

Speciation Characterization and Environmental Stability of Arsenic in Arsenic-Containing Copper Slag Tailing

Chuncaai Zhou (✉ zhoucc@mail.ustc.edu.cn)

Hefei University of Technology

Hexin Shen

Hefei University of Technology

Weiwei Zhang

Hefei University of Technology

Jinke Sun

Hefei University of Technology

Wentao Wu

Hefei University of Technology

Guijian Liu

University of Science and Technology of China

Research Article

Keywords: Mineralogy, Chemical speciation, Environmental mobility, Arsenic, Copper slag tailing

Posted Date: February 23rd, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1297401/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Increasing amounts of arsenic-containing impurities in Cu ores may deteriorate the smelting process and aggravate the environmental impact of slag tailing. Geochemical, mineralogical and chemical speciation characteristics were investigated to elucidate the association and environmental stability of metal(loid)s in copper slag tailing. Results shown that the bulk chemical compositions of the selected slag tailing are Fe_2O_3 (54.8%) and SiO_2 (28.1%). The selected slag tailing may lead to multi-elemental contamination potential for the elevated concentrations of environmental sensitively elements. The mineral phases in slag tailing are silicate (fayalite), oxides (magnetite and hematite), sulfides (galena, sphalerite, arsenopyrite and chalcopyrite). The invariably overlap of silicate, iron, arsenic and oxygen in the elemental distribution suggested that arsenic is existed silicate minerals as Si-Fe-As-O phases. Meanwhile, arsenic is also associated with sulfide minerals and oxides. The percentages of arsenite (As(III)) and arsenate (As(V)) are 59.4% and 40.6% in the selected slag tailing, respectively. The slag tailing is regarded non-hazardous waste for the tiny amounts of toxic elements in leachates. Nevertheless, the slag tailing should be property disposed for the elevated carbonate bound of As and Cu in the slag tailing.

1. Introduction

Copper slag tailing is the primary outlet of pyrometallurgical impurities and mainly composed of silicate matrix (Li et al., 2021b). It is estimated that 2-2.2 ton of slag tailing is generated for every ton of copper production, approximately 40 million ton of slag is generated from world copper production (the copper production was 19.94 million ton in 2017) (Gorai et al., 2003; Piatak et al., 2015; Potysz et al., 2015). Slag tailing is mostly directly stacked close to the center of industrial activity with inappropriate disposal (Zhou et al., 2021b). Re-utilization of slag tailing as additives for building and construction materials, concretes and abrasive materials are recently applied for the excellent soundness characterization, good abrasion resistance and stability of the thermally treated by-products (Fuentes et al., 2020; Labaj et al., 2021; Lu et al., 2020; Pfeifer et al., 2020; Siddique et al., 2020; Zhou & Liu, 2021). However, the environmental safety and inertness should be identified to potential recycle and engineering applications of slag tailing for the elevated concentrations of metal(lid)s (As, Pb, Cu, and Zn) in slag tailing (Agorhom et al., 2015; Li et al., 2021a).

Landfill disposed and engineering applications of slags are exposed to various bio-hydro-climatic conditions (Ganne et al., 2006; Kierczak et al., 2013). Long-term progressive biogeochemical weathering and physical erosion of these materials may lead to the change of chemical and structural as well as to mobilize metallic elements, finally results in deterioration of environmental quality (Cappuyns & Swennen, 2008). Many studied have addressed the mobility mechanisms of metallic elements during weathering, and shown that the redistribution behavior of metallic elements is determined by various parameters i.e. association and chemical speciation of metallic elements, the stability (lattice energy) of their host minerals, and leaching environment (pH, redox potential) (Alter, 2005; Jarosikova et al., 2017; Krol et al., 2020). Meanwhile, the interactions between metallic elements and bulk compositions (especially Fe) play

a significance role in efficient immobilization of metallic elements at the slag-water interface (Li et al., 2020a). It is reached a consensus that the dissolved metallic elements can be trapped and immobilized by precipitation of secondary phases (Lottermoser, 2005). Therefore, the detailed chemical, mineralogical and textural characterizations of slag tailing should be conducted to illuminate the key controls affecting the mobility of metallic elements during disposal and engineering applications.

Arsenic is a naturally occurring toxic element and widely distributed in copper ores as tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) and enargite (Cu_3AsS_4) (Long et al., 2012; Rozendaal & Horn, 2013). Arsenic in copper ores is redistributed among flue dust and slag with the ratios of approximately 76-85% and 7%-17%, respectively (Potysz et al., 2015). Subsequently, the trapped flue dust contains elevated concentrations of arsenic is recycled to smelting process for the high content of Cu (up to 40%). Finally, arsenic is driven to slag to maintain pyrometallurgical balance and avoid the deterioration of Cu matte quality (Guo et al., 2020; Montenegro et al., 2013). The totally concentration of arsenic is up to 7.59% in the slag tailing and pose to potential environmental pressure (Potysz et al., 2015). Nevertheless, the mobility and bioavailability of arsenic is governed by both total concentration and chemical speciation (Jarosikova et al., 2018; Li et al., 2020b). The transformation behavior and bio-toxicity of arsenic is various among different phases of arsenic occurring in slag tailing. The presence of arsenic in sulfide minerals showing relatively high susceptibility to alteration and increasing the mobilization potential of arsenic, while the arsenic in silicate minerals may be retained in the silicate lattice (Zhang et al., 2021a). Therefore, the research on association and chemical speciation of metallic elements (especially As) in slag tailing is extremely significant.

The main objectives of this present work are to: (1) determine the bulk chemical compositions, mineralogical and micromorphological characterization of the selected arsenic-containing slag tailing; (2) illustrate the association and chemical speciation of arsenic in the selected slag tailing; (3) evaluate the potential eco-environmental risks caused by metallic elements in slag tailing. The obtained results may provide important information for the property disposal and utilization of slag tailing.

2. Materials And Methods

2.1 Sampling

The slag tailing was collected from a Cu smelter, where Cu concentrate composed of covellite (CuS), bornite (FeCu_5S_4), chalcopyrite (CuFeS_2), and Cu-As sulfosalts (tennantite, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$) (Zhou et al., 2021a). Concentration, smelting, converting, and refining/electrolysis are critical steps in pyrometallurgical copper, which is presented in Fig. 1. The Cu concentrate mixed with silica flux is smelted in a Outokumpu flash smelting furnace at temperature approximately 1450-1550°C to produce intermediate product (Cu matte with 68% Cu content). The addition of silica flux could improve separation of Fe during smelting. Meanwhile, Ca-based oxides are applied to reduce the viscosity of silica and enhance Cu separation efficiency. The Cu matte is subsequently converted into blister Cu (98.8% Cu) in a flash converting furnace. The waste slags from smelting and converting furnaces are granulated and

re-processed by milling and flotation. After milling and flotation, the waste slags could be subdivided into slag concentrate and slag tailing. Slag concentrate is recycled to the smelting furnace for the high content of Cu (20%). Slag tailing is dewatered and stockpiled close to the industry activity. The flue gas emitted from the furnaces is passed through a series of atmospheric pollution control devices. The trapped flue dust is transported to smelter processes for the high Cu content (40%). However, the trapped flue dust contains large amounts of impurities (especially As) may deteriorate the smelting process and aggravate the problem of slag generation. The off-gas is discharged from stock after satisfied emission standard. Blister Cu is subsequently extracted by refining and electrolysis processes to form pure cathode Cu with purity of 99.9%. According to the flowsheet of pyrometallurgical copper production, it could be found that the slag tailing is the only discharge outlet of various pyrometallurgical impurities. Approximately 5kg of fresh slag tailing was collected from the stockpile and immediately kept in a sealed plastic bag to avoid contamination. The selected slag tailing was air-dried and screened using sieves of 150 (106 μm), 200 (75 μm) and 325 (45 μm) mesh for subsequently analysis.

