Determination of occurrence and leaching toxicity of arsenic in copper flash smelting slags

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Abstract: The efficient and safe disposition of arsenic (As)-containing copper slag depends on the accurate understanding of the As species and their corresponding leaching toxicity. The As species in copper smelting slag were investigated by X-ray fluorescence spectrometry, X-ray diffractometry, electron probe microanalyzer, scanning electron microscopy equipped with energy dispersive spectroscopy, and selectively sequential extraction scheme. Based on the accurate fractionation of As species, the potential source of As toxicity of copper slag was investigated. The results show that As can be associated with smelting slag in the forms of water-soluble As, Cu−As intermetallics, Cu−As sulfides, as well as the As incorporated in fayalite and glassy silicates. The removal of readily soluble As and Cu−As intermetallics from smelting slag by flotation can reduce the As leaching toxicity of slag tailings, making them conform to the USEPA and SEPA regulatory thresholds for As.

Key words: copper flash smelting; arsenic; copper slag; selective sequential extraction; leaching toxicity

1 Introduction

Arsenic (As) has been a continuous center of controversy since its discovery. The values of arsenic in science, medicine and technology have generally been overshadowed by its notoriety as a poison in human beings [1]. Since 2012, As and As compounds have been incorporated into the carcinogenic substance list (Class I) of the International Agency for Research on Cancer (IARC) of the World Health Organization. Arsenic is widely associated with nonferrous metal sulfide ores or concentrates because of their similar element affinity in geology [2,3]. Therefore, the production of nonferrous metals is usually accompanied with the output of As-bearing wastes [4,5]. Copper smelting is a main source of As-bearing wastes. In general, the contents of As and Cu in the copper concentrate ore are approximately 0.2 wt.% and 25 wt.%, respectively [6,7]. The annual output of metal copper from copper ore in China is more than 7 million tons, from which it could be estimated that the total amount of arsenic from copper smelting plants would be more than 56000 tons. Such a large quantity of As-bearing wastes poses great risks to the environment [8−10].

Recently, flash smelting has been one of the most important methods for copper smelting and accounts for approximately 50% of the world's primary copper production [11]. During the pyrometallurgy of the copper ore concentrate, most of the associated As is dislodged by the smelting process and transformed into various As-containing byproducts, such as slags, flue dust, and arsenic cake [12]. Compared with the traditional smelting method, the flash smelting furnace has a remarkable

advantage in promoting the incorporation of As into smelting slag. Some smelters have carried out the practice of returning As-bearing byproducts to the flash smelting furnace [13]. In this way, unstable As can be stabilized in copper slag through slagging reactions. Before the disposal of copper slag, the crushing−flotation process is usually employed to recover the remaining Cu. The recovered Cu-rich slag (slag concentrate) is returned back to the smelting process, and the slag tailings would be the main output of As from the copper production system. To date, the slag tailings from the flash smelting enterprises are commonly dumped into landfill sites, while some studies have also proposed that the slag tailings can be solidified in cement, concrete and backfill materials [14−16]. However, the potential risk of As leakage from slag tailings or solidified materials containing copper slag is still controversial.

The As species in flash smelting copper slag are quite complicated because of the multivalence of As and the complex reactions during matte smelting and slagging. Limited to the inferior sensitivity of analysis technologies or the inadequate understanding of copper metallurgical processes, various occurrences of As in copper slag have been proposed. Some researchers revealed that the arsenic species in copper slag present as arsenates [16], while others indicated the presence of metallic As [17], As sulfide [18,19], and As oxides [17,20]. Meanwhile, some works also showed that As could be solidified in silicate phase [18,21,22]. Researchers developed various solidification technologies to reduce the As leachability of copper slag, but there is a lack of specific understanding of the potential source of As toxicity of copper slag [14−16]. In this work, it is of great significance to identify the various As-bearing phases and clarify their potential toxicities accurately.

In this study, a variety of analytic methods and a selectively sequential extraction scheme were used to investigate the chemical composition and phase constitution of As-bearing species in copper flash smelting slag. The leaching characteristics of the As species during the flotation process and various leaching tests were also studied. The research results will provide a general guideline for the better disposal of As-bearing copper flash smelting slag.

2 Experimental

2.1 Materials

The copper flash smelting slag samples were collected from Jinguan Copper Co., Ltd., Tongling Nonferrous Metals Group in Anhui Province, China. The smelting slag samples were taken from copper flash smelting furnace. The slag concentrate and slag tailing samples were collected from the slag flotation process. The content of remaining Cu in slag tailings was generally controlled below 0.3%. To recover the remaining Cu by flotation, the smelting slag was generally crushed in an ore crusher to ensure that more than 80% of the slag particles were smaller than 200 mesh (0.075 mm). All collected samples were evenly mixed and dried at 60 °C to a constant mass. To assess the leaching toxicity of As species, Cu−As intermetallics and sulfides were prepared through reactive synthesis using elemental As and Cu powder or CuS [17]. All solutions were prepared using analytical grade chemicals and deionized (DI) water.

