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Published in:

Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science

DOI:

[10.1007/s11663-020-01907-8](https://doi.org/10.1007/s11663-020-01907-8)

Published: 01/12/2020

Document Version

Peer reviewed version

Please cite the original version:

Chen, Y., Zhao, Z., Taskinen, P., Liang, Y., Ouyang, H., Peng, B., Jokilaakso, A., Zhou, S., Chen, T., Peng, N., & Liu, H. (2020). Characterization of Copper Smelting Flue Dusts from a Bottom-Blowing Bath Smelting Furnace and a Flash Smelting Furnace. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*, 51(6), 2596-2608. <https://doi.org/10.1007/s11663-020-01907-8>

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Characterization of copper smelting flue dusts from a bottom-blowing bath smelting furnace and a flash smelting furnace

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Abstract

The smelting technology and flue dust treatment have an influence on the physical and chemical characteristics of flue dusts collected in copper smelting. We characterized flue dusts from a Bottom-Blowing Bath Smelting (BBS) process and from a Flash Smelting (FS) process by determining their comprehensive physical, chemical and mineralogical characteristics. Annual flue dust generation data showed that the rate of the BBS process (2-3 %) was clearly lower than that of FS process (5-6 %). The results revealed that copper smelting flue dusts from the FS exhibited a larger entrainment of solids and a smaller particle size than the BBS. The crystallographic and chemical compositions of the samples indicated that the FS flue dusts have a higher degree of crystallinity than those of the BBS. Fe₃O₄, CuSO₄ and PbSO₄, Fe₃O₄, CuFe₂O₈ were the predominant crystalline phases in the FS and BBS flue dusts, respectively. In the FS and BBS flue dusts, amorphous multicomponent Cu-Zn-FeO_x and Cu-Zn-S phases were formed, respectively. Mineralogical examinations and a stepwise chemical extraction confirmed that the majority of arsenic existed in amorphous form and mostly as pentavalent As⁵⁺ arsenate or As₂O₅ except that in BBS-ESPD.

Key words: arsenic, lead, zinc, X-ray photoelectron spectroscopy, speciation

1. Introduction

Copper is an indispensable basic commodity and an important strategic material for the development of national economies. About 80% of the world's copper-from-ore originates from Cu-Fe-S ores, which are not easily dissolved by aqueous solution. Therefore, a vast majority of copper extraction from these minerals is based on pyrometallurgical processing [1]. With the continuous decrease of copper concentrate grades, the increasingly complex compositions and stricter environmental requirements, development of clean and efficient copper extraction methods has become evident [2,3].

There are two main types of modern copper smelting processes: bath smelting, represented in this study by the bottom-blowing bath-smelting (BBS) process, and the suspension smelting, represented here by the flash smelting (FS) process [4]. The FS and the BBS processes have their characteristic features in copper making. The FS technology is advanced, mature and reliable. It is accompanied by advantages of a large single furnace treatment capacity and a long campaign life. However, there are also disadvantages such as drying of the feed mixture, large number of copper water jackets in the furnace vessel, and a high investment cost in small smelter capacities [5-7]. The BBS process is a newly developed smelting technology [8], which is widely applied in China. Its advantages are steady production, simple operation, and a good raw material adaptability [9, 10].

In the smelting, distributions of minor elements, such as arsenic, cadmium, lead and zinc, have important implications to the copper making process. The elements may seriously affect properties of the copper product, and cause severe environmental pollution [11]. Along with increased industry attention to the deportment of arsenic among various material streams in copper smelting, a number of publications on the distribution behavior of minor elements in the pyrometallurgical processing of copper concentrates have been published [12]. Some authors [13-18] used thermodynamic modeling, based on equilibrium calculations to simulate the behavior and distribution of arsenic in the copper smelting. The results show that copper smelting operates close to equilibrium between condensed phases and most arsenic is reporting to the gas phase. This was also confirmed by Chen [19] when investigating the distribution of arsenic in the actual smelting processes. He pointed out that 90 % of As may enter the off gas in the BBS process. According to recent plant analyses, volatilization of arsenic in FSF and FCF (flash smelting furnace and flash converting furnace) is strong [20].

The high As-containing off-gas stream from the smelting furnace carries also solid

particles at high temperatures. The off-gas is treated in a waste-heat boiler (WHB) to separate coarse solids, the waste-heat boiler dust (WHBD), as well as for recovering heat. Then the gas enters the electrostatic precipitator (ESP) for removing the fine particles, the electrostatic precipitator dust (ESPD), leaving an essentially solids-free off-gas stream suitable for acid-making [21]. The dusts typically contain Fe, Cu, As, Pb, Cd and Zn, but vaporization of the elements depends on smelting conditions and its operational parameters [22, 23].

Arsenic is the major impurity in the flue dusts, which in the furnace and its off-gas train is generated by two mechanisms:

- the chemically formed flue dust, vaporizing in the furnace and condensing in the off gas train at lower temperatures [12, 16];
- the mechanically formed dust, produced as a result of entrainment of solid or liquid particles in the smelting furnace [24].

In the industrial operations, the flue dusts are usually recirculated back to the feed-mixture of the smelting. When arsenic content in the flue dust is accumulated to a certain level, affecting the quality of cathode copper, the flue dust circulation is discontinued and the dust treated separately.

