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Electronic Supplementary File

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

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The minerals present in the feed mixtures of the BBS smelter (A0) and the FSF smelter (B0) as identified by the MLA analysis software were collected in Table S-1.

Table S-1. A quantitative phase analysis of minerals in the smelting furnace feed mixtures.

Mineral	Mass fraction/wt.%		Mineral	Mass fraction/wt.%	
	A0	B0		A0	B0
Chalcopyrite	41.9	28.4	Kaolinite	0.02	0.02
Pyrite	19.9	21.3	Tennantite	0.02	0.50
Quartz	7.97	12.9	Brochantite	0.02	0.01
Covellite	7.22	1.22	Spodumene	0.01	0.01
Orthoclase	6.62	1.36	Tetrahedrite	0.01	0.03
Molybdenite	4.81	0.12	Woodhouseite	0.01	0.00
Chlorite	2.90	0.12	Alunite	0.01	0.00
Muscovite	1.31	0.81	Galena	0.01	0.21
Albite	0.10	0.38	Anglesite	0.01	0.08
Bornite	0.94	6.94	Calcite	0.01	0.07
Sphalerite	0.87	1.14	Euchroite -new	0.01	0.01
Biotite	0.85	0.17	Atacamite	0.01	0.00
Plagioclase	0.58	0.24	Grunerite	0.00	0.01
Rutile	0.54	0.08	Svanbergite	0.00	0.00
Goethite	0.46	0.46	Ankerite	0.00	0.01
Magnetite	0.40	1.72	Lead	0.00	0.00
Chalcocite	0.38	3.53	Delafossite-CaO	0.00	11.46
Siderite	0.23	0.23	Serpentine	0.00	0.04
Zoisite	0.21	0.03	Andradite	0.00	0.20
Glass-$Fe_4(SiO_4)_3$	0.13	2.26	Native Copper	0.00	0.14
Ferroactinolite	0.10	0.50	Arsenopyrite	0.00	0.01
Pyrrhotite	0.09	0.36	Anhydrite	0.00	0.02
Apatite	0.09	0.03	Malachite	0.00	0.00
Talc	0.08	0.13	Zircon	0.00	0.00
Fayalite	0.06	2.36	Cuprite	0.00	0.00
Tremolite	0.04	0.17	Svanbergite	0.00	0.00
Ilmenite	0.03	0.01	Others	1.04	0.20
Total	98.81	86.97	Total	1.19	13.03

The calculation of temperature drop rate in the BBS and FS process:

The relationship between the temperature drop rate ($\dot{v}$), temperature change ($\triangle T$) and residence time (τ) in the off-gas train can be defined as follows:

$$\tau = L/(Q/S) \qquad (S1)$$

$$\dot{v} = \triangle T / \tau \qquad (S2)$$

where, L is length of the WHB unit, S is its cross-sectional area, Q is the volumetric gas flow rate in the off-gas train. Assuming the off-gas containing solid particles moving along a straight line, the conditions of equations (S1) & (S2) and the estimated temperature drop rates (average temperature) are shown as listed in Table S-2. It can be seen that the first off-gas temperature drop rate of the BBS process was more than sixfold than that of FS process.

Table S-2. Part of the off-gas train temperature drop rate in the BBS process and FS process.

BBS process			**FS process**		
Quench section:			***Radiation section:***		
Dimensions			Dimensions		
L =	20	m	L =	31	m
S =	8(4×2)	m^2	S =	129.22(18.2×7.1)	m^2
△T =	250	K	△T =	720	K
Gas flow:			Gas flow:		
Q(25 °C) =	35000	Nm^3/h	Q(25 °C) =	40000	Nm^3/h
Q(750 °C) =	120151	m^3/h [1]	Q(950 °C) =	164161	m^3/h [1]
τ =	4.79	s [2]	τ =	88	s [2]
$\dot{v}$ =	52	K/s [3]	$\dot{v}$ =	8	K/s [3]
Horisontal WHB section:			***Convection section:***		
Dimensions			Dimensions		
L =	39	m	L =	20	m
S =	48(12×4)	m^2	S =	40(10×4)	m^2
△T =	250	K	△T =	250	K
Gas flow			Gas flow		
Q(25 °C)=	35000	Nm^3/h	Q(25 °C)=	40000	Nm^3/h
Q(450 °C) =	84916	m^3/h [1]	Q(450 °C) =	97047	m^3/h [1]
τ =	79	s [2]	τ =	30	s [2]
$\dot{v}$ =	3	K/s [3]	$\dot{v}$ =	8	K/s [3]

