Effect of sample preparation on contaminant leaching from copper smelting slag

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ABSTRACT

Currently standardised leaching tests require grain size reduction, which for large fragments of slags could overestimate the leaching results. To assess the effect of the fine-grained fraction generated by sample crushing, a set of leaching experiments was performed on copper smelting slag from the Zambian Copperbelt: (i) EN 12457-2 batch tests (standardised grain size <4 mm; modified procedure with grain size of 4–0.5 mm simulating exposure of larger fragments on the dumps) and (ii) CEN/TS 14997 pH-static tests (standardised grain size <1 mm simulating the possible wind dispersion scenario near the slag crushing facilities or disposal of fine-grained granulated slag; additional grain sizes <5 mm, 5–0.5 mm and 5–0.5 mm after ultrasonic cleaning). A higher proportion of the fine-grained fraction generally led to greater leaching of Cu, Co and Zn. The metal levels in the leachates under circum-neutral conditions were all below the EU limits for non-hazardous waste. However, at pH 4, the presence of fine dust particles dramatically increased the concentrations of metals in the slag leachates. The greater leachability of Cu and Co from slag particles under acidic conditions suggests a risk of their mobilisation in acidic soils in the Copperbelt area.

1. Introduction

A large number of parameters influence the leaching behaviour of solid waste materials. In addition to the chemical composition of the waste and the leaching solution, liquid-to-solid (L/S) ratio, leaching time, the pH and the grain size of the material are the most important factors [1–6]. Testing of the leaching behaviour of solid waste is mandatory in the EU countries to determine the hazardous properties before possible landfilling (EC 1999 [7], EC 2002 [8]). Three possible tests are generally used to evaluate the environmental properties of solid wastes before acceptance at landfills: batch leaching at L/S of 2 L/kg (EN 12457-1) or 10 L/kg (EN 12457-2) [9] or column leaching tests (CEN/TS 14405 [10]). In these protocols, the grain size of the tested material should be <4 mm (95% of particles). The grain size <1 mm (95% of particles) is specified for materials tested using the pH-dependence leaching tests (CEN/TS 14429 [11], CEN/TS 14997 [12]).

Waste products from the smelting industry are of variable grain size. Fine particles of air-pollution-control residues [13] meet the requirements on the particle size. However, other solid wastes such as slags, if not granulated, are tapped off into the large pots

and transported to the dumps after cooling, where they generally occur as fragments several centimetres in size [14–17]. In this case, the monolith leaching test (currently under preparation/standardisation in the EU) used for monolithic or durable materials is not suitable and thus grain size reduction using jaw crushers is required for the standardised leaching testing. Recently, Zandi et al. [18] showed that using the standardised EN 12457-2 [9] 24-h batch leaching protocol, the hazardous properties of the slag from secondary Pb metallurgy can be underestimated when the dust fraction (<0.5 mm) is discarded, as is common practice in commercial laboratories performing leaching tests.

In the footsteps of Zandi et al. [18], who studied the influence of the slag granulometry on single batch leaching, this study is focused on assessment of the pH-dependent leaching behaviour of copper smelter slag using various preparation methods for the sample prior to leaching. The influence of grain size, presence/absence of fine dust particles and the pH on contaminant leaching was investigated. We used the standardised batch EN 12457-2 [9] and pH-stat CEN/TS 14997 [12] protocols as well as the modified pH-stat applied to coarser grain size fractions. The leaching tests performed on the larger slag fractions are more suitable for simulation of the in situ exposure scenario for the slag dumps [14,16], whereas tests performed on material containing fine dusts can simulate the reactivity of fine-grained slag particles dispersed in the environment by wind near the slag re-processing plants (e.g. crushers) or near disposal