2.2 Mineralogical and micromorphological analysis

The mineralogical characterizations of the selected slag tailing were quantified by power X-ray diffraction method (XRD). The XRD pattern was recorded over a 2θ interval of $5-70^\circ$, with a step increment of 0.01° . The minerals in each sample were recognized from the diffractograms by reference to the ICDD Powder Diffraction File. A Tescan MIRA3 field emission scanning electron microscope (SEM) equipped four Energy Dispersive X-ray spectroscopy (EDXs) was applied to investigate the micromorphological characteristics and determine the distribution of elements in soag tailing. The accelerating voltage and beam current was 30kV and 10^{-10}A , respectively. The wavelength of the full-colour cathodoluminescence detector was ranged from 200nm to 850 nm.

2.3 Chemical analysis

The oxides of major elements in the selected slag tailing were determined by X-ray fluorescence spectrometry (XRF). The microwave digestion procedure was conducted to extract the toxic elements (As, Cu, Cr, Ni, Pb and Zn) by an acidic mixture solution of HCl: HNO₃: HF (3:3:2). After digestion and quantify, the concentrations of the selected toxic elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). NIST standard reference materials and blank samples were adopted to ensure the accuracy of the extraction and analytical procedures. The precision is within ± 5 wt. % for all of the selected elements.

2.4 Speciation analysis

The association and speciation behavior of element could be determined by both direct and indirect approach. Both X-ray photoelectron spectroscopy (XPS) and sequential chemical extraction method were conducted to determine the chemical forms and speciation characterization of As and other elements in the selected slag tailing. XPS pattern was recorded by a Thermo-VG Scientific ESCALAB 250 spectrometer using Al K α X-rays as the sputtering source at the power of 150 W. The 284.6 eV was selected as the

standard C (1s) for the calibration of binding energy. A high-resolution scan of As 3d could be recorded with an energy step size of 0.05 eV.

The classic sequential chemical extraction illustrated by Tessier et al. (1979) was used for determination of the speciation behavior of As and other elements in the selected slag tailing (Tessier et al., 1979). The speciation characterization of element could be classified into five fractions according to the extraction procedure listed in Table 1. The concentration of toxic element in each fraction was determined by ICP-MS.

Table 1
Sequential extraction procedure.

Step	Extraction procedure	Speciation
1	1.0 g sample was extracted with 10 ml 1.0 M MgCl ₂ (pH=7.0) under room temperature for 1 h, suspension was achieved by centrifugation at 3500 rpm for 20 min.	Exchangeable
2	The residual solid from step 1 was extracted with 10 ml 1 M sodium acetate (pH=5.0) under room temperature and agitated continuously for 5h, suspension was achieved by centrifugation at 3500 rpm for 20 min.	Carbonate-bound
3	The residual solid from step 2 was treated with 20 ml 0.04 M NH ₂ OH·HCl in 25% (v/v) under room temperature and agitated continuously for 6h, suspension was achieved by centrifugation at 3500 rpm for 20 min.	Fe-Mn oxides bound
4	The residual solid from step 3 was treated with 3 ml 0.02 M HNO ₃ and 5 ml 30% H ₂ O ₂ (pH=2.0) under 85°C for 2 h. A second 3 ml aliquot of 30% H ₂ O ₂ (pH=2.0 with HNO ₃) was then added under 85°C and agitated for 3 h. After cooling, 5 ml of 3.2 M NH ₄ OAc in 20% (v/v) HNO ₃ was added and the sample was diluted to 100ml and agitated continuously for 30 min.	Organic matter bound
5	The residual solid from step 4 was digested with a HCl-HNO ₃ -HF mixture according to the procedure used for bulk samples	Residual

2.5 Environmental stability analysis

In order to evaluate the potential environmental impacts of toxic elements in slag tailing, the solid waste extraction procedure for leaching toxicity (CN-SWEP) according to Chinese standard HJ/T299-2007 was conducted to determine the potential leaching toxicity of toxic elements. The samples were leached at a L/S (liquid/solid) ratio of 10 L/kg in an acidic mixture solution (pH= 3.20 ±0.05) at 23±2°C for 18±2h. The acidic solution was prepared by H₂SO₄ and HNO₃ with the blending ratio of 2:1. The concentrations of toxic elements in leachates were analyzed by ICP-MS.

In addition, the toxicity characteristic leaching procedure (TCLP) suggested by the Environmental Protection Agency (EPA) was also employed to provide information about the environmental risks of toxic elements in the selected slag tailing. Briefly, the samples were extracted by CH₃COOH solution (pH=4.95 ± 0.05) with the L/S ratio of 20 L/kg and agitated continuously at 100±10 rpm for 18±2h. The pH of

solution was adjusted by HCl and HNO₃. The leachate was achieved by centrifugation at 4500 rpm for 10min and determined by ICP-MS.

3. Results And Discussion

3.1 Physico-chemical property of copper slag tailing

Knowledge of chemical, mineralogical and textural characteristics of slag tailing, which determined potential biological toxicity and environmental stability of environmental sensitive elements (As, Pb, Zn, etc.), is particularly significant for the disposal of slag and utilization properly (Piatak et al., 2004; Shu et al., 2021). Variation in smelted ores, fluxes, additives and pyrometallurgical conditions (furnace, atmosphere, temperature, cooling time) causes that the bulk chemical, mineralogical and textural characterizations vary among different smelting plant, and finally affecting the environmental stability of slag tailing (Saez et al., 2003). The bulk chemical compositions of the selected slag tailing are presented in Table 2. The selected slag tailing is mainly composed of Fe₂O₃ (54.8%) and SiO₂ (28.1%), with minor quantity of Al, Ca Na and K oxides, which is different from the previous studies in Australia (Lottermoser, 2005), USA (Piatak et al., 2004), Spain (Saez et al., 2003), Portugal (Mateus et al., 2011), and Poland (Kierczak et al., 2013) (Table 1). The elevated Fe content in slag tailing is originated from the bornite (FeCu₅S₄), chalcopyrite (CuFeS₂) in the Cu concentrate (Mikula et al., 2021). Silica in the slag tailing is derived from both primitive ore and the silica flux which added during smelting processes (Mikula et al., 2021). Alkali oxides in the slag tailing refers to the concentrations of these compounds in gangue minerals of Cu concentrate (Schmukat et al., 2013). Meanwhile, Ca-based oxides are added to reduce the viscosity of silica and enhance Cu separation efficiency during smelting processes (Potysz et al., 2015).

Table 2
The chemical compositions of the selected copper slag.