2.2 Selectively sequential extraction procedure

A selectively sequential extraction (SSE) procedure was employed to evaluate the As partitioning in copper smelting slag. The potential As species in copper slag were classified into six categories, namely, readily soluble As, dissolvable arsenates, sparingly soluble arsenates, As residing in sulfides, arsenopyrite and metal As, as well as the As incorporated into glassy silicates [18,19]. The details of the extraction operations are described in our previous report [17].

2.3 Leaching toxicity test methods

The chemical stability of slag samples was evaluated by the USEPA toxicity characteristic leaching procedure (TCLP) [20], HJ 577—2010 [21] and HJ/T 299—2007 [22] standards. The polytetra-fluoroethylene (PTFE) vessels and a thermo-statically controlled heating block were used for chemical leaching. The reaction vessels and glass wares were cleaned and dried before use. The TCLP tests were performed in a rotary agitator at (30±2) r/min under a liquid–solid ratio (L/S) of 20 L/kg at (23±2) °C. An acetic acid solution with a pH of (2.88±0.05) was used as the extraction fluid.

The extraction time is (18±2) h. The HJ 577—2010 test employs DI water as the leaching agent, which can assess the leaching risk of As in solid wastes when leached by surface water or groundwater. The solid–liquid ratio (S/L) is 100 g/L and the operating time is 8 h. The HJ/T 299—2007 test uses the mixed HNO_3/H_2SO_4 solution to simulate leaching by natural acid rain. The solid–liquid ratio (S/L) is 100 g/L and the operating time is 18 h.

2.4 Flotation simulation experiments

The simulation flotation experiments were designed to assess the As leaching behavior of smelting slag. The smelting slag was also crushed into fine powders with particle sizes less than 0.075 mm. Flotation simulation experiments were performed in a rotary agitator at 150 r/min. The experimental parameters were as follows: slurry concentration 40%−42%, solution pH 8−9, flotation temperature 50−60 °C, and duration 2 h. The reagents and the corresponding additions were butyl xanthate 200 g/t, sodium sulfide 250 g/t and terpenic oil 30 g/t, respectively.

The water used in industrial flotation was neutralized waste acid from the flue gas purification process. The concentrations of F^- and Cl^- in this water can be as high as 300 mg/L and 3000 mg/L, respectively. In flotation simulation experiments, Cl^- and F^- were introduced in the forms of NaCl and NaF. After flotation leaching, the smelting slag particles were filtered, washed and dried at 60 °C to a constant mass. TCLP tests were further performed to evaluate the As toxicity of the processed smelting slag.

2.5 Characterization

The chemical compositions of samples were measured by X-ray fluorescence spectroscopy (XRF, ADVANT'X 4200). The phase analyses were conducted by X-ray diffraction (XRD, Dmax 2500VB) using a Cu K_α source (λ=0.1541 nm). The morphologies of samples were analyzed by scanning electron microscope (SEM, Nova Nano 230) equipped with energy dispersive spectroscopy (EDS, GENENIS 4000). The elemental distribution was obtained by electron probe microanalyzer (EPMA, JEOLJXA−8530F). The cross-section views of the slag samples were prepared by dispersing the slag particles in epoxy resin and then polished by fine diamond spray. Prior to SEM and EPMA analysis, each sample was coated with a 25−30 nm platinum film. The inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Advantage 1000) was employed to determine the concentration of As in leachates.

3 Results and discussion

3.1 Occurrence of As in copper slag

In the copper flash smelting reacting shaft, the fine ore concentrate powders react vigorously with the oxygen-rich atmosphere [23,24]. Herein, As can be oxidized to pentavalent oxide, which can further react with metal oxides to form arsenates. Meanwhile, the micro-molten-pool mechanism and fast continuous smelting operation also lead to insufficient separation of matte and slag; that is, the flash smelting copper slag contains a relatively high content of Cu [25]. As shown in Fig. 1, the As and Cu contents in smelting slag are 0.33% and 2.18%, respectively. The contents of As and Cu in the separated slag concentrate obtained by slag flotation are respectively 1.70% and 16.90%, while those in the slag tailings are respectively 0.13% and 0.31%. Clearly, a considerable proportion of As is recovered back together with Cu, indicating As may be associated with Cu. Meanwhile, the change of S content is consistent with that of As and Cu, indicating As−Cu−S may exhibit a symbiotic relationship.
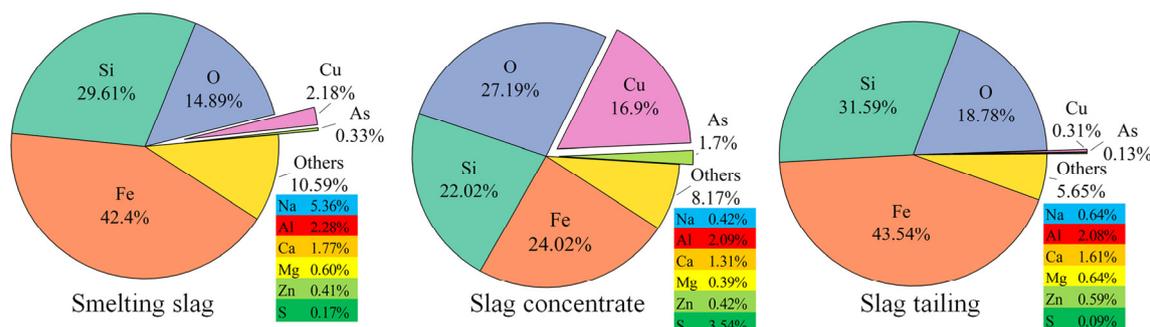