According to current environmental regulations, copper smelting flue dusts are defined as “hazardous materials” due to their high solubility of arsenic in the TCLP (Toxicity Characteristic Leaching Procedure) test [25]. Based on strict environmental regulations, copper smelting flue dusts are receiving growing attention. However, characterization of the flue dust is not common in the literature. Most studies [26-30] focused on the characterization and treatment of a particular metallurgical flue dust. Few researchers have pointed out differences in the flue dusts generated by different smelting processes and technologies.

In this work, a full physical, chemical and mineralogical characterization of copper smelting flue dusts from a BBS process and a FS process will be carried out using various analytical techniques, to properly characterize differences of the flue dusts trapped by the various sections of the smelter off-gas trains and to determine the arsenic speciation in two industrial operations.

2. The smelting process descriptions

Fig. 1 shows flow sheets of the BBS and FS copper smelters studied in this work. In both processes [8, 31-33], copper concentrates with flux, circulated flue dust and slag concentrate are continuously charged by a belt conveyer in the oxidative smelting to produce copper matte, process off-gas and slag. The off-gas from the smelting and converting furnace is cooled and its dust settled in WHB, and the subsequent dust settling chamber (DSC, in

FSF line) prior to ESP, followed by acid-making process. Produced matte is converted into blister copper using a discontinuous and continuous method in the BBS and FS smelter, respectively. The blister copper is transferred into an anode furnace followed by casting operation to copper anodes. Copper cathode is obtained by electrolytic refining of copper anodes in a tank house. The anode slime as a by-product of the electrolytic refining is treated for the precious metals recovery.

Fig. 1. Flow sheets of the bottom-blowing bath smelting and the flash smelting processes and plants.

It was emphasized that characteristics of the flue dusts depend not only on compositions of the feed mixture but also on the smelter operation, such as temperature, oxidation conditions in the furnace and along the off-gas train, and the smelting equipment. The furnace operation conditions of the smelters providing the flue dusts for this study were listed in Table 1. The parameters varied within a certain range to ensure steady operation in the smelting.

The feed mixture of a flash smelting furnace must be well dried and fine for maximum heat recovery and smooth ignition [34]. The bottom-blowing bath-smelting furnace (BBSF) has no strict requirements for the feed material, and no pretreatment is required. In the BBSF, oxygen-rich gas is blown by lances (tuyeres) from bottom of the smelting furnace so that both matte and slag layers are strongly agitated [8]. Oxygen along with the feed mixture is fed by the concentrate burner into the FSF, locating on top of the reaction shaft. In the smelter operations, the slag composition and smelting temperature were adjusted according to the operation point in order to maintain fluidity of the slag. However, due to the dynamic situation in industrial scale furnaces and their operating practices, the slag composition and smelting temperature will fluctuate around the set point rather than keep constant.

3. Experimental

3.1 Sample collection and pretreatment

The flue dust samples were obtained from two Chinese copper smelters operating BBSF and FSF. The high-temperature off-gas from BBSF, mixed with air in the WHB inlet, first entered at 850~900 °C the vertical WHB section, which was about 20 m long and of membrane boiler tube design for heat exchange. Then it entered the acid-making process after passing through the horizontal WHB (600~650 °C) and ESP (< 350 °C). The FSF off-gas was led directly into WHB with a 1 m long duct. Therefore, the off-gas temperature difference between the end of the FSF uptake shaft and the inlet of the WHB was small, and the outlet temperatures in the gas train were given in Fig. 2.

Two different dust samples from the BBSF were obtained. Flue dusts collected from the WHB outlet (WHBD) and from the dust bin of the ESP (ESPD) were obtained from BBSF. The flue dusts of FSF were collected from two sections of the WHB (WHBD, from the radiation and convection sections), followed by DSC (DSCD) and ESP (ESPD).

Fig. 2. Directions of the off-gas flow and the sampling points of the flue dusts in the bottom-blowing bath-smelting plant and the flash smelting plant.

The feed mixtures were collected from the conveyor belt after the concentrate bin and mixed evenly. The samples were dried and ground 40 s in batches with a vibrating mill (XZM-100, Wuhan Exploration Machinery Factory, China). After mixing they were divided into four parts. Samples of 100g from each part were named A0 (BBS) and B0 (FS) for analysis.

The flue dust samples were labelled as A1, A2, and B1, B2, B3, B4 from the BBSF and FSF, respectively, according to the smelting process and its sampling point. The specific sampling locations in the smelting process lines are shown in Fig. 2. The dusts were divided into two after drying. Half was directly used for particle size and SEM analysis. The second half was treated in a similar way as the feed mixture, but homogenized twice for the other analysis in the following sequence: grind→mix→400 g sample→mix→200 g sample→mix→analysis.

3.2 Analytical methods

Mineralogies of the furnace charges containing copper concentrates were analyzed by a Mineral Liberation Analyzer FEI MLA 650 (Thermo Fischer Scientific, USA) equipped with a FEI Quanta 650 scanning electron microscope (Thermo Fischer Scientific, USA) and fitted with an energy dispersive spectrum analyzer Quantax 200 with Dual XFlash 5010 (EDS; Bruker, Germany). The FEI MLA 3.1 software package (Thermo Fischer Scientific, USA) [35] and its mineral standards library was used for the data analysis.

The particle size distributions of the flue dust samples were determined using a Mastersizer 2000 (Malvern, UK) laser diffraction particle size analyzer. Alcohol was used as the dispersant.