Major elements (wt. %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O
This study	28.1±0.54	3.80±0.22	54.8±2.54	3.58±0.68	0.70±0.49	1.35±0.10
Australia (Lottermoser, 2005)	28.7-35.8	3.12-5.41	31.5-43.5	9.12-15.5	0.04-0.26	0.05-1.16
USA (Piatak et al., 2004)	14.5-20.3	1-4.9	21-37	0.83-4.1	0.1-1.9	0.23-1.2
Spain (Saez et al., 2003)	13.8-68.7	0.01-15	6.72-50.6	0.2-7.85	0.11-1.25	0.01-3.05
Portugal (Mateus et al., 2011)	28.5-34.4	1.51-1.97	58.2-58.5	4.95-6.28	0.02-0.15	0.22-0.26
Poland (Kierczak et al., 2013)	31.9-70.7	3.84-11.9	5.58-51.1	0.59-1.68	0.15-2.05	1.25-4.37
Miner elements (mg/kg)	Zn	As	Cu	Pb	Cr	Ni
This study	2034±65	901±124	563±187	341±25	72.7±21.8	35.8±17.7
Australia (Lottermoser, 2005)	12266-58560	24-635	1410-8586	90-51620		0-25
USA (Piatak et al., 2004)	2300-19700	0.5-2	1900-13500	8.1-47	40-276	2.8-27
Spain (Saez et al., 2003)	58-1423	58-8623	1400-280600	16-4562	118-653	53-217
Portugal (Mateus et al., 2011)	>10000	180	3280	>5000		
Poland (Kierczak et al., 2013)	1294-9360	3-315	3030-13400	11-738		

The concentrations of environmental sensitively toxic elements (Zn, As, Cu, Pb, Cr and Ni) are shown in Table 1 and decreasing in the order of Zn> As> Cu> Pb> Cr> Ni. The elevated concentrations of these elements in slag tailing may lead to potential environmental impacts during disposal and utilization. In comparison with other copper slags (Kierczak et al., 2013; Lottermoser, 2005; Piatak et al., 2004; Saez et al., 2003), the selected slag tailing contains elevated As content and should be received greatly concern. Nevertheless, the lowest concentration of Cu in the selected slag tailing suggested that the excellent efficiency of Cu metallurgical processes in the selected furnace.

The selected slag tailing was screened by using sieves of 150 (106 µm), 200 (75 µm) and 325 (45 µm) mesh to investigate the distribution characteristics of particle sizes. The particle sizes fractions of the selected slag tailing in < 45 µm, 45-75 µm, 75-106 µm, and >106 µm are 25.4%, 52.4%, 14.3%, and 7.9%,

respectively. The selected slag tailing is mainly existed in fine particles (<75 µm) with proportions up to 77.8% and primary presented in 45-75 µm (52.4%). The morphology characterizations of the selected slag tailing are presented in Fig. 2. Slag tailing is displayed as angular grains in different size fractions, which is attributed to the milling procedure. The fine amorphous materials are increased with the decreasing of particle sizes.

Metallic elements (Cu, Pb, As, Zn) are mainly associated with copper sulfides in Cu concentrate (Schmukat et al., 2012; Schmukat et al., 2016), which are released and redistributed with the transformation of their host minerals during high temperature smelting processes. The mineral phases of Cu concentrate undergo various complex physico-chemical transformations, i.e. volatilization, decompositions, oxidation, reduction and crystallization, and result in the formation of Cu matte and new phases in the smelting slag (Siddique et al., 2020; Vitkova et al., 2011). Generally, the mineral phases in the slag are regarded as synthetic analogues of naturally minerals, which are formed by anthropogenic activities and determined by smelting conditions (smelting temperature, cooling speed) as well as the chemical compositions of the slag (Pareuil et al., 2011). It is a consensus that the phase variety is more abundant in slower cooled slags than that of cooled at the faster rates (Piatak et al., 2015; Potysz et al., 2016). It is attributed to the closer equilibrium of crystallization of phases in slow cooling. Meanwhile, the phase compositions of slag are greatly influenced by the smelting temperature (Gorai et al., 2003). Spinel, melilite, olivine, pyroxene and glass are formed at different temperature and time. Generally, the mineral phases of slag tailing including silicates (olivine, pyroxene), oxides (magnetite and hematite), sulfides (chalcocite, chalcopyrite, galena, sphalerite and bornite), pure metals, intermetallic compounds and glass matrixes (Li et al., 2021b). The mineralogical characteristics of slag tailing in the different size fractions are depicted in Fig. 3. The mineral phases in slag tailing are fayalite, hematite, magnetite, galena, sphalerite, arsenopyrite and chalcopyrite. Fayalite, hematite and magnetite are the most identified Fe-based minerals, while fayalite and silicate glasses are the mainly silicate phases. Meanwhile, sulfides (galena, sphalerite, arsenopyrite and chalcopyrite) are commonly found in the selected slag tailing with small quantities, which are consistent with previous studies from other furnaces (Kierczak et al., 2013; Mateus et al., 2011). Despite sulfides are volumetrically minor phases in slag tailing, these minerals should be taken fully consideration for the potential environmental risks (Khorasanipour & Esmaeilzadeh, 2016). In comparison with the mineralogical distribution among different size fractions, the peaks of fayalite and hematite are increasing with the decreasing of size fractions, suggesting that these secondly phases are preferred to existed in fine particles.

3.2 Association and chemical speciation of arsenic in copper slag tailing

In smelting furnace, arsenic as an impurity is removed by volatilization and slagging (Safarzadeh & Howard, 2018). Arsenic sulfide and elemental arsenic are oxidized to arsenic trioxide during high temperature smelting processes (Montenegro et al., 2013). Arsenic trioxide is volatilized and condensed on the surface of fine particulates in the smoke dust collection processes. Subsequently, arsenic trioxide could react with oxygen to form non-volatilized arsenic pentoxide under oxidizing environment (Ganne et

al., 2006). It has been reported that the volatilization ratio is approximately 76-85% with 7%-17% existed in slag during flash smelting processes (Potysz et al., 2015). For the high Cu content (up to 40%) in the collected dust, the collected arsenic-containing dust is recycled to the smelting furnace and resulted in the deterioration of Cu matte. Therefore, smelting slag is the only discharge outlet of various pyrometallurgical impurities (As, Zn, Pb, and Ni) to ensure the pyrometallurgical quality. The release and environmental mobility of elements from slags are controlled by various factors, i.e. geochemical/mineralogical compositions of slags, association and speciation of elements, and disposal processes (Long et al., 2012; Rozendaal & Horn, 2013). Among them, the association and chemical speciation can provide greatly significant information about the toxicity and bioavailability of As. Therefore, SEM-EDS, XPS and sequential chemical extraction procedures are applied to illustrate the association and chemical speciation of As.

The two-dimensional distribution images of elements in the slag tailing and in different size fractions are present in Fig. 4 and Fig. S1. According to Fig. S1, arsenic is mainly existed in the fine particles (<75 μm). The overlap area of silicate, iron, arsenic and oxygen in the EDS images suggested that As may be associated with silicate minerals as Si-Fe-As-O phases (Zhou et al., 2021a). According to the distributions of elements in different size fractions (Fig. S1), the Si-Fe-As-O phases are mostly found in the fine particulates (<75 μm). Many studies reported that As-O phases disseminated in the silicate minerals are the primary Si-Fe-As-O phases in slag tailing (Montenegro et al., 2013; Zhang et al., 2021a). Meanwhile, the overlap areas of arsenic and sulfur are also found in the selected slag tailing, suggested that the arsenic sulfides are existed in the slag tailing. Therefore, arsenic is mainly existed in silicate minerals, sulfide minerals and oxides in the slag tailing.