Fig. 1 XRF analysis results of smelting slag, slag concentrate, and slag tailing samples (wt.%)

Figure 2 shows the XRD patterns of copper slag samples. Since both slag concentrate and slag tailings are separated from the smelting slag, the diffraction peaks of those three slag samples show a certain consistency. It is found that fayalite (Fe_2SiO_4, PDF #71-1671), magnetite (Fe_3O_4, PDF #00-5841), jadeite (PDF #01-0470) and quartz (PDF #01-2692) are the main phases presented in slag samples, which corresponds to previous studies [26,27]. A broad XRD peak in the 2θ range of 10°−30° can be attributed to the amorphous silicates [28]. Meanwhile, minor phases of Cu_5FeS_4 (PDF #42-0586), $Cu_{12}As_4S_{13}$ (PDF #11-0102) and Cu_2S (PDF #72-1071) can be detected in smelting slag and slag concentrate samples, while they are invisible in slag tailings. Cu_3As (PDF #72-1329) and Cu_5As_2 (PDF #46-1394) can only be detected in slag concentrate. This suggests that Cu and As may be actually associated together as complex composite sulfides and intermetallics. Other As-related minerals are almost undetectable in all slag samples due to the relatively low detection limit of XRD.
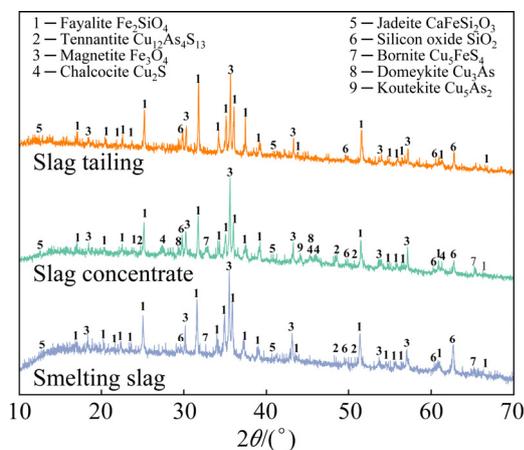

Fig. 2 XRD patterns of smelting slag, slag concentrate, and slag tailing samples

Figures 3(a, b) show sectional morphologies of slag samples, and the corresponding EDS mapping results are provided in Figs. S1 and S2 (Supplementary information). It is seen that the slag samples are mainly composed of fayalite, magnetite and silicate matrix [29]. Especially, copper matte particles can be widely found in slag concentrate samples, while only some small-size matte particles that are difficult to be separated by flotation can be observed in slag tailings. Meanwhile, bulk Cu−As particles as well as minor disseminated Cu−As−S

granules are also found in the slag concentrate sample, which are speculated to be Cu−As intermetallics and Cu-As sulfides. This explains the fact that As and Cu are together recovered and enriched in slag concentrate by slag flotation process.
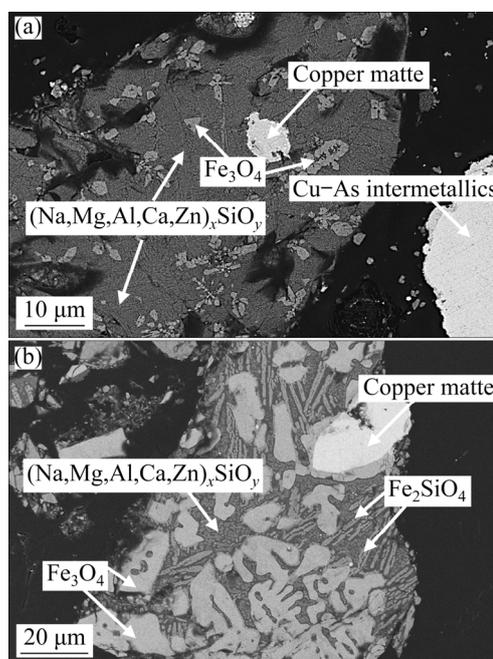