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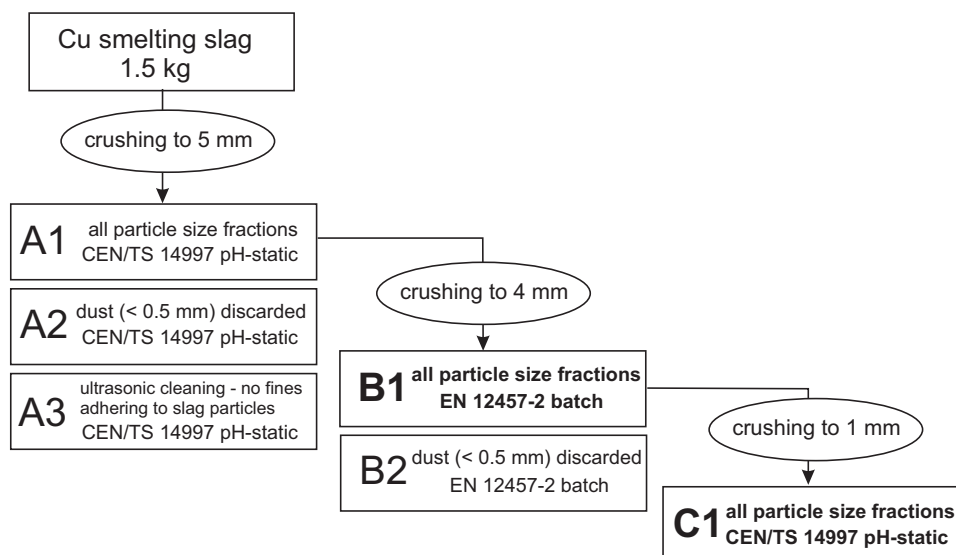
Fig. 1. Scheme of the sample processing prior to the leaching experiments. Letters (A–C) represent different stages of crushing; numbers (1–3) indicate different portions of dust particles. The standardised procedures are given in bold.

sites for granulated slags, both of which are common scenarios observed at numerous smelting sites in Africa [15,19,20].

2. Materials and methods

2.1. Slag sample preparation and characterisation

The copper smelting slag from the Nkana smelter located at Kitwe, Copperbelt Province (Zambia) was used as a testing material. It occurred as black-to-grey fragments up to 7 cm in size and was collected on the piles (S 12°50′20″, E 28°12′40″) in the vicinity of the smelter. A composite sample weight of approximately 1.5 kg has been processed.

Fig. 1 indicates the sample treatment for this study. The particle size distributions of the individual samples are given in Table 1. The sample was crushed using jaw crushers to <5 mm (A), <4 mm (B) and <1 mm (C) and sieved using the series of stainless steel sieves (Retsch, Germany) with mesh 5 mm, 4 mm, 2 mm, 1 mm, 0.5 mm and 0.1 mm to check the individual granulometric fractions.

Sample A was prepared by crushing to <5 mm (95% of particles) and separated into three subsamples: A1 – all fractions; A2 – the <0.5 mm fraction was discarded according to Zandi et al. [18]; A3 – the <0.5 mm fraction was discarded and the coarse fraction was ultrasonically cleaned (60 min in alcohol, the solution was refreshed every 10 min) in order to remove fine particles formed by crushing and adhering on the surfaces of larger grains [14] (Fig. 1).

Sample B was prepared by crushing to <4 mm (95% of particles) and divided into two subsamples: B1 – all fractions according to the standardised EN 12457-2 [9] experimental protocol; B2 – fraction <0.5 mm was discarded according to Zandi et al. [18] (Fig. 1).

Sample C was prepared according to the standardised CEN/TS 14997 [12] experimental protocol and crushed to <1 mm (95% of particles) (denoted as C1 with all fractions included).

As the chemical compositions of subsamples A1, B1 and C1 (and A2 = B2) are assumed to be identical (Fig. 1), only subsamples A1, A2 and A3 were analysed for the bulk chemical composition to obtain information about the effect of the fine-grained fraction on the sample chemistry. The A subsamples were pulverised in an agate mortar (Fritsch Pulverissette, Germany) prior to chemical and mineralogical analyses. The bulk chemical composition of the samples was determined after digestion in mineral acids ($HClO_4$, HF, HNO_3) and/or sintering according to Ettler et al. [15]. Subsequent chemical analysis was performed using gravimetric and volumetric analyses and photometry to determine the major elements. Trace elements were determined by flame atomic absorption spectrometry (FAAS, Varian SpectrAA 280FS, Australia) and inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6500 radial, UK). The content of total sulphur was determined using an ELTRA CS 530 analyser (ELTRA, Germany). Procedural blanks were run simultaneously for all the determinations. The analyses were controlled by USGS standard reference material G2 with accuracy better than 10% of the relative standard deviation.

