient of As is as high as 4.524, while the concentrations of other elements do not exceed the limiting values similar to those of TCLP tests. The results also indicate that, the arsenic compounds in this residue are dissolved easily in oxidizing strong acid medium (sulfuric acid and nitric acid).

4 Process for valuable metals recovery

As shown by above studies, it is clear that the resource value of this residue is fairly high for the contents of some valuable metals, such as W, Sn, Nb, and Bi. On the other hand, the residue contains some toxic elements (mainly As and Pb), and is classified as hazardous waste. Therefore, the clean utilization and safe disposal of this residue is in great necessity. The occurrence state analysis of the main valuable metals by MLA indicates that it is difficult to extract these valuable metals from the existing minerals by conventional acid leaching. In addition, the treatment process will be complicated by doing arsenic removal from leaching solution since arsenic is dissolved easily in sulfuric acid solution (see Table 5). According to the above analysis, a potential process for valuable metals recovery from this residue has been designed, and the simplified flowsheet is shown in Fig. 5. The characteristics of this proposed route are the combination of carbothermal reduction smelting, low temperature alkaline smelting, and hydrometallurgical process to realize the comprehensive utilization of valuable metals and low value components. One outstanding advantage of the process is that toxic metals As and Pb flow into the flue dust during the carbothermal reduction smelting, the small amount of flue dust simplifies

Table 5 Leaching concentrations and environmental risk coefficients of main harmful elements

Method	Index	As	Pb	Zn	Cr	Cu	F
TCLP	Leaching concentration/(mg·L^{-1})	0.18	0.0078	0.0042	0.0028	0.45	6.88
	Limiting value$^{\#}$/(mg·L^{-1})	5.0	5.0	N	5.0	15.0	N
	γ	0.036	0.0016	N	0.0006	0.03	N
CSLT	Leaching concentration/(mg·L^{-1})	22.62	0.052	0.0057	0.0185	0.11	9.54
	Limiting value*/(mg·L^{-1})	5	5	100	15	100	100
	γ	4.524	0.0104	0.0001	0.0012	0.0011	0.0954

$^{\#}$The limiting value of US; *The limiting value of China; N: Not limited in the standard

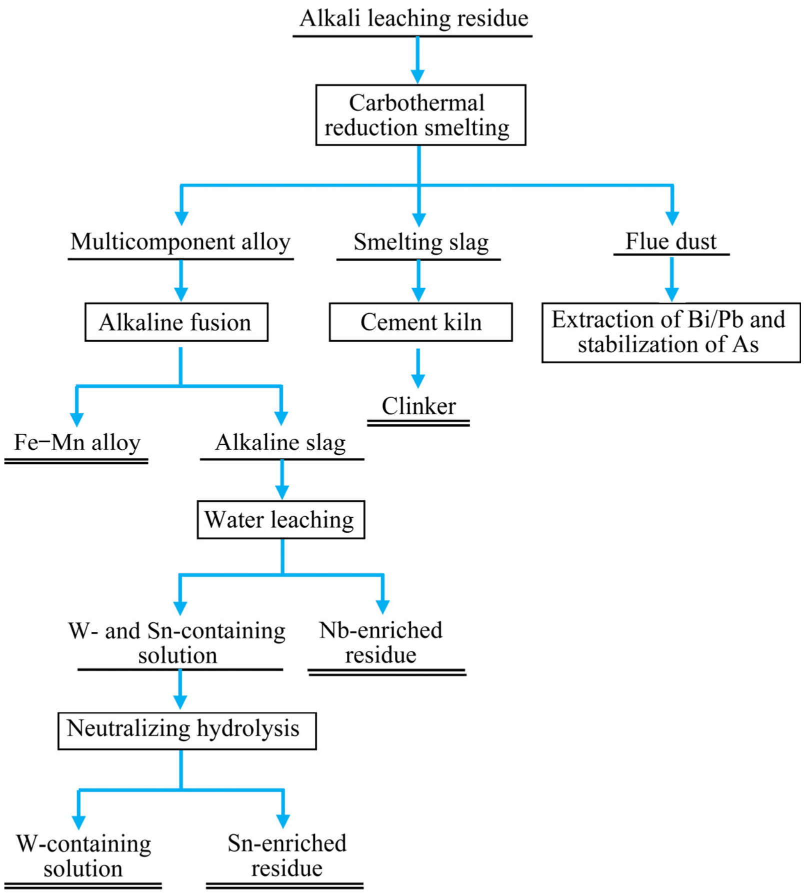

Fig. 5 Simplified flowsheet of designed process for alkali leaching residue treatment

the subsequent treatment of As and Pb.