Fig. 3 SEM images of slag concentrate (a) and slag tailing (b) samples

Figure 4 shows the EPMA mapping result of the slag concentrate sample, indicating the accurate distributions of Fe, Si, O, Cu, S and As. From these images, the fayalite (Zone 1), magnetite (Zone 2), copper matte particles (Zone 3) and silicate matrix (Zone 4) can be clearly identified [26,27]. The observed As species can be partitioned into several portions. Firstly, a handful of As is solubilized in fayalite phase (Zone 1) and glassy silicates (Zone 4). During the smelting, the molten silica anions with various metal oxides can accelerate the surface adsorption of As oxides. The adsorbed AsO_4^{3-} ions can be further integrated into the $[SiO_4]^{4-}$ chain structures of silicates. Secondly, the copper matte particles with different Cu grades (Zone 3) dissolve a certain content of As [25,30]. Thirdly, As can be associated with Cu in the form of Cu−As intermetallic phases. Such intermetallic particles could be transformed from Cu−As sulfides ($Cu_{12}As_4S_{13}$ and Cu_3AsS_4) via a series of complicated redox reactions similar to the process of matter converting [13]. Obviously, these Cu−As intermetallics and Cu−As sulfides can account for

the enriched As in the recovered slag concentrate (Fig. 1).

As shown in Fig. 5, fayalite (Zone 1), silicate matrix (Zone 2) and magnetite (Zone 3) are also the major phases in the slag tailing sample. Specifically, Ca participates into the formation of the glassy matrix, while Mg is associated with the fayalite phase. It is noteworthy that the content of As in the glassy silicate matrix is higher than that in the fayalite phase, indicating the glassy silicates with higher contents of Si and Ca possess better performance for As solidification. Meanwhile, some copper matte as well as Cu−As intermetallic particles with a particle diameter less than 10 μm (Zone 4) can be found in the slag tailings sample. These small Cu-rich particles disseminated in the silicate matrix are hard to be separated and recovered by floatation. Obviously, in addition to
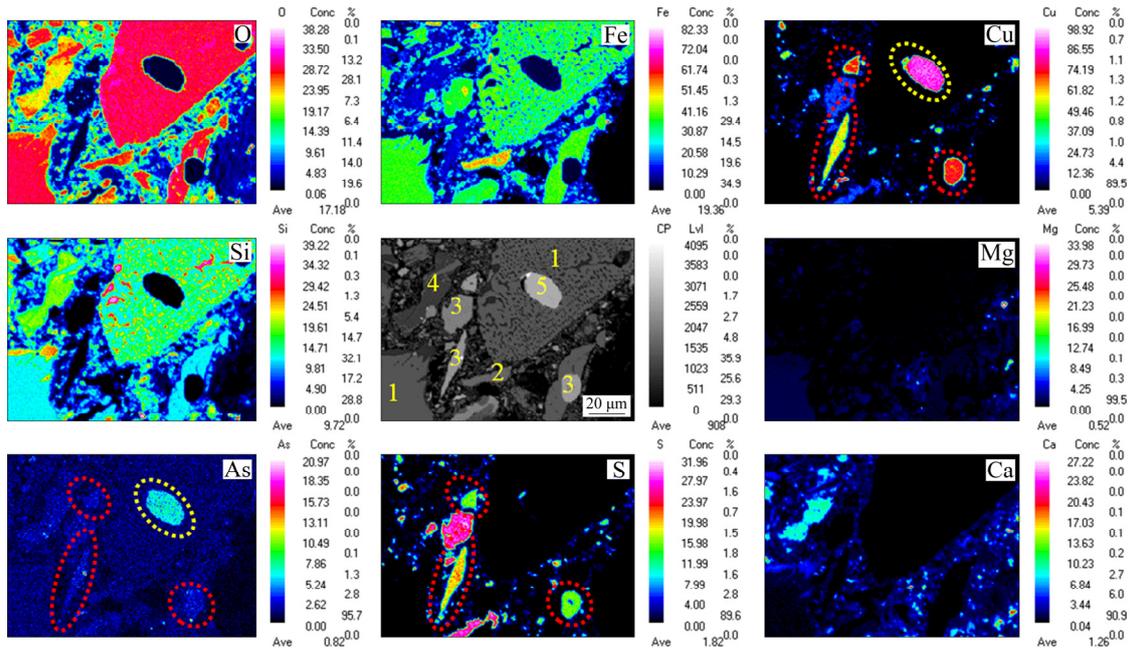