[1]: this is the volumetric flow rate at average temperature of the unit (from ideal gas law); [2]: calculated at the average temperature of the unit; [3]: from the temperature drop at average residence time.

The TCLP leaching procedure used in this study:

In some copper smelting plants, there is some escaping SO_2 gas emitted into the air under some special cases (such as equipment maintenance), causing acid rain around the plant. Therefore, the toxicity characteristic leaching procedure (TCLP) was employed to assess the stability of the impurity elements. This was used to simulate the environmental pollution caused by the unprocessed flue dusts accumulated in the factory under acid rain conditions.

TCLP was used to simulate the leaching of flue dusts [1]. The TCLP was performed in a rotary agitator at 30 ± 2 rpm using a liquid-solid ratio (L/S) of 20 L/kg. An acetic acid solution with a pH of 2.88 ± 0.05 was used as the extraction fluid. Leaching experiments included addition of 50 g of solid sample in a polyethylene bottle, followed by addition of 1 L of the extraction fluid. The mixture was agitated for 18 h and then filtered. The concentrations of As, Cd, Pb and Zn elements were determined by an Agilent 5100 ICP-OES (inductively coupled plasma-optical emission spectroscopy; Agilent, USA). Each experiment was conducted in triplicate and the average results were presented in this paper to minimize the random errors.

The leaching results show that the copper concentrations in the leaching solution were more than 5000 mg/L. As a general practice, the flue dusts are usually recirculated back to the feed-mixture of the smelting to recycle copper. Copper is the main and valuable element of the flue dusts, while As, Cd, Pb and Zn are impurity elements for copper smelting. Therefore, in the manuscript, only the non-major and impurity elements leaching results were listed out.

The leachable harmful elements, As, Cd, Pb and Zn, concentrations of the copper smelting flue dusts obtained in this study were presented in Table 4. According to the present hazardous waste characterization standards (with the leaching limits of As ≤5mg/L, Cd ≤1mg/L, Pb ≤5mg/L, Zn: not available) [2], the flue dusts were hazardous materials. The leachable elements were higher than the acceptable threshold values, except for Zn in the sample A1. This is because in the A1 flue dust sample, the multicomponent copper-zinc-sulfur residue may inhibit the leaching of zinc.

The leaching rate (R) of an element was calculated using the following equation:

$$R=100\times M_{1,ij}/ M_{2,ij}\% \qquad \text{(S3)}$$

in which the i represents a certain dust sample i, j represents one of the studied heavy metals, $M_{1,ij}$ is the leached mass of harmful elements (mg), and $M_{2,ij}$ is the total mass of harmful elements (mg) in the analyzed sample [3].

The calculated results of the leaching rates were also collected in Table 4. For the BBS flue dusts, the leaching rates of As, Cd, Pb and Zn in A2 (≥92.7 %) were higher than those of A1 (≤ 22.6 %). For the FS flue dusts, the four leaching rates obtained were as follows: R_{Pb} (0.5 %-1.9 %) < R_{As} (5.6 %-15.7 %) < R_{Zn} (52.5 %-83.5 %) < R_{Cd} (97.3 %-99.5 %) and $R_{B1} < R_{B2} < R_{B3} < R_{B4}$.

Therefore, it can be concluded that the Cd and Pb in the flue dusts were the most easily and most difficult to be leached out. Besides, in combination with the particle sizes of the flue dusts, a regular pattern in the samples was that the harmful elements leaching rates increased with decrease of the particle size.

For the behavior of arsenic, it is worth noting that the leaching of arsenic from A2 was as high as 92.7 %, which was much higher than in the other samples. This can be explained by the observed chemical speciation of arsenic (Fig. 11).