Table 1
Granulometry of the subsamples related to a given experimental protocol (in cumulative %).

Granulometry	Subsample				
	A1	A2/A3[a]	B1	B2	C1
<0.1 mm	5.1	–	4.8	–	12.6
0.1–0.5 mm	15.1	–	15.7	–	46.0
0.5–1 mm	23.6	10.0	25.3	11.3	98.5
1–2 mm	42.4	32.1	51.3	42.2	100.0
2–4 mm	69.3	63.8	97.6	97.2	
4–5 mm	90.8	89.2	100.0	100.0	
>5 mm	100.0	100.0			
Leaching	CEN/TS 14997	CEN/TS 14997	EN 12457-2 batch	EN 12457-2 batch	CEN/TS 14997 pH-static
protocol	pH-static	pH-static	95% particles <4 mm	95% particles <4 mm	95% particles <1 mm

[a] Identical granulometry (A3 is cleaned ultrasonically).

The mineralogical investigation was performed using X-ray diffraction analysis (see Vítková et al. [21] for details).

2.2. Leaching procedures

Slag subsamples B1 and B2 were subjected to the batch leaching test according to European standard EN 12457-2 [9]. A mass of 5 g of solid was placed in the HDPE reactor and 50 ml of MilliQ+ deionised water (Millipore® Academic purifying system, USA) were added in order to maintain an L/S (liquid/solid) ratio of 10 L/kg. The leaching test was performed at $20 \pm 4\,°C$ for 24 h and the reactors were continuously agitated using a horizontal shaker. After the experiments, the supernatants were filtrated to 0.45 μm (Millipore®) and the pH, Eh and specific conductivity were measured immediately.

Subsamples A1, A2, A3 and C1 were subjected to a pH-static experiment according to European standard CEN/TS 14997 [12]. Preliminary determination of the acid and base consumptions (acid neutralisation capacity and base neutralisation capacity) was performed before the pH-static leaching using manual titration and pH measurement every 30 min. Two suspensions were prepared, one for acid titration (HNO_3) and the other for alkaline titration (NaOH), with an initial L/S of 9.8 L/kg to prevent exceeding the limit value of 11 L/kg [12]. The pH-static experiments were carried out at $20 \pm 4\,°C$ for 48 hours. A mass of 5 g of solid was placed in a 100 ml PE bottle and 48 ml of MilliQ+ deionised water was added to maintain an L/S ratio of 9.6 with a final ratio of about 10 after the addition of acid/base. Nine values were selected in the pH range from 4 to 12 (4, 5, 6, 7, 8, 9, 10, 11, 12). Acid (14 M, 1 M or 0.1 M HNO_3) or base (1 M, 2 M or 5 M NaOH) was added to adjust the pH values. During the initial period (4 h), strong acid and base (the strength of the reagent depends on the specific pH) were added to obtain the predefined pH values, followed by a continuous pH control and acid/base titration using primarily 0.1 M or 1 M HNO_3 and 0.1 M or 1 M NaOH. An experiment at the natural pH of each sample (i.e., without addition of acid/base) was included in all cases. The reactors were continuously agitated (except for the time of pH control and titration). After 48 h, the suspended solids were allowed to settle for about 10 min and the physical–chemical parameters (pH, Eh, specific conductivity) were immediately measured in the leachate before filtration (Millipore® 0.45 μm).

The values of pH and Eh were determined using a Schott Handylab 1 pH meter (Schott Gerätte, Germany) equipped with a BlueLine 28 pH combined electrode and a Schott PT 737 A (Pt–Ag/AgCl) redox electrode, respectively. The temperature and specific conductivity were measured using a Schott Handylab LF 1 conductometer equipped with a LF 513 T measuring cell and a temperature detector. The devices were calibrated by standard calibration procedures using Hamilton Duracal Buffers (a two point calibration) for pH electrode, Fisher Scientific redox standard solution (250 mV) for Eh measurements and Fisher Scientific conductivity solution (1413 μS/cm) for conductivity measurements. All the experiments were performed in duplicate and with procedural blanks.