Fig. 4 EPMA mapping results of slag concentrate sample (1−Fayalite; 2−Iron oxide; 3−Copper matte particles; 4−Silicate matrix; 5−Cu−As intermetallic)
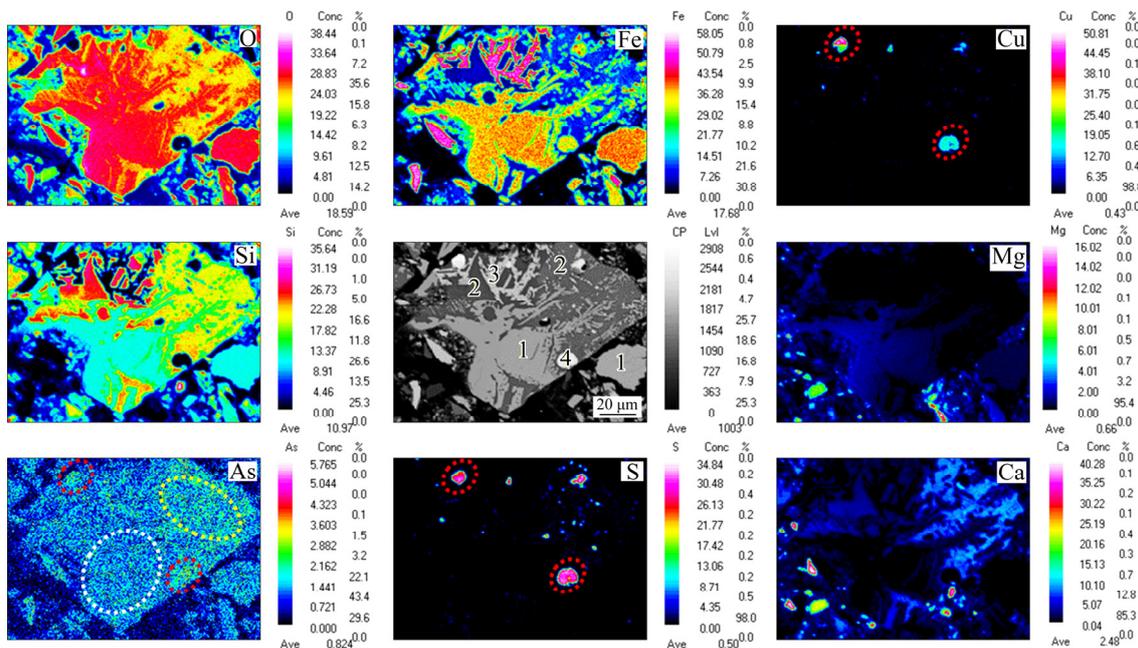

Fig. 5 EPMA mapping results of slag tailing sample (1−Fayalite; 2−Silicate matrix; 3−Iron oxide; 4−Copper matte particles)

the As associated with the silicate matrix and the fayalite phase, the remaining Cu−As intermetallics and Cu−As sulfide particles should be responsible for a portion of As in slag tailings. Moreover, due to the coexistence of Cu and As, the contents of As in slag concentrate and slag tailings would be affected by the recovery of Cu.

3.2 As partitioning and leaching toxicity

Figure 6(a) shows the As fractionation results obtained by the SSE method. According to the selective leaching principles, the As-related species in copper slag include readily soluble As (namely, arsenic oxides and potassium/sodium arsenates), dissolvable arsenates (Mg/Zn/Ca/Al arsenates), sparingly soluble arsenates (Fe/Cu arsenates), As residing in sulfides, arsenopyrite and metal As (Cu−As intermetallics), as well as As incorporated into glassy silicates [17]. As for the smelting slag, the majority of As (56%) is distributed in the glassy silicates, meanwhile a portion of As associated with sulfides (18%) and intermetallics (12%) besides arsenates is also detectable. In the slag concentrate, most of As is resided as sulfides (41%) and metallic As (52%), while these kinds of As species are much reduced in slag tailings. It is noteworthy that the proportion of As incorporated in silicates accounts for the dominant part of As, indicating most of the solidified As in copper slag should be quite immovable. The SSE result accords well with the SEM–EDS and EPMA analysis results. The reproducibility of the SSE results is acceptable, and the standard deviation of this procedure can refer to Ref. [17].

Figure 6(b) shows the leaching results of As from the slag samples by different toxicity characteristic leaching tests. It can be seen that the leached As concentrations of slag samples by HJ 557—2010 and HJ/T 299—2007 tests are relatively low, while the TCLP tests liberate the highest concentrations of As from the slag samples. Generally, the amount of the released As increases with the decrease of pH value of leaching agents [31,32]. The TCLP test employs organic acid (citric acid) as leaching agent, which can further contribute to the dissolution of As via complexation. Among these leaching tests, the As contents in the leachates from slag tailings are all below 5.0 mg/L, conforming to the USEPA and SEPA regulatory thresholds; while the concentrations of As released
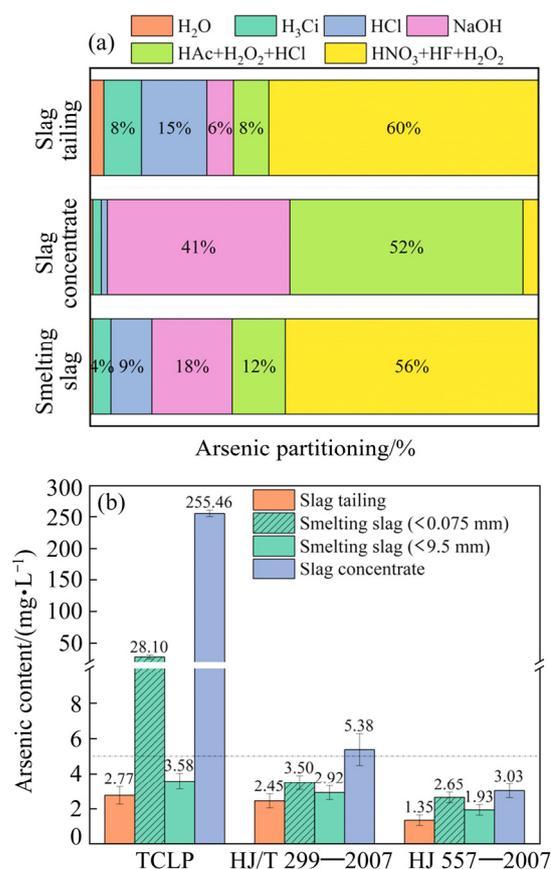