The dust generation rates:

The dust generation rates in 2017 of Chinese BBS and FS copper smelter were calculated from process data on a monthly basis, shown as Fig. S-1

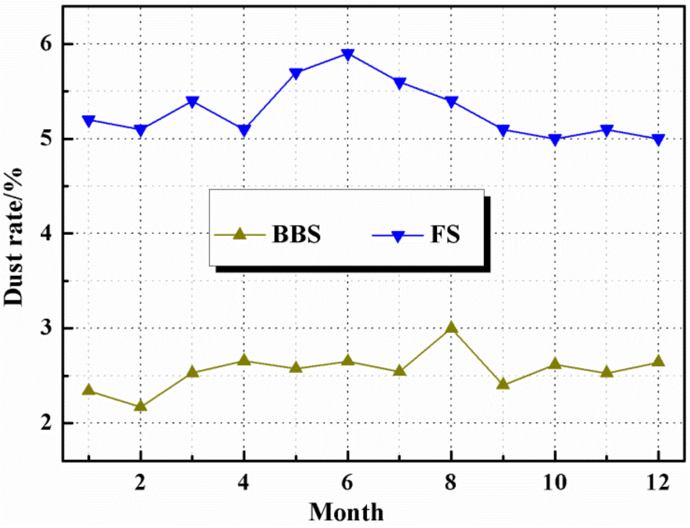

Fig. S-1 A comparison of the monthly dust generation rates of the BBS and FS smelters.

The sequential extraction procedure for the arsenic species:

The leaching steps and used lixiviants in the sequential extraction for arsenic used in this study are described in detail in Fig. S-2. The obtained results show that in flue dust sample A2 (BBSF-ESP), 72.5 % of the total arsenic existed as simple arsenic oxides. Fig. 11 also shows that in the other flue dust samples, more than 89 % of total arsenic existed in various forms of pentavalent arsenates. The high leaching rate of arsenic from sample A2 in the TCLP tests explain fully why As was easily leached out.

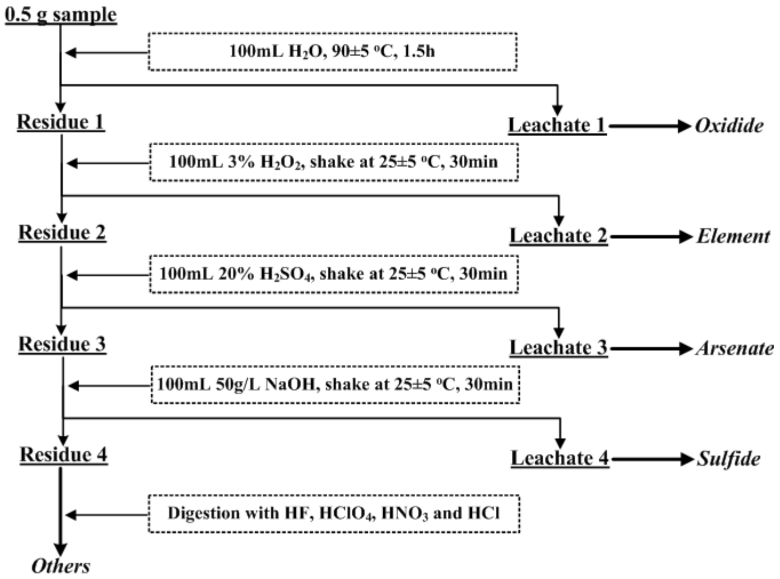

Fig. S-2 Flow chart for the sequential extraction of As from the flue dusts.

The EDS analysing spots/areas of the dust samples in Fig. 7:

The mineralogy of the dust is complex and it was not possible to determine the mineralogy of all components. However, based on the characterization of the dust and mass balance, a simplified mineralogical composition of the dusts was proposed, as shown in Table S-3. Minor impurities in the substances were not considered.

Table S-3. The atomic percentage of elements and the possible existing phases at the related spots/areas in Fig. 7.