Microstructures of the samples were examined using a Nova NanoSEM 230 FEI scanning electron microscope (SEM; Thermo Fischer Scientific, USA). Polished sections from selected dust samples were further examined by an electron probe microanalyzer JXA-8530F (EPMA; JEOL, Japan) to characterize the cross sections of the flue dusts particles. The operation conditions for EPMA were as follows: the accelerating voltage 15 kV; the probe current 20 nA (2.0×10^{-8} A); the beam diameter $< 1 \mu\text{m}$. The external standards used for the analysis were InAs for As, chalcopyrite (CuFeS_2 , Sudbury Ontario) for Cu, Fe and S, willemite ($(\text{Zn}, \text{Mn})_2\text{SiO}_4$, Franklin Furnace, NJ, USA) for Zn, crocoite (PbCrO_4 , Dundas, Tasmania, Australia) for Pb and O, bustamite ($\text{CaMnSi}_2\text{O}_6$, Broken Hill, NSW Australia) for Ca. A ZAF correction program was employed for the matrix effects.

The flue dust samples mixed with resin and hardener were cast into polypropylene mold ($\phi 30 \text{ mm}$) and baked at 55°C for 5 h. Then, the specimens were polished with #300, #800, #1200 and #1500 emery papers in sequential order along the longitudinal direction and washed with ethanol, followed by polishing.

The crystalline phase compositions of the samples were identified by a D/Max 2500 VB+ 18 KW X-ray diffractometer (XRD; Rigaku, Japan) using Cu (40 kV, 300 mA)

radiation, with the steps of 0.02° and scanning speed of $10^\circ \cdot \text{min}^{-1}$ in the 2θ range from 10° to 80° . The phase identification was done with the MDI Jade 6.0 software (Jade 6.0, MDI, Livermore, CA, USA) interfaced with the PDF2 powder database [36].

The elemental compositions of the flue dust samples were determined by an X-ray fluorescence spectrometer 1800 (XRF; Jindao, Japan) using Rh anode radiation and a standard slit at 36.5°C .

X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo Scientific ESCALAB 250Xi (Thermo Fisher Scientific, USA) using an Al K α X-ray source (1486.6 eV). To compensate for the charging effects, all XPS spectra were calibrated with graphitic carbon as the reference, at the binding energy (BE) of 284.8 eV.

4. Results and discussion

4.1 Analyses of the feed mixtures

The elemental compositions of the feed mixtures of the BBSF (A0) and FSF (B0) were determined by XRF. The concentrations of the main elements and some impurity trace elements are presented in Table 2. The analysis shows that Cu, Fe, O and S were main elements of the copper concentrate mixtures.

Fig. 3. Mineral liberation chart for the feed mixtures of the BBSF (A) and FSF (B) smelting processes; a & c: backscattered electron image; b & d: the final MLA analysis image.

Mineral liberation results and quantitative analysis of feed mixture minerals, generated by a SEM-EDS-based MLA, combined with the image analysis software are shown in Fig. 3 and supplementary Table S-1 (electronic supplementary material), respectively. They give

useful information about mineral properties of the feed mixtures, such as particle size, texture, mineral surfaces, mineral associations, and characteristics of the mineral assemblages on a μm -to-mm scale [37].

As shown in the supplementary material (supplementary Table S-1), the ore minerals in the two feed mixtures were similar, but the mineral compositions were obviously different. In the feed mixtures A0 and B0, concentration of chalcopyrite was the highest followed by pyrite and quartz. The contents of the three main minerals in A0 and B0 were as follows: 41.9 % (chalcopyrite, CuFeS_2), 19.9 % (pyrite, FeS_2) and 7.90 % (quartz, SiO_2) for A0, and 28.4 % (chalcopyrite), 21.3 % (pyrite) and 12.9 % (quartz) for B0, respectively. As can be seen in Fig. 3, the minerals of A0 show a coarser average particle size (d_{50}) than those of B0. The observation was confirmed by the particle size analysis. Fig. 3 shows in detail that small fractions of chalcopyrite and pyrite in A0 and B0 occurred together with other minerals, whereas the other minerals were fully liberated throughout the polished sections studied.

4.2 Dust generation rates

The Chinese BBS and FS copper smelter operations were characterized in more detail and their dust generation rates in 2017 were calculated on a monthly basis, supplementary Fig. S-1. It can be seen that the dust rate of the BBS process (2-3 % of the dry feed) was clearly lower than that of the FS process (5-6 %). The elemental compositions of the flue dusts from the BBSF and FSF were determined by XRF. The chemical assays of the flue dusts obtained were collected in Table 3.

The low volatility of silicon at the smelting temperatures is well-documented, and it can therefore be used as a tracer for the mechanical entrainment of the feed or the smelting bath by gas flow. That is, a high silicon concentration in the dust means a high entrainment rate. In this sense, it can be concluded from Table 3 that the entrainment rate of the FS furnace was much higher than that of the BBS furnace.

The FSF deals with a fine feed mixture, and the smelting process is carried out in a gas-solid suspension [5]. Not only un-melted particles were carried away by the furnace off-gas, but also some molten droplets originating from the reaction shaft. The process gas leaving the furnace was cooled in the off-gas train and dust was collected in WHB, DSC and ESP, as shown in Fig. 2 [31-33]. Particle size of the feed mixture of the BBSF was larger, and most particles dissolved into the furnace bath. In the BBSF, only a small fraction of the charge was carried away by the smelter off-gas.