Fig. 6 As fractionation results for smelting slag, slag concentrate and slag tailings by selectively sequential extraction procedure (a) and leached As contents of slag samples by different toxicity characteristic leaching tests (b)

from the smelting slag and slag concentrate samples are out of the limit of TCLP test. To be specific, the As concentration of the leachate from the crushed smelting slag (<0.075 mm) reaches 28.10 mg/L, while the concentration of the leached As from the coarse smelting slag particle sample (TCLP standard <9.5 mm) is only 3.58 mg/L. Therefore, the leaching toxicity of As is also affected by the particle size of slag samples. Moreover, it is worth noting that the concentration of the leached As from the slag concentrate sample reaches as high as 255.46 mg/L. Regarding to the SSE results, it can be inferred that the Cu−As intermetallics and Cu−As sulfides, which account for over 90% of As in slag concentrate, could be responsible for the high leaching toxicity of As. In this work, it is also plausible that the low As toxicity of slag tailings could be attributed to removing the most of Cu−As intermetallics and Cu−As sulfides during flotation,

and the remaining As species are actually quite immovable against leaching.

3.3 Leaching toxicities of As species in copper slag

The flash smelting plants generally employ flotation to recover the remaining Cu in smelting slag. Therefore, the flotation process may also have an effect on the leaching toxicity of As. Researchers have proposed using the flotation process to remove As from mine tailings [33], coal [34], gold ore [35], etc, while the knowledge about the change of As toxicity of copper slag after flotation is scarce. Figure 7 shows the As contents in flotation solutions and the corresponding TCLP test results of the treated smelting slag samples. It can be seen that the leached As concentration by TCLP for the untreated smelting slag is 28.1 mg/L, while the values for the smelting slag samples after simulated flotation are much reduced. Meanwhile, it is worth noting that the concentrations of As in the slag processing water reach ~15 mg/L, indicating a proportion of As in the smelting slag has been leached out during flotation. As discussed above, the fraction of As species assigned in the SSE process corresponds to the water-soluble As, including arsenic oxides and potassium/sodium arsenates. Regarding this, the As toxicity of smelting slag can be reduced by the pre-removal of the portion of water-soluble As. Especially, as shown in Figs. 7(a, b), the introduction of Cl^- and F^- enhances the leachability of readily soluble As species compared with deionized water, but excess addition seems inoperative. According to reported chemicals used for sequential extractions [36,37], the usage of chlorine and fluorine salts can favor the exchange of adsorbed arsenates and reduce the re-adsorption or precipitation of the extracted As. The experiments with the addition of flotation agents show that these industrial flotation agents only have slight influence on the As concentrations in the flotation solutions and the subsequent TCLP test solutions (see Fig. 7(c)). This may due to their small dosages. From the above results, it can be deduced that the decreased As toxicity of slag tailings could be ascribed to the water scrubbing during flotation process.