Samples	Spots/ areas ID	As (at%)	Cu (at%)	Fe (at%)	Zn (at%)	S (at%)	Pb (at%)	O (at%)	Ca (at%)	Possible Phases
A1 (BBS-WHBD)	1	0.18	38.63	1.00	6.56	37.27	0.02	15.81	0.53	$CuSO_4$+Me_xS
	2	8.89	7.12	8.69	2.10	3.12	1.02	***67.42***	1.64	Me_xAsO_4+$CuSO_4$+Me_xO
	3	0.12	33.61	1.96	4.75	28.79	0.00	30.52	0.24	$CuSO_4$+Me_xS+Me_xO
	4	0.48	44.59	3.53	4.38	33.68	0.39	12.68	0.28	$CuSO_4$+Me_xS+Me_xO
	5	0.09	6.67	29.49	1.36	0.18	0.07	***62.15***	0.00	Fe_3O_4+Me_xO
	6	9.67	8.99	12.54	1.39	0.78	0.60	65.60	0.44	Me_xAsO_4+$CuSO_4$+Me_xO
	7	13.47	7.99	3.34	1.24	6.72	7.26	59.51	0.47	Me_xAsO_4+AsO_x+$PbSO_4$ +$CuSO_4$+Me_xO
	8	0.41	33.87	2.26	1.87	29.88	0.07	31.48	0.17	$CuSO_4$+Me_xS+Me_xO
	9	0.44	36.34	1.13	2.44	23.92	0.19	35.38	0.16	$CuSO_4$+Me_xS+Me_xO
	10	3.75	17.64	1.98	0.80	18.74	6.24	50.45	0.40	Me_xAsO_4+AsO_x+$PbSO_4$ +$CuSO_4$+Me_xS+Me_xO
	11	0.18	36.06	0.91	2.97	34.65	0.03	24.99	0.22	$CuSO_4$+Me_xS
	12	0.27	37.64	1.11	2.75	32.55	0.00	25.50	0.18	$CuSO_4$+Me_xS
	13	0.27	37.62	0.97	2.57	30.42	0.01	27.93	0.20	$CuSO_4$+Me_xS