According to (TCLP) leaching results (Table 4), both the FSFD and BBSFD show

characteristics of toxicity and were classified as hazardous wastes. A large particle size of the flue dust and a high entrainment rate can inhibit harmful elements leaching rates.

4.3 Characterization of the flue dusts

4.3.1 Microstructures and particle size distributions

The collected flue dusts were characterized by a laser diffraction particle size analyzer. An ultrasonic pretreatment in alcohol was used to disperse the sample and to avoid its potential dissolution in water. This eliminated errors of physical agglomeration and chemical reactions in the particle size measurements.

The cumulative particle size distributions obtained are shown in Fig. 4. It can be seen that the median particle sizes (d_{50}) gradually decrease along with the distance in the off-gas train. In the BBS the mean particle sizes were: WHBD (A1) > ESPD (A2) and in the FS: WHBD (B1, B2) > DSCD (B3) > ESPD (B4). The flue dust particle sizes of the two smelting processes with almost similar gas trains were as follows: BBS > FS. The particle sizes of the flue dusts were confirmed by the SEM micrographs in Fig. 5 (a~f).

Fig. 4. Cumulative particle size distributions of the flue dusts studied (a:BBSFD; b:FSFD).

It can be seen in Fig. 5 (g~l) that the flue dust particle shapes were irregular. The surfaces of the flue dust particles from the BBSF were smooth and those from the FSF were faceted. It indicates that crystallinity of the dust particles from the FSF was higher than that from the BBSF.

Fig. 5. SEM secondary electron images of the flue dust surface morphologies.
(a&g: BBS-WHBD; b&h: BBS-ESPD; c,d,i&j: FS-WHBD; e&k: FS-DSCD; f&l: FS-ESPD)

4.3.2 Mineralogy of the phases

Cu, Fe, O and S were the main elements of the copper concentrates (Table 2). In addition, the volatile impurity elements, such as As, Pb and Zn, enrich in the flue dust to a certain extent during cooling of the gas and condensate along the off-gas train. Thus, concentrations of such elements in the flue dusts were relatively high compared to the feed mixtures. Despite the similar elemental concentrations in flue dusts of the two smelters, their main crystalline phases were different. Typical X-ray diffractograms of the studied flue dusts are shown in Fig. 6.

As can be seen in Fig. 6, the diffraction patterns of the BBSFDs were diffuse. However, those of the FSFDs showed relatively narrow peaks, although there was also a small number of diffuse peaks. This indicates that the FSFDs have a higher degree of crystallinity than the BBSFDs. This was consistent with the SEM observations. This may be due to the fact that

the first period of the off-gas train temperature drop rate in the FS process was much lower than that in the BBS process, which promotes the crystallization of particulate matter.

Before the sampling point of the first BBS process dust sample (A1), the off-gas went through two cooling processes: the vertical quench section and the horizontal WHB section, as described in chapter 3.1. During the quench section, the entrainment solid or liquid particles and some higher melting point compounds, which are supposed to condense first, would appear. The especially large particles would settle in the BBSF due to the gravity leaving some relatively small particles into the horizontal WHB accompanying the off-gas. However, in the FS process, the WHB inlet temperature is essentially the same as the smelting temperature.

The off-gas train temperature drop rate in the BBS and FS process were calculated according to the length of the WHB unit, cross-sectional area, average temperature change and volumetric gas flow rate in the off-gas train. The parameters and results are shown in supplementary Table S-2. It can be concluded that the biggest off-gas temperature drop rate of the BBS process was more than sixfold than that of FS process.

Fig. 6. XRD patterns of the smelting flue dusts from an industrial BBSF (a) and FSF (b).

Fe₃O₄ and CuSO₄ were the predominant crystalline phases in the FSF flue dust samples. PbSO₄, Fe₃O₄ and CuFe₅O₈ were identified in the BBSFD samples and besides some weak peaks, such as Pb₂As₂O₇ and Zn₂Cu(AsO₄)₂ exhibiting some overlapping with some main peaks, appeared in the XRD patterns. This made the firm identification of its minor phases difficult [38]. Therefore, in order to fully characterize the arsenic-containing phases in the flue dusts it was necessary to employ additional analytical methods. XPS, a sequential chemical extraction and EPMA were applied for this purpose.

4.4. Enrichment of elements in flue dust

Twenty back-scattered electron micrographs from polished sections of the flue dust

samples are shown in Fig. 7. The contents of arsenic, copper, iron, zinc, lead, sulfur and oxygen in selected regions in atomic percentages were collected in supplementary Table S-3.

As shown in Fig. 7, the black areas represented spots with more than 2.3 at.% zinc containing at the same time high copper and sulfur, and low oxygen as well as iron. It was assumed that zinc and copper in these areas form sulfides, which were mainly present in BBSD samples. The areas marked with red areas were enriched in more than 1.6 at.% Zn, and contained high at.% oxygen and iron, and low at.% copper and sulfur. A Cu-Zn-FeO_x phase was assumed to exist in these regions, mainly in FSD samples.

In the areas with yellow shadow, the oxygen atom was very high in the measured atoms content (arsenic, copper, iron, zinc, sulfur, oxygen and lead). During these atoms, sulfur and arsenic can occupy oxygen with high atomic ratio (1:4). However, they were not abundant to combine with all the oxygen, resulting in excess oxygen being vacated. Therefore, it is inferred that the Me_xSiO₄ or SiO₂ may exist in these regions. According to chapter 4.2, a high silicon concentration in the dust means a high entrainment rate. From the areas with yellow shadow, we can conclude that mechanically formed particles in FSD samples were more than that in BBSD samples, consistent with XRF results (Table 3).