However, the leached-As concentration of smelting slag after water scrubbing still exceeds the TCLP regulatory threshold. As shown in Fig. 6, the
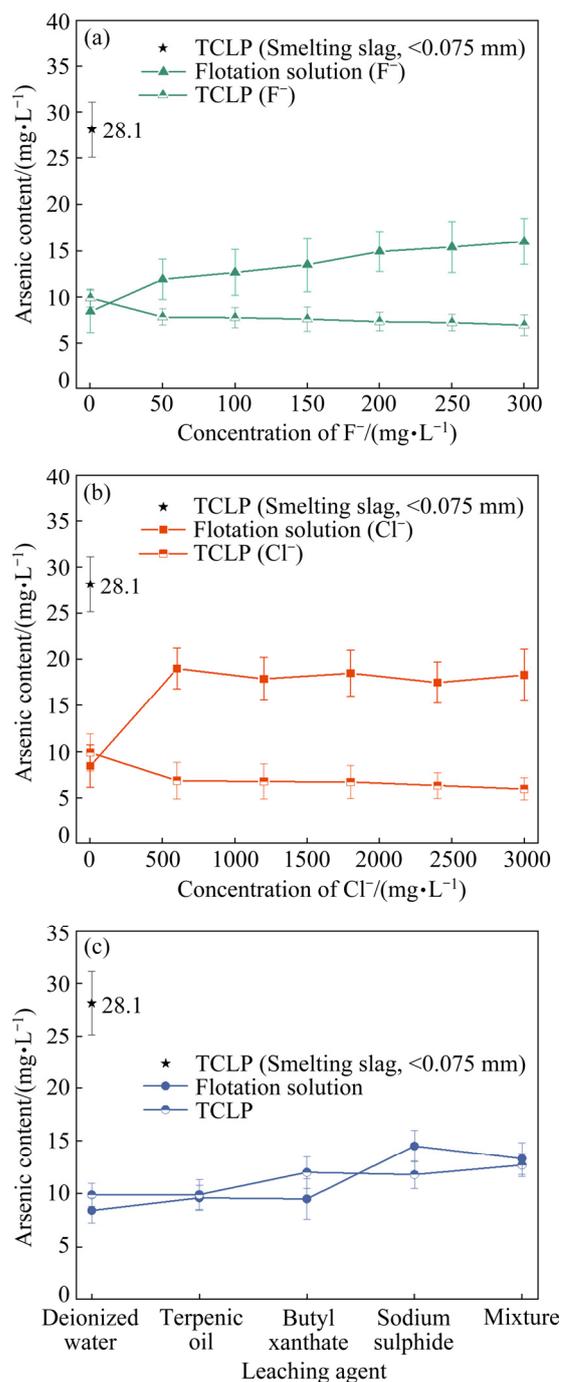

Fig. 7 Arsenic contents in flotation solutions and TCLP test solutions of smelting slag treated with different concentrations of F^- (a), Cl^- (b), and different flotation reagents (c)

excess As leached by TCLP may be highly related to the presence of Cu−As intermetallics and Cu−As sulfides in copper slag. To further confirm this, the slag concentrate was added back to slag tailings to assess the variation of As toxicity. It is shown in Fig. 8(a) that with the increase of slag concentrate addition in the mixture, the leaching contents of Cu

and As in the leaching solutions also increase. Note that when the addition of slag concentrate is 2.0 wt.%, the leached-As concentration from the mixture reaches 5.9 mg/L, which is higher than the TCLP limit. According to the common compositions of copper slags, the contents of As and Cu in smelting slag are comparable to those in a mixture of 90% slag tailings and 10% slag concentrate. The corresponding concentrations of As and Cu by TCLP are 18.59 and 197.30 mg/L, respectively, which are somewhat similar to those of the smelting slag after water scrubbing. Notably, As and Cu are leached synchronously during TCLP tests of copper slag. This also conforms to our inference.
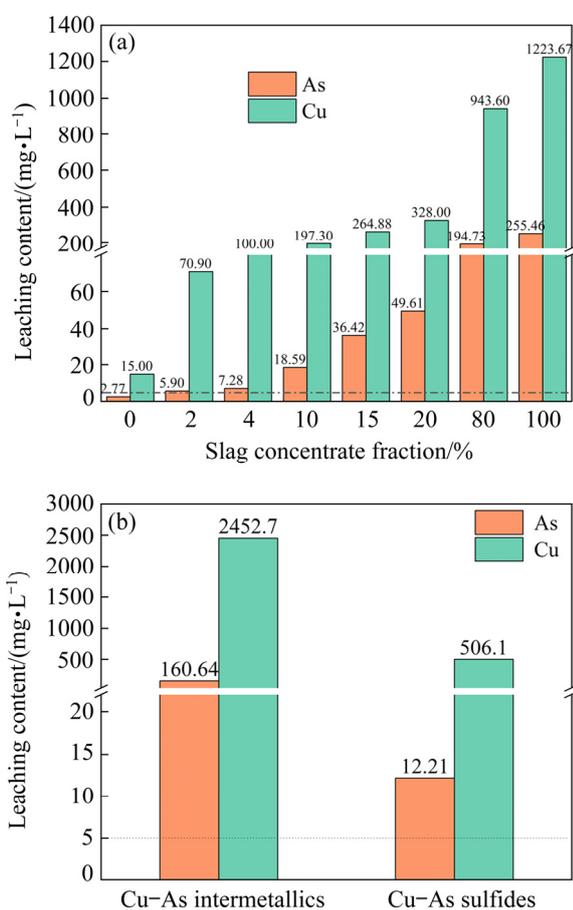

Fig. 8 Contents of As and Cu in TCLP test solutions from slag mixtures (a) as well as synthesized Cu−As intermetallics and Cu−As sulfides (b)