The associations of As determined by sequential chemical extraction are presented in Fig. 5. As is mainly existed in residual (82.1%), Fe-Mn oxides bound (9.6%), and organic matter bound (6.2%). The elevated fractions of As in residue and Fe-Mn oxides bound suggested that As are mainly associated with silicate minerals. The organic matter bound of As may be explained by the adsorption of unburned organic matter.

The chemical speciation of As provides extremely information for the toxicity and bioavailability of As in slag tailing. According to the valence states of As, As compounds could be clustered into arsine (As^{-3}), elemental As (0), arsenite (As^{+3}), arsenate (As^{+5}) (Zhou et al., 2021a). Among them, arsenite (As(III)) and arsenate (As(V)) are the mainly valence states of As in slag tailing (Zhang et al., 2021b). The As3d peaks obtained by XPS spectral are conducted to illustrate the chemical speciation of As and shown in Fig. 6. As3d₃ and As3d₅ are known as the two peaks of As3d peaks. Two separated peaks are found at 49.98 eV and 44.53 eV, which are regarded as the As3d of metallic arsenic. It is obviously found that As in slag tailing could be existed in both As(III) and As(V) with the proportions of 59.4% and 40.6%, respectively. For the high toxicity of As(III), the environmental risks of slag tailing caused by As deserve further concern.

3.3 Potential environmental risks of copper slag tailing

Under natural weathering condition, the environmental risks of environmental sensitively elements in slag tailing are related to both total concentration and chemical speciation (Ganne et al., 2006). Determination of the total concentrations of elements in slag tailing provide important information about pollution levels. Nevertheless, the environmental stability and toxicity of elements are greatly determined by the leaching potential and duration.

The results of CN-SWEP and TCLP leaching tests are listed in Table 3. It could be found that the leaching of elements (As, Cu, Zn, Pb, Ni and Cr) in the selected slag tailing is far below the legislation limits and could be considered as non-hazardous inert wastes. Meanwhile, the results of sequential chemical extraction procedure may be applied as an indication to evaluate the potential environmental risk. The risk assessment code (RAC) determined that element could be considered safe (no risk) to the ecosystem when the exchangeable and carbonate bound fractions are less than 1% of the total value. On the contrary, the element can have a strong environmental impact (very high risk) when the aforementioned fractions of any of these elements are more than 50% of the total value. Meanwhile, 1-10%, 11-30% and 31-50% of RAC values are regarded as low risk, medium risk and high risk, respectively. The fractionation characteristics of elements in slag tailing are presented in Fig. 5. The selected environmental sensitively elements are primary existed in residual. The RAC values of Zn, Pb, Cr and Ni reveal that the environmental impacts of these elements could be regarded as negligible. However, speciation patterns of As and Cu show a low risk and medium risk, respectively. Therefore, the environmental impacts induced by these elements in slag tailing should be taken into consideration during disposal and utilization.

Table 3
Leaching of toxic elements from the selected copper slag as obtained by
CN-SNEP and TCLP (mg/L).

Methods	As	Cu	Zn	Pb	Ni	Cr
CN-SNEP	2.512	24.150	2.478	0.274	0.112	0.034
TCLP	2.529	8.056	0.521	0.013	0.020	ND
China limitation	5	100	100	5	5	1
USA limitation	5	20	250	5	5	1

The results of leaching tests are difference to that of RAC model, which may be explained by the interaction between exchangeable element and Fe. High content of Fe in form of Fe^{2+} is existed in slag tailing, Fe^{2+} is quickly oxidized to Fe^{3+} in the water phase, and other elements are co-precipitated with Fe during the formation of iron (hydr)oxide colloids. Finally, the dissolved elements (Cu and As) could be reduced effectively during leaching tests.

4. Conclusions

The bulk chemical compositions of the selected slag tailing are Fe_2O_3 (54.8%) and SiO_2 (28.1%), with minor quantity of Al, Ca Na and K oxides. In comparison with other Cu smelting furnaces, the low Cu content in slag tailing indicates the excellent pyrometallurgical efficiency of the selected smelting furnace. The mineral phases in slag tailing are fayalite, hematite, magnetite, galena, sphalerite, arsenopyrite and chalcopyrite. The peaks of fayalite and hematite are increasing with the decreasing of size fractions, suggesting that these secondly phases are preferred to existed in fine particles. As-O phases disseminated in the silicate minerals are the primary Si-Fe-As-O phases in slag tailing. Meanwhile, arsenic is also associated with sulfide minerals and oxides. As in slag tailing could be existed in both As(III) and As(V) with the proportions of 59.4% and 40.6%, respectively. The results of CN-SWEP and TCLP leaching tests suggested that the selected slag tailing could be considered as non-hazardous inert wastes. However, the high proportions of carbonate bound of As and Cu indicated that the release of As and Cu from slag tailing may lead to potential environmental issues if no countermeasures are adopted.

Declarations

Acknowledgements

We acknowledge editors and reviewers for polishing the language of the paper and for in-depth discussion.

Author contribution

Zhou Chuncai: Conceptualization, Methodology, Writing –original draft preparation. **Zhang Weiwei**: Investigation, Data Curation. **Shen Hexin**: Software, Investigation. **Sun Jinke**: Data curation. **Wu Wentao**: Funding acquisition **Liu Guijian**: Reviewing and Editing.

Funding

This work is supported by the National Key Research and Development Project of China (2020YFC1908601), the National Natural Science Foundation of China (41702166), the Key Research and Development Program of Anhui Province (201903a07020011 and 202004b11020016), the Anhui Provincial Natural Science Foundation (1908085MD113) and Project of Linhuan Coking Industry Company.

Data availability

The data sets supporting the results of this article are included within the article and its additional files.