At high temperatures, a large fraction of arsenic was present in the off-gas as gaseous species, and only a small fraction of arsenic was dissolved in condensed particulates, such as spots #2 and 6 in Fig. 7. Thus, the arsenic contents of the WHBDs were relatively low. When the gas temperature drops below the dew point of an arsenic-containing phase, it can precipitate and enrich in the flue dust, as shown in the bright white areas in Figs. 7 A2-1~A2-6.

The arsenic content in the FSFD particles was generally low. However, similar to BBSFD, sulfur contents of the high-arsenic particles were low indicating that arsenic in FSF gas train was precipitated in the form of a simple arsenic oxide or as arsenates.

In order to clearly observe the enrichment differences of different elements, the relationships between the atomic percentage of sulfur, oxygen, arsenic at different spots/areas in Fig. 7 versus that of copper, iron, lead and zinc are shown in Fig. 8 based on supplementary Table S-3. The assays in the granules were classified into three categories: oxide (I: low-sulfur & high-oxygen region), sulfate (II: medium-sulfur & high-oxygen region), and sulfide (III: high-sulfur & low-oxygen region) by their sulphur and O contents.

Fig. 7. Electron micrographs of the copper smelting flue dusts studied and the EDS

analysing areas of each sample; the sampling position of each flue dust at the smelter is shown in the legend (A1-1, A1-2, A1-3, A1-4: BBS-WHBD; A2-1, A2-2, A2-3, A2-4, A2-5, A2-6: BBS-ESPD; B1-1, B1-2, B1-3, B2: FS-WHBD; B3-1, B3-2, B3-3: FS-DSCD; B4-1, B4-2, B4-3: FS-ESPD).

As can be seen in Fig. 8(a), the distribution characteristics of arsenic in BBSFD particles can be divided into three categories: the low-arsenic particles with high copper (26 at. %-44 at. %) (III) and the higher arsenic particles with a low-copper content (0.3 at. %-9.0 at. %) (I). As for the trend of arsenic content in particles with medium-copper is not clear (II). In addition, the zone of a high oxygen content was linked a high arsenic content, indicating that arsenic was present in the particles as a simple oxide or an arsenate. Their specific ratios could be obtained through the speciation analysis. Most high-copper low-arsenic zone and the low-copper high-arsenic zone may have been formed in WHB (in the high temperature zone) and in ESP (in the low temperature zone), respectively.

Both in the BBSFD and FSFD flue dusts, copper was enriched in regions II and III particles, while iron was mainly enriched in region I, easy to form iron oxides. However, the enrichment domains of zinc in BBSFD and FSFD were different. Zinc was enriched in regions I (oxides) and III (sulfides). Converting the corresponding at. % to wt. % in Figs. 8(a), (b) and (d), the points with a high copper content (27 wt. %-37 wt. %) were coexisting with zinc and sulfur in some BBSFD particles. From the previous analysis, we know that they were from BBS-WHB, indicating reducing conditions in the WHB. In some areas, a high iron content (up to 50 wt. %) combined with zinc and oxygen could be found in few

FSFD particles. It can be explained that zinc can be selectively condensed as oxides at approximately 1100 °C with a limited amount of leakage air and as sulfides at about 900 °C with no leakage air [39], corresponding to the conditions in the WHB of FS and the BBS furnace (between the top of slag and the furnace off-gas outlet), respectively. However, the two phases were not found by XRD in Fig. 6, suggesting that the phases were not present in crystalline form but were amorphous. This result is consistent with Stefanova et al. [40], who investigated phase compositions of the WHBD from FSF smelting and pointed that copper and zinc may form amorphous phases with iron oxides.

It can be seen in Fig. 8(c) that lead content of the FSFD was generally low. In the BBSFD particles, high lead was easily enriched in region II as lead sulfate, according to the XRD results shown in Fig. 6. The particles in the dust consisting of oxides and sulphates indicated that the particles reacted with leakage or injected air in the off gas stream.

Fig. 8. Distributions of arsenic between copper (a), iron (b), zinc (c) and lead (d) compounds in the flue dusts.

4.5. Phase distribution analysis for arsenic

To confirm the chemical states of the flue dust surfaces (A1-A2, B1-B4), an X-ray photoelectron spectroscopy (XPS) analysis was performed. The C 1s peak at 284.8 eV was used as a reference to correct the binding energies.

Fig. 9. The XPS survey spectra of the flue dust samples (a) A1 and A2 as well as (b) B1, B2, B3 and B4.

A summary of the obtained XPS spectra (Figs. 9(a) and (b)) revealed the existence of C, O, S, Fe, Cu, Zn, Cd, Pb and As in all samples. It should be pointed out that the main focus in measuring chemical states of the flue dust surfaces was the speciation of arsenic. As depicted in Fig. 10(a), the high-resolution As 3d XPS spectrum of sample A1 could be divided into two peaks at 45.16 eV and 45.94 eV. Generally, the binding energy of As^{3+} is lower than As^{5+} by about 1 eV [41]. The former peak can be ascribed to the As^{3+} species, while the latter can be assigned to As^{5+} .