2.3. Analytical determinations

Leachate samples from each experiment were analysed for Na, K, Ca, Mg, Fe, Al, Si, Ba, Sr and total S by ICP-OES (Thermo Scientific iCAP 6500, UK), for Mn, Co, Ni, Cu, Zn, As, Se and Mo by quadrupole-based inductively coupled plasma mass spectrometer (ICP–MS; Thermo Scientific XSeries II, UK), and for the Cl^-, SO_4^{2-} and NO_3^- anions by high-performance liquid chromatography (HPLC; Dionex ICS-2000, USA). The accuracy of the determinations was controlled using a Merck IV solution (ICP multielement standard IV, Merck, Germany), CRM CZ9102 (Analytika, Czech Republic) and NIST SRM 1943d (Trace elements in water, NIST, USA). The alkalinity of the

Table 2
Chemical composition of the studied slag subsamples.[a]

Component	Units	A1[b]	A2[c]	A3
SiO_2	wt.%	38.1 ± 0.01	38.5 ± 0.06	38.4 ± 0.18
TiO_2	wt.%	0.44 ± 0.01	0.46 ± 0.00	0.46 ± 0.00
Al_2O_3	wt.%	6.11 ± 0.01	6.31 ± 0.02	6.31 ± 0.04
Fe_2O_3	wt.%	8.63 ± 0.21	8.61 ± 0.04	9.16 ± 0.04
FeO	wt.%	23.5 ± 0.12	23.2 ± 0.05	23.0 ± 0.14
MnO	wt.%	0.07 ± 0.00	0.07 ± 0.00	0.07 ± 0.00
MgO	wt.%	2.64 ± 0.01	2.66 ± 0.01	2.67 ± 0.00
CaO	wt.%	10.8 ± 0.18	10.8 ± 0.04	11.2 ± 0.07
Na_2O	wt.%	0.12 ± 0.01	0.12 ± 0.01	0.12 ± 0.00
K_2O	wt.%	2.13 ± 0.09	2.19 ± 0.00	2.22 ± 0.01
P_2O_5	wt.%	0.35 ± 0.01	0.34 ± 0.00	0.34 ± 0.00
C_{tot}	wt.%	0.47 ± 0.00	0.40 ± 0.00	0.56 ± 0.01
S_{tot}	wt.%	0.66 ± 0.00	0.67 ± 0.00	0.38 ± 0.00
As	mg/kg	92 ± 0.00	88 ± 0.23	82 ± 1.22
Ba	mg/kg	554 ± 4.75	576 ± 2.25	592 ± 3.00
Cu	mg/kg	$18,278 \pm 238$	$18,390 \pm 10.00$	$12,783 \pm 72.50$
Co	mg/kg	$12,263 \pm 47.5$	$12,280 \pm 25.0$	$11,998 \pm 57.50$
Cr	mg/kg	337 ± 2.17	381 ± 9.02	357 ± 9.40
Mo	mg/kg	44 ± 0.35	40 ± 1.08	42 ± 0.18
Ni	mg/kg	36 ± 0.98	34 ± 0.40	34 ± 2.50
Sb	mg/kg	12 ± 0.00	12 ± 1.68	$<DL$[d]
Sr	mg/kg	280 ± 2.02	281 ± 1.30	298 ± 1.07
V	mg/kg	39 ± 0.60	38 ± 0.80	42 ± 1.13
Zn	mg/kg	211 ± 1.48	205 ± 1.70	210 ± 0.50

[a] Mean ± standard deviation ($n = 2$).
[b] Identical chemical composition for subsamples B1 and C1.
[c] Identical chemical composition for subsample B2.
[d] Sb: DL = 10 mg/kg, other elements below detection limit (Bi: DL = 25 mg/kg; Cd: DL = 1.1 mg/kg; Pb: DL = 7.5 mg/kg; Se: DL = 10 mg/kg; Tl: DL = 25 mg/kg).

samples with pH > 4.5 was measured by back titration (0.05 M HCl) using a Schott TitroLine Easy automatic titrator.

2.4. Speciation-solubility modelling

Speciation-solubility modelling was carried out using the PHREEQC-2 geochemical code, version 2.17 for Windows [22] to determine the speciation of the contaminants in the leachates and the degree of leachate saturation with respect to the solubility-controlling phases as a function of the pH. The minteq.v4.dat thermodynamic database was used for all the calculations.