Declarations

Ethics approval and consent to participate Not applicable

Consent to publish Not applicable

Competing interests The authors declare no competing interests

References

1. Agorhom E. A., Lem J. P., Skinner W., Zanin M. Challenges and opportunities in the recovery/rejection of trace elements in copper flotation-a review. **Minerals Engineering**, 2015, 78, 45-57.
2. Alter H. The composition and environmental hazard of copper slags in the context of the Basel Convention. **Resources Conservation and Recycling**, 2005, 43(4), 353-360.
3. Cappuyns V., Swennen R. The application of pH(stat) leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials. **Journal of Hazardous Materials**, 2008, 158(1), 185-195.
4. Fuentes I., Ulloa C., Jimenez R., Garcia X. The reduction of Fe-bearing copper slag for its use as a catalyst in carbon oxide hydrogenation to methane. A contribution to sustainable catalysis. **Journal of Hazardous Materials**, 2020, 387, 121693.
5. Ganne P., Cappuyns V., Vervoort A., Buve L., Swennen R. Leachability of heavy metals and arsenic from slags of metal extraction industry at Angleur (eastern Belgium). **Science of the Total Environment**, 2006, 356(1-3), 69-85.
6. Gorai B., Jana R. K., Premchand. Characteristics and utilisation of copper slag - a review. **Resources Conservation and Recycling**, 2003, 39(4), 299-313.
7. Guo L., Lan J. R., Du Y. G., Zhang T. C., Du D. Y. Microwave-enhanced selective leaching of arsenic from copper smelting flue dusts. **Journal of Hazardous Materials**, 2020, 386, 121964.
8. Jarosikova A., Ettler V., Mihaljevic M., Drahota P., Culka A., Racek M. Characterization and pH-dependent environmental stability of arsenic trioxide-containing copper smelter flue dust. **Journal of Environmental Management**, 2018, 209, 71-80.
9. Jarosikova A., Ettler V., Mihaljevic M., Kribek B., Mapani B. The pH-dependent leaching behavior of slags from various stages of a copper smelting process: Environmental implications. **Journal of Environmental Management**, 2017, 187, 178-186.
10. Khorasanipour M., Esmaeilzadeh E. Environmental characterization of Sarcheshmeh Cu-smelting slag, Kerman, Iran: Application of geochemistry, mineralogy and single extraction methods. **Journal of Geochemical Exploration**, 2016, 166, 1-17.
11. Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Neel C., Ettler V., Mihaljevic M. Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland). **Journal of Geochemical Exploration**, 2013, 124, 183-194.
12. Krol A., Mizerna K., Boiym M. An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. **Journal of Hazardous Materials**, 2020, 384, 121502.
13. Labaj J., Blacha L., Jodkowski M., Smalcerz A., Frohlichova M., Findorak R. The use of waste, fine-grained carbonaceous material in the process of copper slag reduction. **Journal of Cleaner Production**, 2021, 288, 125640.

14. Li Y. K., Qi X. J., Li G. H., Wang H. Efficient removal of arsenic from copper smelting wastewater via a synergy of steel-making slag and $KMnO_4$. **Journal of Cleaner Production**, 2021a, 287, 125578.
15. Li Y. K., Zhu X., Qi X. J., Shu B., Zhang X., Li K. Z., Wei Y. G., Hao F. Y., Wang H. Efficient removal of arsenic from copper smelting wastewater in form of scorodite using copper slag. **Journal of Cleaner Production**, 2020a, 270, 122428.
16. Li Y. K., Zhu X., Qi X. J., Shu B., Zhang X., Li K. Z., Wei Y. G., Wang H. Removal and immobilization of arsenic from copper smelting wastewater using copper slag by in situ encapsulation with silica gel. **Chemical Engineering Journal**, 2020b, 394, 124833.
17. Li Z., Ma G. J., Zhang X., Li J. L. Characteristics and chemical speciation of waste copper slag. **Environmental Science and Pollution Research**, 2021b, 28, 20012–20022.
18. Long G., Peng Y. J., Bradshaw D. A review of copper-arsenic mineral removal from copper concentrates. **Minerals Engineering**, 2012, 36-38, 179-186.
19. Lottermoser B. G. Evaporative mineral precipitates from a historical smelting slag dump, Rio Tinto, Spain. **Neues Jahrbuch Fur Mineralogie-Abhandlungen**, 2005, 181(2), 183-190.
20. Lu S. J., Li J., Chen D. L., Sun W., Zhang J., Yang Y. A novel process for silver enrichment from Kaldos smelting slag of copper anode slime by reduction smelting and vacuum metallurgy. **Journal of Cleaner Production**, 2020, 261, 121214.
21. Mateus A., Pinto A., Alves L. C., Matos J. X., Figueiras J. Neng, N. R. Roman and modern slag at S. Domingos mine (IPB, Portugal): Compositional features and implications for their long-term stability and potential reuse. **International Journal of Environment and Waste Management**, 2011, 8, 133-159.
22. Mikula K., Izydorczyk G., Skrzypczak D., Moustakas K., Witek-Krowiak A., Chojnacka K. Value-added strategies for the sustainable handling, disposal, or value-added use of copper smelter and refinery wastes. **Journal of Hazardous Materials**, 2021, 403, 123602.
23. Montenegro V., Sano H., Fujisawa T. Recirculation of high arsenic content copper smelting dust to smelting and converting processes. **Minerals Engineering**, 2013, 49, 184-189.
24. Pareuil P., Hamdoun H., Bordas F., Joussein E., Bollinger J. C. The influence of reducing conditions on the dissolution of a Mn-rich slag from pyrometallurgical recycling of alkaline batteries. **Journal of Environmental Management**, 2011, 92(1), 102-111.
25. Pfeifer A., Skerget M., Colnik M. Removal of iron, copper, and lead from aqueous solutions with zeolite, bentonite, and steel slag. **Separation Science and Technology**, 2020, DOI: 10.1080/01496395.2020.1866607.
26. Piatak N. M., Parsons M. B., Seal R. R. Characteristics and environmental aspects of slag: A review. **Applied Geochemistry**, 2015, 57, 236-266.
27. Piatak N. M., Seal R. R., Hammarstrom J. M. Mineralogical and geochemical controls on the release of trace elements from slag produced by base- and precious-metal smelting at abandoned mine sites. **Applied Geochemistry**, 2004, 19(7), 1039-1064.

28. Potysz A., Kierczak J., Fuchs Y., Grybos M., Guibaud G., Lens P. N. L., van Hullebusch E. D. Characterization and pH-dependent leaching behaviour of historical and modern copper slags. **Journal of Geochemical Exploration**, 2016, 160, 1-15.
29. Potysz A., van Hullebusch E. D., Kierczak J., Grybos M., Lens P. N. L., Guibaud G. Copper Metallurgical Slags - Current Knowledge and Fate: A Review. **Critical Reviews in Environmental Science and Technology**, 2015, 45(22), 2424-2488.
30. Rozendaal A., Horn R. Textural, mineralogical and chemical characteristics of copper reverb furnace smelter slag of the Okiep Copper District, South Africa. **Minerals Engineering**, 2013, 52, 184-190.
31. Saez R., Nocete F., Nieto J. M., Capitan M. A., Rovira S. The extractive metallurgy of copper from Cabezo Jure, Huelva, Spain: Chemical and mineralogical study of slags dated to the third millenium BC. **Canadian Mineralogist**, 2003, 41, 627-638.
32. Safarzadeh M. S., Howard S. M. Thermal removal of arsenic from copper concentrates: Three-dimensional isothermal predominance diagrams for the Cu-As-S-O system **Journal of Hazardous Materials**, 2018, 347, 371-377.
33. Schmukat A., Duester L., Ecker D., Heining P., Ternes T. A. Determination of the long-term release of metal(loid)s from construction materials using DGTs. **Journal of Hazardous Materials**, 2013, 260, 725-732.
34. Schmukat A., Duester L., Ecker D., Schmid H., Heil C., Heining P., Ternes T. A. Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength. **Journal of Hazardous Materials**, 2012, 227, 257-264.
35. Schmukat A., Duester L., Goryunova E., Ecker D., Heining P., Ternes T. A. Influence of environmental parameters and of their interactions on the release of metal(loid)s from a construction material in hydraulic engineering. **Journal of Hazardous Materials**, 2016, 304, 58-65.
36. Shu J. C., Lei T. Y., Deng Y. L., Chen M. J., Zeng X. F., Liu R. L. Metal mobility and toxicity of reclaimed copper smelting fly ash and smelting slag. **Rsc Advances**, 2021, 11(12), 6877-6884.
37. Siddique R., Singh M., Jain M. Recycling copper slag in steel fibre concrete for sustainable construction. **Journal of Cleaner Production**, 2020, 271, 122559.
38. Tessier A., Campbell P. G. C., Bisson M. Sequential Extraction Procedure for the Speciation of Particulate Trace-Metals. **Analytical Chemistry**, 1979, 51(7), 844-851.
39. Vitkova M., Ettler V., Mihaljevic M., Sebek O. Effect of sample preparation on contaminant leaching from copper smelting slag. **Journal of Hazardous Materials**, 2011, 197, 417-423.
40. Zhang H. B., Wang Y. N., He Y. Z., Xu S. H., Hu B., Cao H. Z., Zhou J., Zheng G. Q. Efficient and safe disposition of arsenic by incorporation in smelting slag through copper flash smelting process. **Minerals Engineering**, 2021a, 160, 106661.
41. Zhang S. H., Zhu N. W., Mao F. L., Zhang J. Y., Huang X. X., Li F., Li X. Y., Wu P. X., Dang Z. A novel strategy for harmless and reduction of copper smelting slags by alkali disaggregation of fayalite (Fe_2SiO_4) coupling with acid leaching. **Journal of Hazardous Materials**, 2021b, 402, 123791.