Based on the arsenic speciation analysis by XPS and XRD, the As^{3+} species is As_2O_3 , whereas the As^{5+} species can be attributed to pentavalent arsenate AsO_4^{3-} and arsenic(V) - oxide As_2O_5 . As_2O_5 could not be observed in XRD pattern, evidently due to its low content. Similar results were obtained in the As 3d XPS spectra of the A2, B1, B2, B3 and B4 flue dust samples. It is worth noting that elemental As^0 was found in the sample B1, which is in agreement with the chemical phase analysis of arsenic (listed in Fig. 11).

In Fig. 10(b), the binding energies of S 2p spectrum for the sample A1 at 169.07 and 170.29 eV correspond to the S 2p_{3/2} and S 2p_{1/2}, assigned to the SO_4^{2-} species that can be further confirmed by the existence of PbSO_4 and CuSO_4 [42]. This is in good agreement with the XRD results obtained in this study. The S 2p peak shifted towards lower binding energies may be caused by changes of sulfate contents in the flue dusts. Note that the S^{2-} was not detected in any of the samples in their S 2p XPS spectra. It indicated that sulfides were not present on the flue dust surfaces, but wrapped within cores of the dust particles. This could

be confirmed by the EPMA results above.

Fig. 10. High-resolution deconvoluted XPS spectra of (a) As 3d and (b) S 2p for the samples A1, A2, B1, B2, B3, and B4 representing presence of sulfate only.

The stepwise chemical extraction technique was employed for analyzing the phases carrying As in the flue dusts. The extraction procedure flow chart used is shown in supplementary Fig. S-2 [43,44]. The obtained arsenic distributions between the phases were depicted in Fig. 11. It could be discovered in Fig. 11, that most arsenic in the copper smelting dusts existed in arsenate phases, except that in the BBSF-ESP dust where arsenic mainly existed as simple (binary) trivalent oxides. In addition, only a very small fraction of arsenic existed in sulfidic form and as elemental arsenic.

The chemical phase extraction results confirmed the high-resolution XPS data of the arsenic distribution on the flue dust particles. According to the above XRF, XRD, EPMA data and the chemical phase extraction results obtained, the majority of arsenic existed in amorphous form of AsO_x ($x = 1.5$ and 2.5) in the BBSFD (A2) taken from the ESP of the BBSF.

According to the thermodynamic studies of Cu/Fe-As-S(O) system and copper smelting processes, the speciation of arsenic will be affected by many factors, such as temperature, atmosphere, the compositions of the co-condensed phases and so on [45-47]. In present day plant practice, in order to control the concentration of SO_3 in the off gas in the waste heat boiler/electrostatic precipitator, a certain amount of air is leaked or injected into the off gas [39]. It will lead to different oxygen partial pressures affecting the arsenic valence and speciation. In this investigation, the amount of added air in the off gas streams of the two

smelters were not obtained. Therefore, no conclusions between the conditions and arsenic valence can be drawn in this work.

Fig. 11. Chemical speciation and distributions of As in the flue dusts.

5. Conclusions

A comprehensive physical, chemical and mineralogical characterization of copper smelting flue dusts from a BBS smelter and a FSF smelter was carried out. The results show that the dry and fine feed mixture of the flash smelting process causes a larger entrainment rate of flue dust than the wet feed in the bottom-blowing bath smelting process. Along with a higher dust generation rate of the FSF, a smaller average particle size in its flue dust was evident.

Fe_3O_4 , CuSO_4 and PbSO_4 , Fe_3O_4 , CuFe_5O_8 were the predominant crystalline phases in the FS and the BBS flue dusts, respectively. Crystallographic data and chemical compositions of the waste-heat boiler and electrostatic precipitator flue dusts showed that the FS operation point generated a higher degree of crystallinity than the BBS. Besides, zinc may form amorphous phases with iron oxides in flue dust particles in the FS off-gas train. In the BBS flue dust particles, complex copper-zinc-sulfur melts were formed in the WHB. The majority of arsenic oxide existed in amorphous form in the ESPD from BBS. Due to the added of oxygen in the off-gas, arsenic in the flue dusts was oxidized and no presence of elemental arsenic was detected, except in the WHBD from FSF radiation section. Its oxidation degree was mostly pentavalent arsenate in FSF-ESP, whereas in BBS-ESP it was mostly simple AsO_x ($x = 1.5$ and 2.5). This will have a major impact on the hydrometallurgical processing of flue dusts and the arsenic recovery.

In summary, in the sulfide smelting of copper the circumstances in the process off-gas train and the dust collection have a clear impact on physical and chemical characteristics of

the forming flue dusts. An important difference between the bath smelting and flash smelting off-gases is the mechanically entrained flue dust and its carry over compared with the chemically formed dust in different sections of the off-gas train. It is essential to understand the mechanisms of formation as well as the characteristics of the copper smelting flue dusts for their recycling, utilization and safe treatment.

Acknowledgements

The authors gratefully acknowledge financial support from the National Key R&D Program of China (2017YFC0210405), the key project of National Natural Science Foundation of China (51634010), National Natural Science Foundation of China (51722407) and the “Double First Class” Funding Project of Central South University (31801-160170002).