3. Results

3.1. Slag chemistry and mineralogy

The chemical composition of three slag subsamples A was very similar (Table 2). The main components were SiO_2 (38.1–38.5 wt.%), FeO (23.0–23.5 wt.%), CaO (10.8–11.2 wt.%), Fe_2O_3 (8.61–9.16 wt.%) and Al_2O_3 (6.11–6.31 wt.%) with relatively high concentrations of Cu (12.8–18.4 g/kg) and Co (12.0–12.3 g/kg). The content of Cu significantly decreased as the fine particles were removed by ultrasound; a slight decrease was observed for As, Co and Sb (Table 2). The slags were principally composed of clinopyroxenes corresponding to diopside-hedenbergite ($CaMgSi_2O_6$–$CaFeSi_2O_6$) solid solution. Magnetite (Fe_3O_4), olivine (($Fe,Mg)_2SiO_4$) and a certain portion of the amorphous fraction were observed in each subsample. Detailed mineralogical investigation of primary and secondary phases of the Nkana slags was reported by Vítková et al. [21].

3.2. Physical–chemical parameters and granulometry

The pH value gradually decreased as the dust fraction was removed while additional crushing to 1 mm (Table 1) resulted in an increase in the pH. The natural pH of sample A1 was 6.7, while this value dropped to 6.3 (A2) and 6.2 (A3) after the dust removal and ultrasonic cleaning, respectively. Similarly, the natural pH of
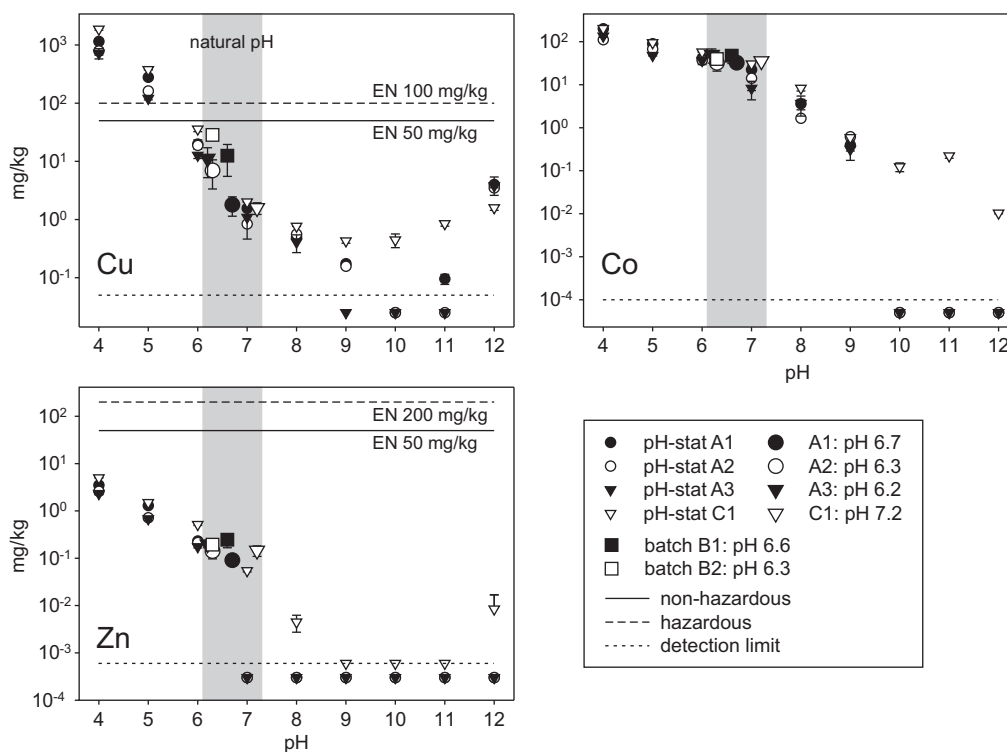
Fig. 2. Results of batch (EN 12457-2) and pH-static (CEN/TS 14997) leaching experiments including leaching at natural pH (larger symbols) and comparison with regulatory concentration limits for non-hazardous and hazardous waste [8]. The region of natural pH values of the individual sample fractions is indicated by a grey background; symbols with vertical bars represent mean and standard deviation of the measurements.