42. Zhou H. H., Liu G. J., Zhang L. Q., Zhou C. C. Mineralogical and morphological factors affecting the separation of copper and arsenic in flash copper smelting slag flotation beneficiation process. **Journal of Hazardous Materials**, 2021a, 401, 123293.
43. Zhou H. H., Liu G. J., Zhang L. Q., Zhou C. C., Mian M. M., Cheema A. I. Strategies for arsenic pollution control from copper pyrometallurgy based on the study of arsenic sources, emission pathways and speciation characterization in copper flash smelting systems. **Environmental Pollution**, 2021b, 270, 116203.
44. Zhou Y. Q., Liu W. W. Application of granulated copper slag in massive concrete under saline soil environment. **Construction and Building Materials**, 2021, 266, 121165.

Figures

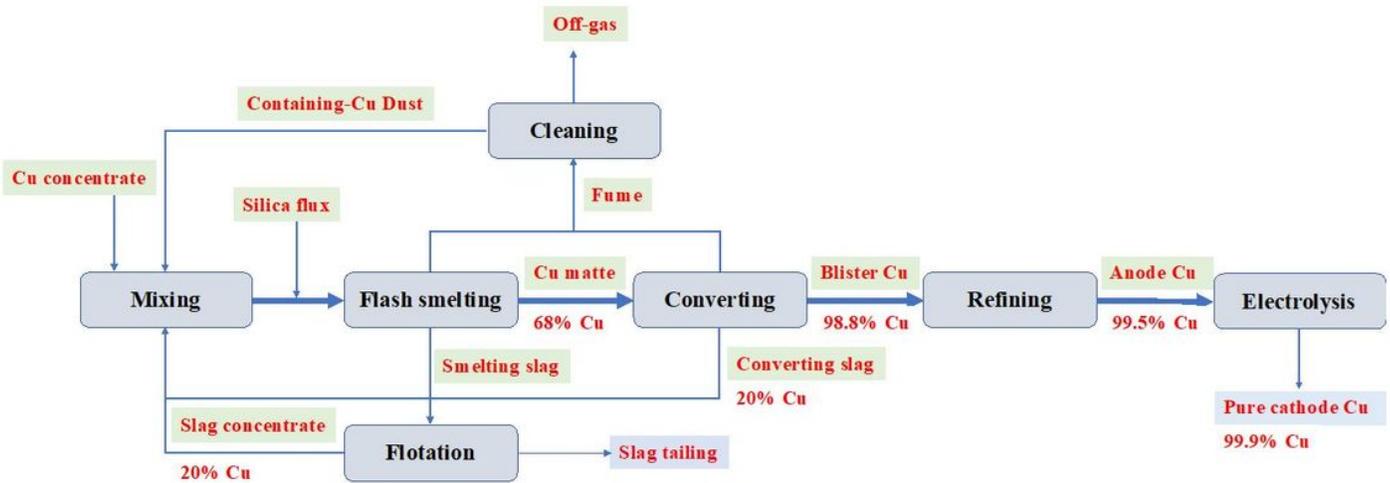


Figure 1

Flowsheet of pyrometallurgical copper production

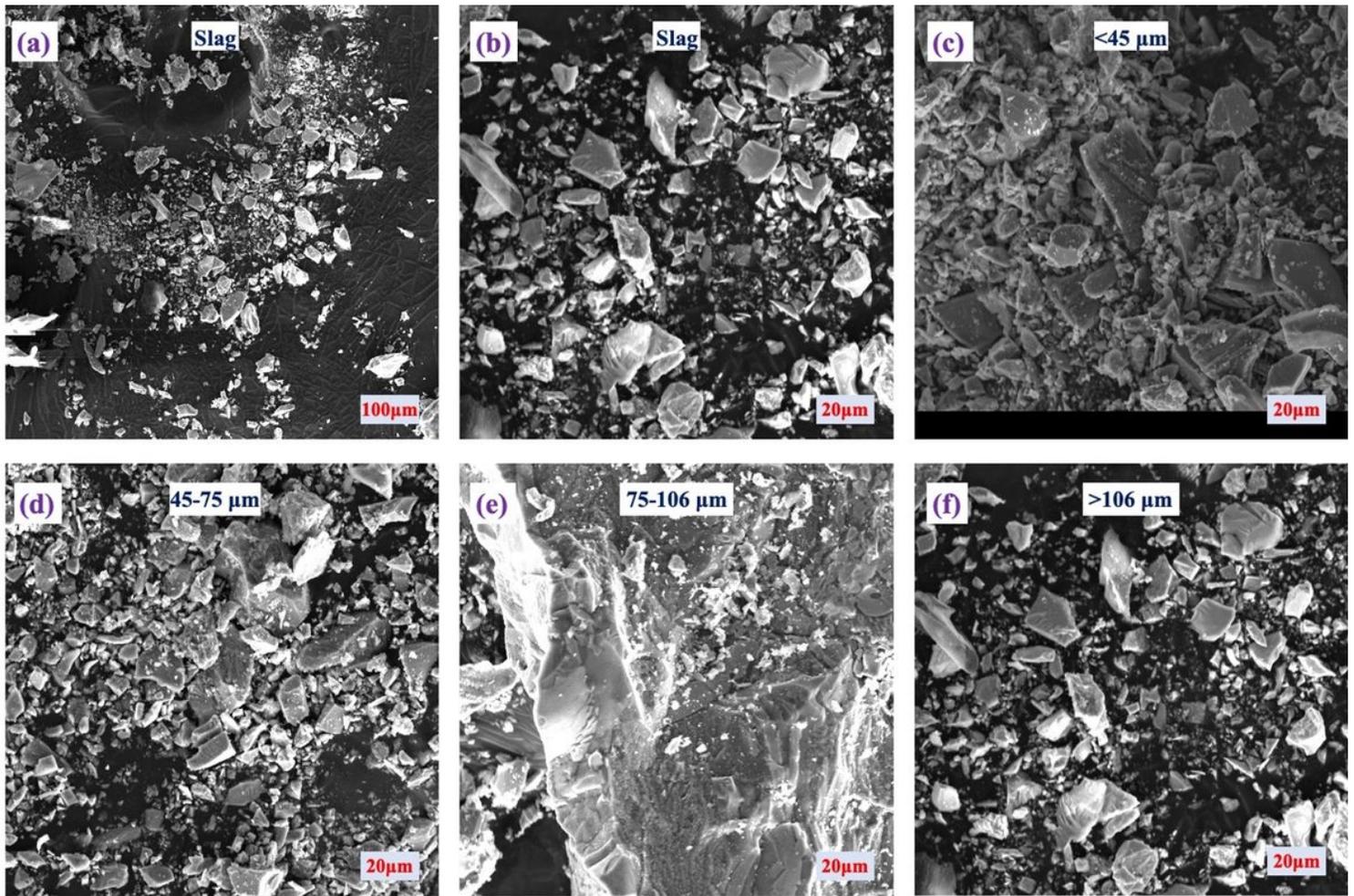


Figure 2

The morphology characterization of the slag tailing.