References

- [1] Schlesinger M. E., King M. J., Sole K. C., & Davenport W. G.: Elsevier, 2011, pp. 2.
- [2] Guo X., Wang Q., Liao L., Tian Q., & Zhang Y.: Nonferr. Metals Science Engineering, 2014, Vol. 5, pp. 28-34.
- [3] Guo X., Song Y., & Wang Y.: Res. Conserv. Recycling, 2008, Vol. 52, pp. 871-882.
- [4] Li M., Tong C., Huang J., & Wang J.: Chinese J. Process Engin., 2016, Vol. 16, pp. 1028-1037.
- [5] Zhou S.: Xiangguang: Nonferrous Metals, 2009, pp.11-20 (in Chinese).
- [6] Liu J., Gui W., Xie Y., & Yang C.: Appl. Mathem. Modell., 2014, Vol. 38, pp. 2206-2213.
- [7] He Y.: World Non-ferrous Metals, 2018, pp. 7-10 (in Chinese).
- [8] Coursol P., Mackey P., Kapusta J., Kapusta, N., & Cardona V.: JOM, 2015, Vol. 67, pp. 1066-1074.
- [9] Liu L., Yan H., Zhou J., Gao Q., Zhang Z., Liu F., & Cui Z.: Chinese J. Nonferr. Metals, 2012, Vol. 22, pp. 2116-2124.
- [10] Yu Y., Wen Z., Liu X., Su F., Lan H., & Hao X.: Appl. Mechan. Mater., 2014, Vol. 602-605, pp. 546-553.
- [11] Sohn H., Fukunaka Y., Oishi T., Asaki Z., & Song H.: Metall. Mater. Trans. B, 2004, Vol. 35, pp. 651-661.
- [12] Chen C., Zhang L., & Jahanshahi S.: Metall. Mater. Trans. B, 2010, Vol. 41, pp. 1175-1185.
- [13] Wang Q., Guo X., Tian Q., & Jiang T.: Metals, 2017, Vol. 7, pp. 1-11.
- [14] Wang Q., Guo X., Tian Q., Chen M., & Zhao B.: Metals, 2017, Vol. 7, pp. 1-12.
- [15] Chen H., Mei Z., Xie K., Li X., Zhou J., Wang X., & Ge Z.: Trans. Nonferr. Metals Soc. China, 2004, Vol. 14, pp. 631-636.
- [16] Itagaki K., & Yazawa A.: Mater. Trans. JIM, 2007, Vol.23, pp. 759-767.
- [17] Mendoza D., Hino M., & Itagaki K.: Mater. Trans. B, 2001, Vol. 42, pp. 2427-2433.
- [18] Swinbourne D., & Kho T.: Metall. Mater. Trans. B, 2012, Vol. 43, pp. 823-829.
- [19] Chen Z.: China Nonferr. Metall., 2009, pp. 16-22 (in Chinese).
- [20] Kaur R., Nexship C., Wilson M., & George-Kennedy D.: In: Proc. Copper 2010. DGBM, Clausthal-Zellerfeld, Germany, 2010, pp. 2415-2432.
- [21] Balladares E., Kelm U., Helle S., Parra R., & Araneda E.: Dyna, 2014, Vol. 81, pp. 11-18.
- [22] Montenegro V., Sano H., & Fujisawa T.: Mater. Trans., 2008, Vol. 49, pp. 2112-2118.
- [23] Montenegro V., Sano H., & Fujisawa T.: Miner. Engin., 2013, Vol. 49, pp. 184-189.

- 485 [24] Samuelsson C., & Carlsson G.: CIM Bulletin, 2005, Vol. 94, pp. 111-115.
- 486 [25] Jarošíková A., Ettler V., Mihaljevič M., Drahotka P., Culka A., & Racek M.: J. Environm.
487 Managem., 2018, Vol. 209, pp. 71-80.
- 488 [26] Zhong D., Li L., & Tan C.: Metall. Mater. Trans. B, 2017, Vol. 48, pp. 1308-1314.
- 489 [27] Tae K.-H., Bok H.-K., Kye S.-P., & Debasish M.: Separ. Purif. Techn., 2015, Vol. 142, pp. 116-
490 122.
- 491 [28] Wu J., Chang F., Wang H., Tsai M., Ko C.-H., & Chen C.-C.: Environm. Technol., 2015, Vol. 36,
492 pp. 2952-2958.
- 493 [29] Csavina J., Taylor M., Omar F., Rine K., Sáez A., & Betterton E.: Sci. Total Environm., 2014,
494 Vol. 493, pp. 750-756.
- 495 [30] Morales A., Cruells M., Roca A., & Bergó R.: Hydrometallurgy, 2010, Vol. 105, pp. 148-154.
- 496 [31] Li Z., & Xu B.: Metallurgy Technology of Copper, Chemical Industry Press, Beijing, 2012, pp.
497 7.
- 498 [32] Ren H.: Non-ferrous Metal Bath Smelting, Metallurgical Industry Press, Beijing, 2001, pp. 2-6.
- 499 [33] Zhu Z., & He J.: Modern copper smelting, Science Press, Beijing, 2003, pp. 23-45.
- 500 [34] Talja J., Chen S., Mansikkaviita H., & Berg C.: In: Proc. Copper 2013, vol. III (Book 1), Santiago,
501 Chile. Ch IMM, 2013, pp. 67-77.
- 502 [35] FEI MLA software, Thermo Fischer Scientific, USA; accessed in October 2019 at:
503 <https://www.fei.com/materials-science/minerals-mining/> .
- 504 [36] Toby B. H.: J. Appl. Cryst., 2005, Vol. 38, pp. 1040-1041.
- 505 [37] Redwan M., Rammlmair D., & Meima J.: Sci. Total Environ., 2012, Vol. 414, pp. 480.
- 506 [38] Stathopoulos V., Papandreou A., Kanellopoulou D., & Stournaras C.: J. Haz. Mater., 2013, Vol.
507 262, pp. 91-99.
- 508 [39] Samuelsson C., & Björkman B.: Thermodynamic studies. Scand. J. of Metall., 1998, Vol. 27, pp.
509 64-72.
- 510 [40] Stefanova V., Shentov D., Mihailova I., & Iliev P.: Russ. J. Non-Ferr. Metals, 2012, Vol. 53, pp.
511 26-32.
- 512 [41] Carol A., Martinson, & Reddy K.: J. Colloid Interface Sci., 2009, Vol. 336, pp. 406-411.
- 513 [42] Nasef M., Saidi H., Nor H., & Yarmo M.: J. Appl. Polymer Sci., 2000, Vol. 76, pp. 336-349.
- 514 [43] Zhang H.: Chemical Phase Analysis of Ores and Industrial Products: Nonferrous Metals Industry
515 Analysis Series, Metallurgical Industry Press, Beijing, 1992, pp. 50-53 (in Chinese).
- 516 [44] Yang W., Tian S., Wu J., Chai L., & Liao Q.: JOM, 2017, Vol. 69, pp. 1077-1083.
- 517 [45] Safarzadeh M., Miller J., & Huang H.: Metall. Mater. Trans. B, 2014, Vol. 45, pp. 568-581.
- 518 [46] Chen C., Zhang L., & Jahanshahi S.: Metall. Mater. Trans. B, 2010, Vol. 41, pp. 1175-1185.
- 519 [47] Cheng R., Zhang H., & Ni H.: Processes, 2019, Vol. 7, pp. 754-1-12.