A2 (BBS-ESPD)	14	4.32	1.95	27.92	0.51	1.20	0.18	63.61	0.31	$AsO_x+Fe_3O_4+Me_xO$ $+CuSO_4$
	15	2.89	28.74	0.12	4.05	27.67	0.12	35.74	0.67	$CuSO_4+AsO_x+Me_xS$ $+Me_xO$
	16	4.55	2.85	1.51	0.73	11.27	9.22	69.37	0.50	$AsO_x+PbSO_4+CuSO4$ $+Me_xO$
	17	1.69	16.53	0.34	1.55	17.00	0.69	61.82	0.38	$AsO_x+PbSO_4+CuSO_4$ $+Me_xO$
	18	24.33	3.37	1.01	0.79	4.77	2.37	62.94	0.41	$Me_xAsO_4+AsO_x+PbSO_4$ $+CuSO_4+Me_xO$
	19	1.29	15.63	0.54	1.08	15.23	1.82	64.16	0.26	$AsO_x+CuSO_4+Me_xO$
	20	5.35	2.13	2.41	0.57	12.46	10.46	65.65	0.96	$Me_xAsO_4+AsO_x+PbSO_4$ $+CuSO_4+Me_xO$
	21	1.25	26.26	0.26	3.61	24.57	1.56	41.54	0.95	$AsO_x+CuSO_4+Me_xS$ $+Me_xO$
	22	1.15	17.26	0.16	1.23	16.62	0.06	63.22	0.29	$AsO_x+CuSO_4+Me_xO$
	23	1.96	20.43	0.31	2.25	20.16	0.04	54.34	0.51	$AsO_x+CuSO_4+Me_xS$
	24	6.66	2.28	2.75	0.76	9.97	8.40	68.88	0.31	$Me_xAsO_4+AsO_x+CuSO_4$ $+Me_xO$
	25	3.07	19.70	0.32	1.70	15.31	0.11	59.41	0.37	$AsO_x+CuSO_4+Me_xS$
	26	22.19	3.99	0.14	1.82	14.61	0.00	57.25	0.00	$AsO_x+AsS_x+CuSO_4$ $+Me_xS$
	27	0.05	0.11	0.02	0.00	0.02	0.01	***80.87***	18.92	$AsO_x+CuSO_4+Me_xO$ $+Me_xS$
	28	16.58	4.54	0.29	0.30	11.85	0.12	55.55	10.78	$AsO_x+AsS_x+CuSO_4$ $+Me_xS$
	29	9.82	5.09	14.84	0.27	0.32	0.35	***69.20***	0.10	$Me_xAsO_4+Fe_3O_4+Me_xO$
	30	13.34	16.46	2.88	0.50	1.24	0.53	63.18	1.88	$Me_xAsO_4+CuSO_4+Me_xO$
	31	9.31	16.47	1.62	1.06	11.17	3.76	56.12	0.50	$AsO_x+AsS_x+CuSO_4$ $+Me_xO$
	32	30.11	5.62	8.60	1.77	7.96	3.28	42.66	0.00	$AsO_x+AsS_x+Me_xO$
	33	0.47	0.39	37.05	0.10	0.11	0.02	61.73	0.14	$Me_xAsO_4+FeO_x$
	34	9.72	2.61	4.38	0.71	9.81	9.71	63.07	0.00	$PbSO_4+AsO_x+Me_xO$
B1 (FS-WHBD1)	35	0.41	9.21	3.43	1.12	0.41	0.37	***84.87***	0.18	$Fe_3O_4+Me_xO$
	36	0.02	4.87	27.19	2.20	0.19	0.01	***65.48***	0.03	$Fe_3O_4+Me_xO$
	37	0.78	23.64	7.62	0.96	22.85	0.19	43.75	0.22	$Fe_3O_4+Me_xO$
	38	0.39	3.99	3.95	2.20	2.41	0.50	***86.30***	0.27	$Fe_3O_4+Me_xO$
	39	0.62	11.03	3.21	1.15	13.57	0.29	***69.96***	0.17	$CuSO_4+Fe_3O_4+Me_xO$
	40	0.58	11.85	23.37	1.60	0.60	0.06	***61.89***	0.04	$CuSO_4+Fe_3O_4+Me_xO$
	41	0.15	5.67	3.07	0.32	18.92	0.33	71.36	0.18	$Me_xSO_4+Me_xO$
	42	0.08	2.82	27.86	1.89	0.12	0.03	***67.21***	0.00	$Fe_3O_4+Me_xO$
	43	0.26	35.22	4.55	0.98	0.47	0.30	***58.22***	0.00	$Fe_3O_4+Me_xO$
	44	0.01	2.46	29.86	1.76	0.03	0.00	***65.88***	0.00	$Fe_3O_4+Me_xO$
	45	0.07	19.33	16.65	0.15	0.23	0.12	***63.43***	0.01	$Fe_3O_4+Me_xO$
	46	0.66	16.18	12.35	1.53	1.53	0.21	***67.47***	0.06	$Fe_3O_4+Me_xO$
	47	1.67	15.77	4.51	2.53	21.52	0.13	53.44	0.43	$CuSO_4+Fe_3O_4+Me_xO$ $+Me_xS$
	48	0.14	0.94	33.37	0.07	0.16	0.00	***65.29***	0.01	$Fe_3O_4+Me_xO$
	49	0.29	11.33	1.63	1.28	14.99	0.09	***70.26***	0.13	$CuSO_4+Me_xO$