sample B decreased from 6.6 (B1) to 6.3 (B2), while the pH value of sample C1 was 7.2 as a result of crushing. Changes in the pH were in a good agreement with differences and/or similarities in granulometry of the individual samples (Table 1). The proportions of particles <0.5 mm yielded 15.1%, 15.7% and 46% for samples A1, B1 and C1, respectively. The maximum Eh values were measured for samples B1 and B2 yielding 585 mV and 593 mV, respectively. Under acidic conditions (pH 4–6), the Eh values slightly increased with increasing pH yielding 509–548 mV (A1), 516–565 mV (A2), 531–583 mV (A3) and 496–539 mV (C1). In contrast, the Eh values decreased with increasing pH in the alkaline region (pH 7–12) yielding 520–238 mV (A1), 538–230 mV (A2), 543–247 mV (A3) and 526–212 mV (C1). The specific conductivity in the leachates without pH adjustments dropped from 227 μS/cm (A1) to 116 μS/cm (A2) and from 193 μS/cm (B1) to 92 μS/cm (B2) when the dust fraction was discarded. This indicates the influence of the fine particles on the slag reactivity and the release of elements into the leachate.

3.3. Leaching behaviour

3.3.1. Leachability and speciation of contaminants

Fig. 2 illustrates the leaching behaviour of the most important contaminants (Cu, Co and Zn) as a function of the pH and granulometry and comparison of the leaching data with the regulatory levels. Further discussion will be focused on Cu, Co and Zn, since other possible contaminants were present in relatively low concentrations, often close to the detection limits. The EU regulatory limits established for the acceptance of waste at landfills (EC 2002 [8]) applicable to EN 12457-2 [9] at $L/S = 10$ L/kg were used, because no criteria are stated in the CEN/TS 14997 protocol [12]. Therefore, only the values for leachates at the natural pH of the material are the most relevant for comparison. Unfortunately, no limits are given for Co [8].

The results of pH-static experiments exhibited a common trend with maximum concentrations at pH 4 decreasing towards pH 7 and, in some cases, increasing slightly again at pH 11 and 12. Generally, the leaching of Cu, Co and Zn was accelerated by an increased proportion of dust particles and the concentrations hence decreased in the sequence C1–A1–A2–A3 (Fig. 2). Copper exhibited a more or less U-shaped leaching trend, similar to the leaching behaviour of Cu in other waste materials [5]. The maximum concentrations of Cu were released at pH 4, yielding 1872–1151–788–720 mg/kg following the sequence, and dropped rapidly to 2.00–1.56–0.84–1.09 mg/kg at pH 7 with a minimum in the range of pH 9–11. The Cu concentrations in all the leachates increased again at pH 12. The leaching of Co exhibited a gradual decrease with increasing pH (Fig. 2) with maximum concentrations at pH 4 (202–199–111–135 mg/kg). The highest concentrations of Zn were released at pH 4–6, while values below the detection limit were detected in leachates A1, A2 and A3 at pH 7–12.

The leachable concentrations of Cu and Zn in the batch leachates (24 h) as well as in the pH-stat leachates at their natural pH (48 h) did not exceed the regulatory limits (Fig. 2). However, the variation in the concentrations of Cu and Zn in the leachates not adjusted for pH was affected by the actual pH value dependent on the granulometry of the samples. The leaching of Cu exhibited the most significant differences. Thus, despite the highest portion of the dust particles in samples A1 and C1, leached concentrations of only 1.80 and 1.58 mg Cu/kg were detected, while the concentrations were higher for A2 and A3 (dust fraction removed) due to the slightly lower natural pH (Fig. 2). The maximum leached Cu concentration for all samples without pH adjustments was 28.5 mg/kg (leachate B2). Similar behaviour was observed for Co and Zn, where the highest concentrations for samples without pH adjustments were 49.8 mg Co/kg and 0.25 mg Zn/kg in leachates A3 and B1, respectively.

Table 3
Saturation indices of selected solubility-controlling phases calculated by PHREEQC-2 for leachates at specific pH values. Oversaturation of the leachates with respect to the solid phases is indicated in bold.