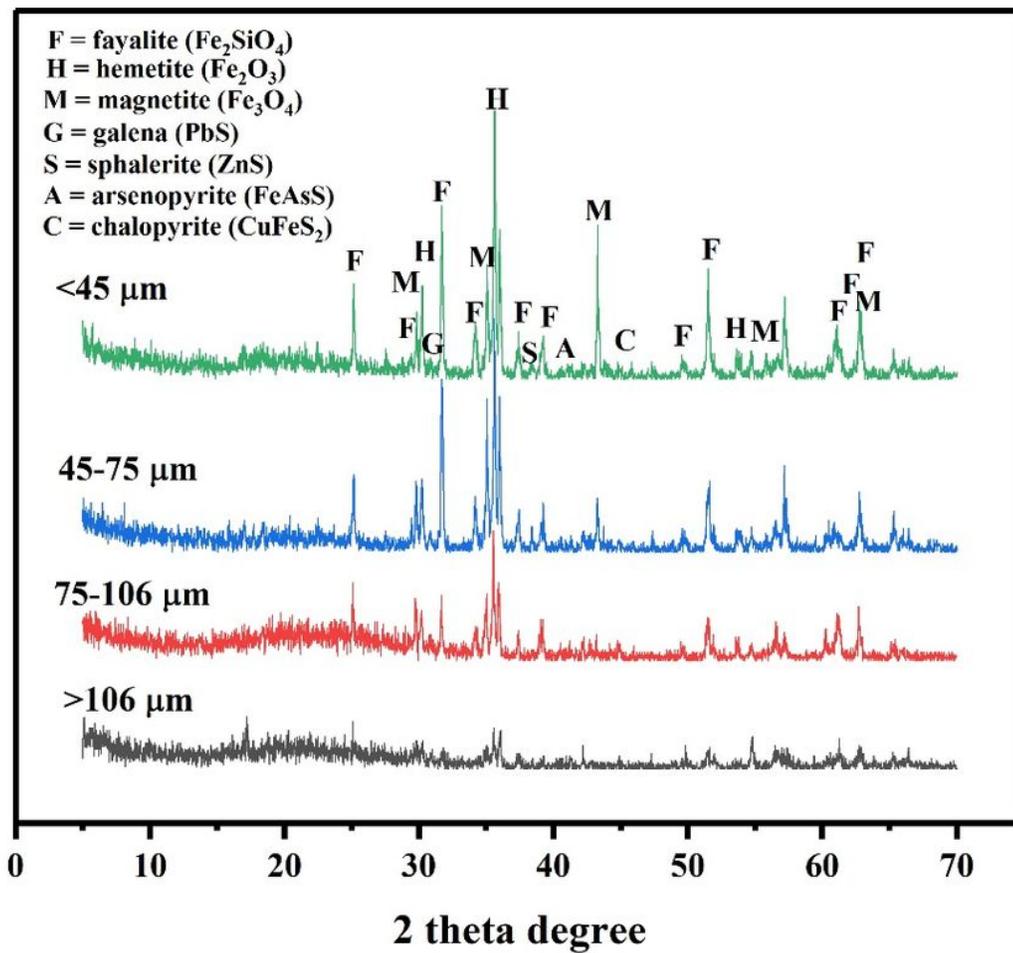


Figure 3

The mineralogical characterizations of the selected slag.

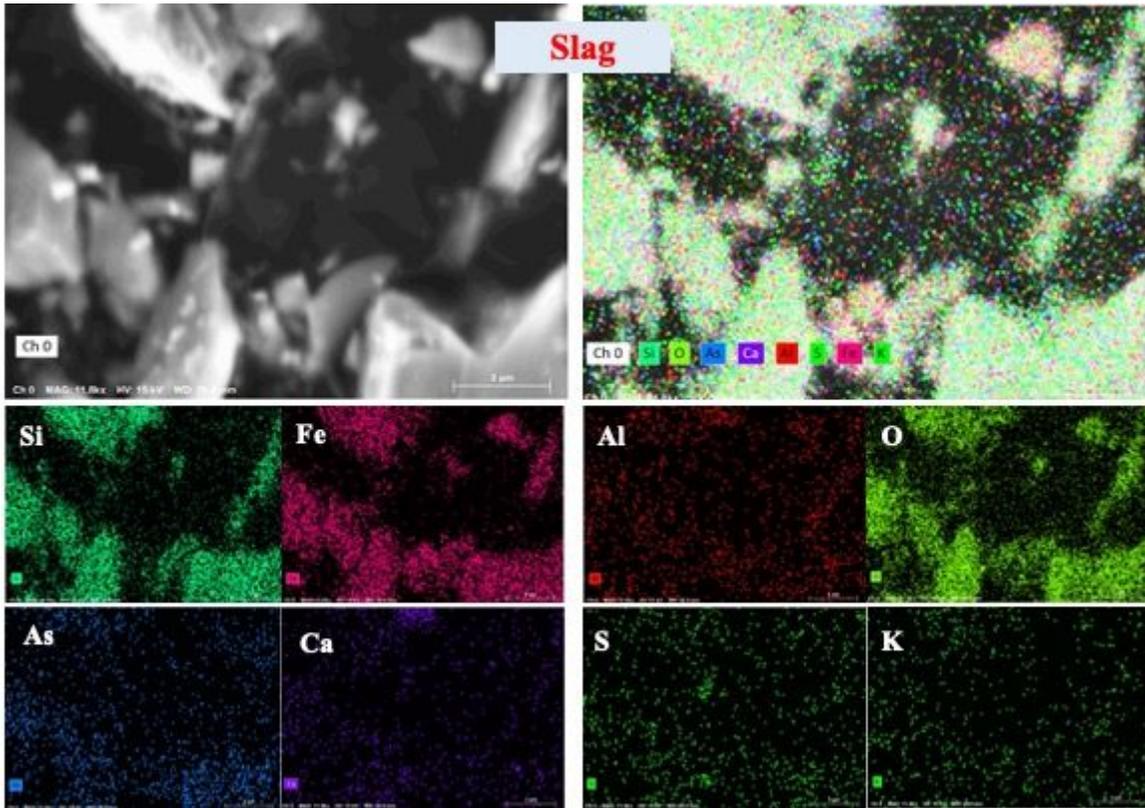


Figure 4

Two-dimensional distribution of elements in slag tailing.