Table 1 Operation parameters of the smelting furnaces

Parameter	BBSF	FSF
Processing capacity (t/h)	90-100	120-260
Concentrate pre-treatment	No drying (<10 % water)	Drying (<0.3% water)
Smelting temperature (°C)	1160-1200	1280-1320
Slag tapping temperature (°C)	1080-1180	1290-1310
Oxygen concentration in feed (%) ^a	70-73	78-85
Oxygen pressure in feed (MPa)	0.58-0.64	0.015-0.022
SO ₂ concentration in off-gas (%)	30-32	44-48
Copper matte grade (%)	52-60	67-70
Cu in smelting slag (%)	3.0-4.0	0.95-1.20
Cu in flotation tailing slag (%)	≤0.32	0.24-0.35
Fe/SiO ₂ (w/w) ^b	1.60-1.80	1.2-1.4
Slag ratio (w/w) ^c	3.05-3.75	2.9-3.2

^a: Volumetric ratio; ^b: weight of Fe in the smelting slag/weight of SiO₂ in the smelting slag; ^c: weight of smelting slag and converting slag/weight of copper.

Table 4. Heavy metal contents (TCLP) and the leached fractions (% R) of the flue dusts.

Sample ID	As		Cd		Pb		Zn	
	TCLP (mg/L)	R (%)	TCLP (mg/L)	R (%)	TCLP (mg/L)	R (%)	TCLP (mg/L)	R (%)
A1 (BBS-WHBD)	657	22	20	8	15	0.7	82	8
A2 (BBS-ESPD)	6127	92	822	99	174	3	1989	99
B1 (FS-WHBD1)	43	5.5	243	97	3.8	0.5	638	53
B2 (FS-WHBD2)	69	7.5	343	99	8.8	0.9	727	59
B3 (FS-DCSD)	109	13	374	99	9.7	2	799	65
B4 (FS-ESPD)	144	16	405	99	8.6	4	942	83

Table 2. Elemental analysis of the feed mixtures into the BBSF (A0) and the FSF (B0).

Furnace feed	Elemental composition (wt.%)															
	Cu	O	Fe	S	As	Pb	Zn	Cd	Bi	Si	Ca	K	Na	Mo	Al	others
A0	21.1	17.5	19.0	23.3	-*	0.1	0.9	-*	-*	9.1	0.6	3.0	1.4	0.6	3.2	0.4
B0	25.1	9.9	23.7	23.4	0.1	0.4	1.5	-*	-*	9.5	1.6	0.9	0.5	0.2	2.1	1.1

-*: below detection limit ≤ 0.01 .

Table 3. Elemental analysis of the flue dusts at different sampling points.

Smelting dust	Element composition (wt.%)															
	Cu	O	Fe	S	As	Pb	Zn	Cd	Bi	Si	Ca	K	Na	Mo	Al	others
A1	27.7	24.5	15.2	13.6	7.9	5.4	2.6	0.7	0.7	0.6	0.4	-*	-*	0.1	0.1	0.6
A2	19.7	30.2	2.2	14.1	14.3	12.2	2.2	1.8	1.7	0.2	0.3	-*	-*	0.2	0.1	0.7
B1	29.2	20.5	18.3	15.8	2.5	2.8	3.6	0.9	0.2	3.3	1.2	0.6	-*	0.5	0.6	0.1
B2	26.8	20.1	19.0	15.2	2.9	3.0	3.6	1.1	0.2	3.7	1.2	1.2	0.6	0.5	0.8	0.1
B3	27.0	20.0	18.9	15.5	3.0	3.1	3.7	1.1	0.2	3.7	1.2	1.2	-*	0.5	0.8	0.1
B4	25.6	22.1	16.6	15.9	4.2	2.9	3.3	1.4	0.2	3.7	1.0	1.1	-*	0.6	0.8	0.6

-*: below detection limit ≤ 0.01 .