The specific TCLP leaching behaviors of Cu−As intermetallics and Cu−As sulfides were further investigated using synthetic materials. As shown in Fig. 8(b), the TCLP test solutions from both compounds contain considerable amounts of As and Cu. Especially, the Cu−As intermetallics

show much higher As toxicity than Cu−As sulfides, suggesting that Cu−As intermetallics should be primarily responsible for the As toxicity of copper slag. Because the TCLP tests are performed under conditions not strictly isolated with oxygen, Cu−As intermetallics are more likely to be oxidized and then dissolved by acetic acid. However, the matte or As sulfides are difficult to be digested with non-oxidizing acids [38]. This may be the reason for the selective dissolution of Cu−As intermetallics. Figure 9 shows the backscattered electron images of the smelting slag before and after TCLP test and the EDS analysis results for the special sites in Fig. 9 are presented in Table 1. It is seen that the Cu−As intermetallics with the core−shell structure is segregated from the matte matrix due to the immiscibility of the high-temperature Cu−As−S system [13]. After TCLP test, the precipitated Cu−As intermetallic phase was completely dissolved, while the matte phase dissolving some As was almost insoluble in TCLP test. This result confirms the above speculation.
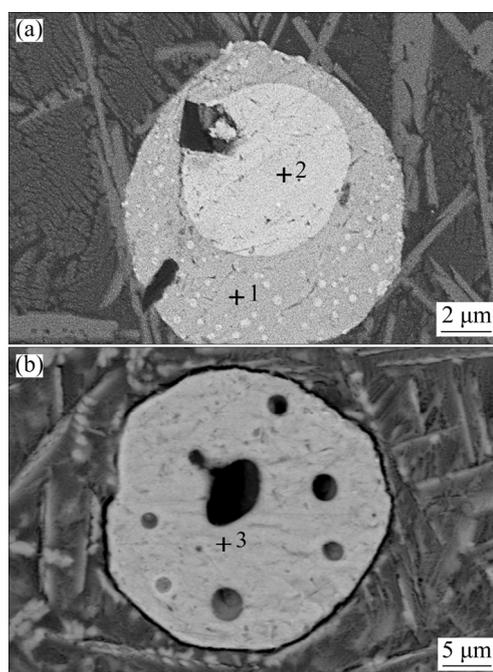

Fig. 9 SEM images of copper smelting slag before (a) and after (b) TCLP test

Table 1 EDS results of labeled areas in Fig. 9 (wt.%)

Position	S	Fe	Cu	As
1	29.86	8.43	59.27	2.45
2	2.22	−	72.60	25.18
3	40.13	3.10	55.78	0.99

As discussed above, it can be concluded that the As toxicity of copper slag can be reduced from two aspects. Firstly, the flash smelting process could be modified to increase the separation efficiency of copper slag and copper matte to reduce the inclusions of Cu, especially Cu−As intermetallics. Secondly, the flotation process should be carefully controlled to remove the water-soluble As species and recover the remaining Cu as much as possible.

4 Conclusions

(1) A comprehensive analysis of the As species in copper flash smelting slag has been carried out. The confirmed As species include arsenates, Cu−As intermetallics, As dissolved into copper matte, Cu−As sulfides, and As incorporated in fayalite and glassy silicates.

(2) The majority of As (56%) in slag tailings is distributed in glassy silicates after removing the most of As resided in Cu−As sulfides and intermetallics by flotation. Both the smelting slag and slag tailings can meet the requirements of TCLP, HJ 557—2010 and HJ/T 299—2007 tests for As.

(3) Water scrubbing during flotation can reduce the As toxicity of copper slag. The introduction of Cl^- and F^- enhances the leachability of the readily soluble As species compared with deionized water.

(4) The As toxicity of copper slag can be highly related to the presence of Cu−As intermetallics, which can be selectively dissolved by acetic acid used in TCLP test.

Supplementary information

The supplementary information can be found at: http://tnmsc.csu.edu.cn/download/22-p0293-2021-1113-Supplementary_information.pdf.

Acknowledgments

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铜闪速熔炼渣中砷的赋存状态和浸出毒性

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摘 要：铜冶炼含砷炉渣的高效安全处置取决于对其含砷物相及其浸出毒性的准确认识。采用 X 射线荧光光谱、X 射线衍射、电子探针显微分析、扫描电子显微术和选择性逐级提取法对铜熔炼渣中的含砷物相进行鉴定，并基于对炉渣中不同含砷物相的选择性逐级提取结果探讨渣中砷浸出毒性的可能来源。结果表明，砷以水溶性砷、铜砷金属间化合物、铜砷硫化物以及固化在铁橄榄石和硅酸盐玻璃相中的砷等形式赋存在熔炼渣中。浮选过程可以去除熔炼渣中的水溶性砷并回收铜砷金属间化合物，降低渣尾矿的砷浸出毒性，使其符合 USEPA 和 SEPA 标准要求。

关键词：铜闪速熔炼；砷；铜炉渣；选择性逐级提取；浸出毒性

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