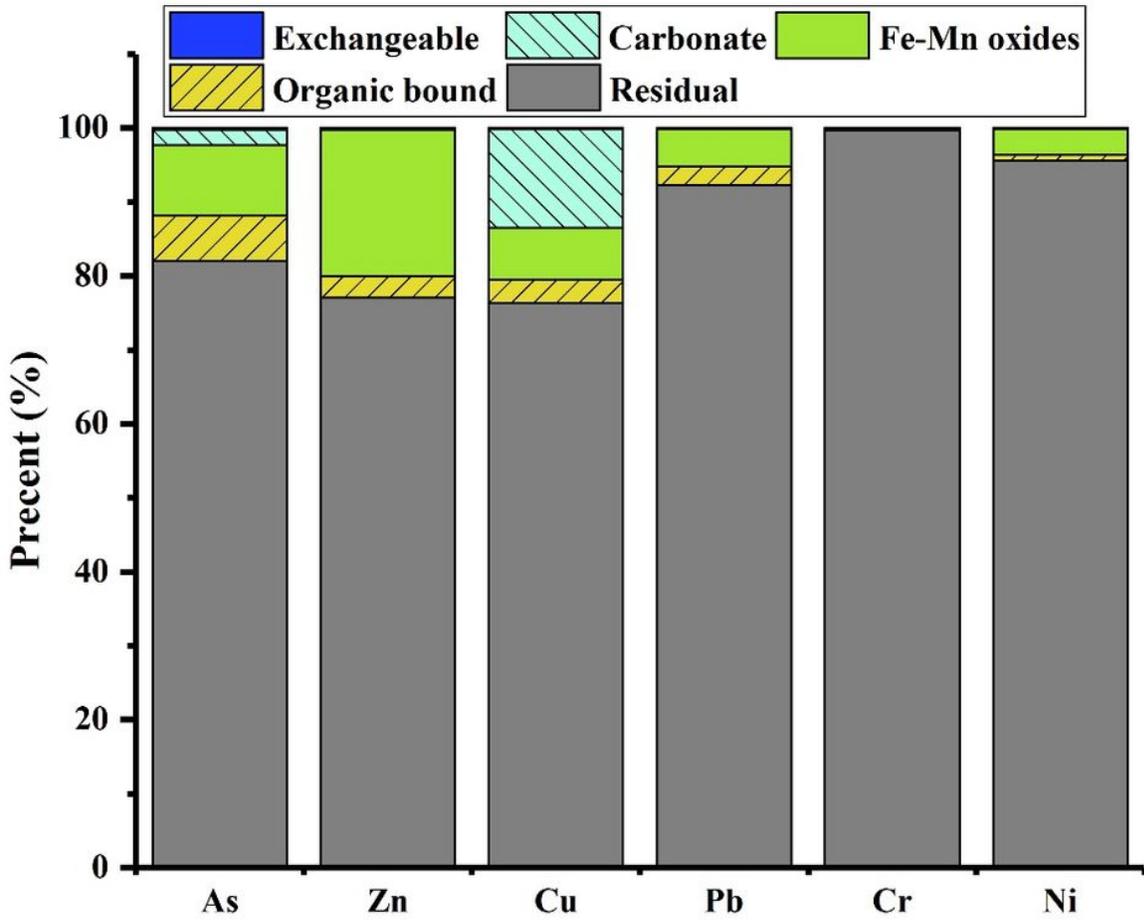


Figure 5

Association of toxic elements in the selected slag.

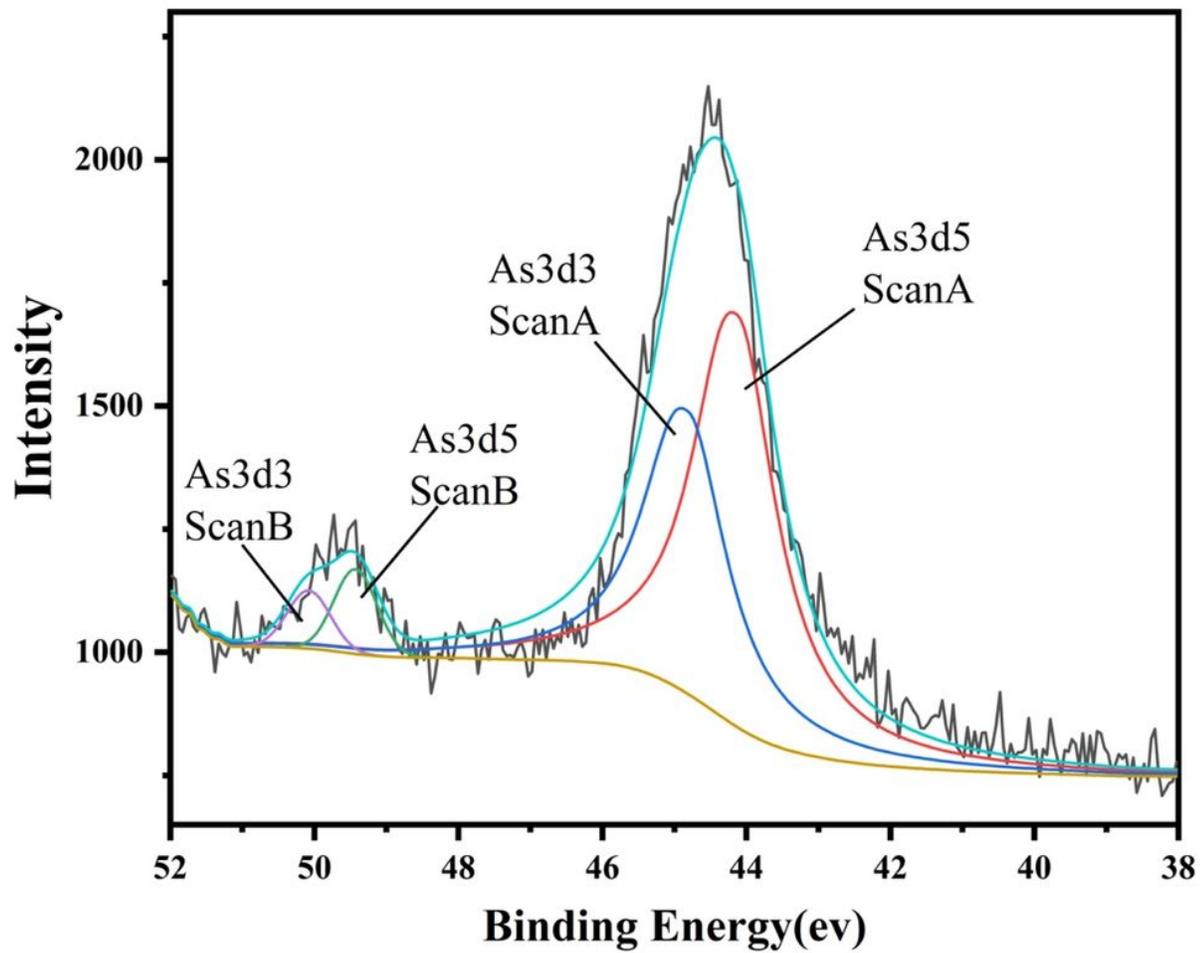


Figure 6

Chemical speciation and valence state of arsenic in the selected slag.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supportinformation.docx](#)