	50	0.28	12.54	1.66	1.34	16.06	0.04	***67.96***	0.11	$CuSO_4+Me_xO$
	51	0.79	3.77	27.42	2.13	2.09	0.44	***63.25***	0.10	$Fe_3O_4+Me_xO$
	52	3.64	1.22	23.60	0.11	0.86	0.14	***70.40***	0.02	$Fe_3O_4+Me_xO$
	53	0.09	7.38	1.91	0.68	0.37	0.25	***89.29***	0.04	$Fe_3O_4+Me_xO$
B2 (FS-WHBD2)	54	0.05	4.88	30.27	2.79	0.02	0.01	***61.96***	0.03	$Fe_3O_4+Me_xO$
	55	0.58	15.55	13.43	0.19	1.65	0.50	***68.07***	0.02	$Fe_3O_4+Me_xO$
	56	1.75	25.24	5.06	1.09	23.29	0.07	43.34	0.16	$CuSO_4+Fe_3O_4+Me_xO+Me_xS$
B3 (FS-DCSD)	57	2.36	24.16	5.86	0.75	16.41	0.18	50.07	0.21	$CuSO_4+Fe_3O_4+Me_xO+Me_xS$
	58	0.43	11.15	25.12	1.33	1.58	0.01	***60.29***	0.10	$Fe_3O_4+Me_xO$
	59	0.56	23.17	35.26	2.23	4.92	0.07	33.65	0.15	CuSO4+MexO
	60	0.08	7.61	27.02	1.02	0.14	0.01	***64.04***	0.08	$Fe_3O_4+Me_xO$
	61	1.96	13.60	4.15	0.50	14.88	1.66	62.83	0.43	$CuSO_4+Fe_3O_4+Me_xO+Me_xS$
	62	0.02	5.01	30.07	2.83	0.01	0.01	61.99	0.06	$Fe_3O_4+Me_xO$
	63	6.09	20.05	5.74	0.34	3.87	0.74	63.14	0.04	$Me_xAsO_4+Me_xO$
	64	2.75	23.36	9.39	0.50	3.64	0.89	59.35	0.12	$Me_xAsO_4+CuSO_4+Fe_3O_4+Me_xO$
	65	0.57	16.36	9.44	0.48	4.63	0.84	***67.52***	0.15	$CuSO_4+Fe_3O_4+Me_xO$
	66	0.01	3.07	30.61	3.67	0.04	0.00	62.58	0.01	$Fe_3O_4+Me_xO$
	67	0.82	15.95	7.68	1.10	8.62	0.93	64.77	0.13	$CuSO_4+Fe_3O_4+Me_xO$
	68	0.10	25.73	8.75	1.90	14.86	0.86	47.51	0.28	$CuSO_4+Fe_3O_4+Me_xO$
	69	1.24	17.33	4.49	1.01	28.82	0.15	46.76	0.20	$CuSO_4+Me_xS$
B4 (FS-ESPD)	70	0.07	12.26	35.80	1.45	0.05	0.00	50.30	0.06	$Fe_3O_4+Me_xO$
	71	0.03	8.99	32.94	2.36	0.04	0.02	55.55	0.06	$Fe_3O_4+Me_xO$
	72	2.35	20.64	38.14	3.06	1.90	0.30	33.45	0.16	$Fe_3O_4+Me_xO+Me_xS$
	73	0.14	5.70	26.32	1.90	0.33	0.04	***65.53***	0.04	$Fe_3O_4+Me_xO$
	74	0.12	7.77	27.04	1.74	0.24	0.02	***63.02***	0.05	$Fe_3O_4+Me_xO$
	75	0.29	6.60	11.69	0.73	6.53	5.42	***68.66***	0.08	$Fe_3O_4+Me_xO$
	76	0.02	12.61	1.15	0.54	11.27	0.00	***74.31***	0.09	$CuSO_4+Me_xO$
	77	2.98	6.95	17.07	0.90	3.17	0.62	***68.26***	0.05	$Me_xAsO_4+CuSO_4+Me_xO$
	78	1.25	8.75	24.83	1.50	1.05	0.11	***62.43***	0.09	$Fe_3O_4+Me_xO$
	79	2.56	6.60	7.54	3.34	1.99	0.30	***77.57***	0.09	$Me_xAsO_4+CuSO_4+Me_xO$
	80	2.35	9.09	21.95	1.63	2.41	0.69	61.77	0.11	$Me_xAsO_4+CuSO_4+Me_xO$
	81	1.02	7.98	27.99	1.94	2.01	0.61	58.38	0.07	$Me_xAsO_4+CuSO_4+Me_xO$

References:

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