Preliminary experiments have been carried out to treat the residue with the proposed process, and the results are listed in Table 6. Carbothermal reduction smelting is firstly conducted with the reduction temperature of 1500 °C, reaction time of 60 min, and carbon dosage of 16% (mass fraction of residue). A multicomponent alloy can be obtained, and the recoveries of W, Fe, Mn, Sn, and Nb in the alloy are 91.84%, 90.64%, 56.95%, 65.09%, and 82.98%, respectively. The As, Pb, and Bi flow into flue dust during smelting. As mentioned before, the small amount of flue dust containing As and Pb simplifies the subsequent extraction of Bi and Pb, and the solidification/stabilization of As. The smelting slag can be utilized as supplementary raw material of cement, as the main components of smelting slag (SiO_2, CaO, Al_2O_3, and a certain amount of iron oxide) are similar to those of cement raw material. This is an appropriate way for the comprehensive utilization of the low value component. Alkaline fusion with smelting temperature of 800 °C, reaction time of 90 min, NaOH and $NaNO_3$ as alkali medium, is then conducted on crushed multicomponent alloy. W, Sn and Nb are transformed into fused salt (Na_2WO_4, Na_2SnO_3, Na_5NbO_5) during alkaline fusion, and a Fe−Mn alloy with 69.28% Fe and 20.82% Mn can be obtained, the final recoveries of Fe and Mn are 90.63% and 56.95%, respectively. After water leaching of salt slag, the insoluble Na_5NbO_5 is separated with water-soluble Na_2WO_4 and Na_2SnO_3, Nb-enriched residue with 47.92% Nb and a recovery of 73.31% is obtained. Then through further neutralizing hydrolysis of W- and Sn-containing solution under pH value of 8, Sn is separated and the Sn-enriched residue with 60.02% Sn and a recovery of 56.29% is obtained. The final Na_2WO_4 solution can be transported to ammonium paratungstate (APT) production system for tungsten extraction. The preliminary results show that, the valuable metals can be extracted effectively from the residue by the proposed technological process. Further investigations will be carried out systematically to realize comprehensive utilization of the residue.

Table 6 Preliminary results of valuable metals recovering experiments

Product	Index	W	Fe	Mn	Sn	Nb
Multicomponent alloy	Content/wt.%	5.31	62.36	18.73	3.47	1.63
	Recovery/%	91.84	90.64	56.95	65.09	82.98
Fe−Mn alloy	Content/wt.%	0.08	69.28	20.82	0.05	0.06
	Recovery/%	0.93	90.63	56.95	0.84	2.75
Nb-enriched residue	Content/wt.%	0.58	−	−	0.96	47.92
	Recovery/%	0.30	−	−	0.54	73.31
Sn-enriched residue	Content/wt.%	0.12	−	−	60.02	0.08
	Recovery/%	0.10	−	−	56.29	0.20

All the indexes are calculated based on the raw material (alkali leaching residue)

5 Conclusions

(1) The residue is with fairly high resource value for the high contents of some valuable metals (W 1.22%, Fe 18.24%, Mn 17.25%, Sn 0.74%, Nb 0.61%), while the content of the toxic element As is also high (0.75%). Mineralogical analysis shows that, W exists in both wolframite and scheelite; Fe exists as pyrite, hematite and oxide colloids; Mn exists as vernadite and oxide colloids; Sn mainly exists as cassiterite; Nb mainly exists as pyrochlore; As mainly exists as arsenopyrite. The particle size of the residue is ultrafine. Although the existing minerals of the investigated elements mainly occur as monomer particles, it is difficult to extract these valuable metals by conventional acid leaching due to their mineral properties. The residue is in good thermal stability below 469 °C.

(2) The release of As from the residue increases over time even in neutral environment. The leaching concentrations of all the investigated harmful elements through TCLP are within the limiting values of US, while the leaching concentration of As through CSLT exceeds the limiting value of China by more than 4 times, and the residue is classified as hazardous solid waste by the Chinese standard.

(3) A potential process for valuable metals recovery from this residue was proposed. The preliminary experiment results indicated that the main valuable metals could be extracted effectively: the Fe−Mn alloy with 69.28% Fe, 20.82% Mn, Fe and Mn recovery of 90.63% and 56.95% was obtained; the Nb-enriched residue with 47.92% Nb and a recovery of 73.31% was obtained; the Sn-enriched residue with 60.02% Sn and a recovery of 56.29% was obtained; the Na_2WO_4 solution could be used for tungsten extraction.

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黑钨精矿碱浸渣理化与环境特性及有价金属回收工艺

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摘　要：采用 XRD、SEM−EDS、化学物相分析、MLA 和 TG−DSC 等方法研究黑钨精矿碱性浸出渣的理化特性和矿物学特性，并采用批次浸出实验、毒性浸出程序(TCLP)实验、国家标准毒性浸出测试(CSLT)分析浸出渣毒性元素的环境释放特性。结果表明，浸出渣中 W、Fe、Mn、Sn、Nb 等有价金属含量高，具有很高的资源价值，同时也含有高含量毒性元素 As。有价金属矿物主要以单体形式存在，但由于矿物性质，难以通过常规酸浸工艺提取有价金属。浸出渣中 As 向环境的释放量随时间增长而增加。TCLP 结果表明，所有毒性元素浸出浓度均未超标；而 CSLT 结果表明，As 浸出浓度超过国家标准限值 4 倍以上。因此，该浸出渣被列为危险固体废物。提出一种从浸出渣中回收有价金属的工艺。实验结果表明，采用该工艺可有效回收浸出渣中的有价金属。

关键词：碱性浸出渣；理化特性；环境特性；有价金属回收

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