		EN 12457-2		CEN/TS 14997			
		B1	B2	C1-natural pH	C1-pH 4	C1-pH 5	C1-pH 10
pH		6.62	6.33	7.24	4.04	5.05	9.96
Phase	Composition						
Antlerite	$Cu_3(SO_4)(OH)_4$	−1.12	−0.54	−2.12	−4.97	−2.52	−2.58
Azurite	$Cu_3(CO_3)_2(OH)_2$	**0.49**	**1.20**	−0.22	−	−3.91	−0.83
Brochantite	$Cu_4(SO_4)(OH)_6$	**0.45**	**1.18**	−0.44	−6.23	−2.39	**0.75**
Calcite	$CaCO_3$	−1.97	−2.81	−1.09	−	−4.83	**0.83**
Co(OH)$_2$	$Co(OH)_2$	−4.29	−4.66	−3.04	−9.00	−7.03	−1.12
Co$_3$O$_4$	Co_3O_4	**5.00**	**3.75**	**7.62**	−17.15	−9.45	**13.45**
CoCO$_3$	$CoCO_3$	−1.42	−1.68	−0.70	−	−4.22	−1.56
CoO	CoO	−4.78	−5.15	−3.53	−9.49	−7.52	−1.62
Cu(OH)$_2$	$Cu(OH)_2$	−0.68	−0.52	−0.56	−3.50	−2.11	**1.09**
CuCO$_3$	$CuCO_3$	−0.71	−0.43	−1.12	−	−2.19	−2.25
Cuprousferrite	$CuFeO_2$	−	−	−	**8.66**	**9.56**	**10.98**
Diaspore	$AlO(OH)$	−	−	**2.10**	**0.64**	−0.81	**0.42**
Gibbsite	$Al(OH)_3$	−	−	**0.68**	−0.78	−2.23	−1.00
Gypsum	$CaSO_4·2H_2O$	−1.95	−2.82	−1.90	−1.83	−1.88	−2.60
Ferrihydrite	$Fe(OH)_3$	−	−	−	**1.12**	**1.53**	**2.34**
Langite	$Cu_4(SO_4)(OH)_6·2H_2O$	−1.82	−1.08	−2.70	−8.50	−4.65	−1.52
Lepidocrocite	$FeO(OH)$	−	−	−	**2.94**	**3.35**	**4.16**
Maghemite	Fe_2O_3	−	−	−	**2.23**	**3.06**	**4.68**
Malachite	$Cu_2(CO_3)(OH)_2$	**1.09**	**1.53**	**0.80**	−	−1.82	**1.32**
Smithsonite	$ZnCO_3$	−3.69	−3.99	−3.12	−	−6.00	−
Tenorite	CuO	**0.35**	**0.51**	**0.47**	−2.47	−1.08	**2.12**

Symbols used: − not calculated.

Speciation modelling (PHREEQC-2) indicated the variation in the metal speciation as a function of the pH and the presence of the dust fraction. The free ionic form of Co prevailed in the leachates (87–99% of the total speciation); the portion of the $CoSO_4^0$ complex increased with increasing pH and/or dust portion (1.3–9.6% of the total speciation); the carbonate form $CoHCO_3^+$ was present in the leachates with pH > 5 (up to 4.6%). The free ionic form of Cu predominated in the batch leachates (i.e., B1–B2: 67–75%) and at pH 4–6 (60–98%), while the $CuCO_3^0$ complex prevailed at pH 7–9 (54–86%) and $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$ or $CuOH^+$ species were present at pH 10–12 (47–100%). A variable fraction of the neutral $CuSO_4^0$ complex was present in the leachates with pH 4–9 (up to 7% of the total speciation). The free ionic form of Zn prevailed (89–98% of the total speciation) and up to 9.5% of $ZnSO_4^0$ complex was present in the leachates under acidic conditions. The carbonate form $ZnHCO_3^+$ was calculated for the leachates with pH > 5 (up to 1.5%). Zinc leachate concentrations yielding <10^{-2} mg/L (involves all the leachates with pH 8–12) were not calculated in the speciation modelling.

3.3.2. Solubility-controlling phases

Possible solubility-controlling phases and their saturation indices (SI) as calculated by PHREEQC-2 are listed in Table 3. Various Cu- or Co-bearing carbonates, hydroxides, oxides or sulphates exhibited positive or close-to-zero SI values under near neutral pH conditions in the B and C leachates and under more alkaline conditions (pH 10) for leachate C (Table 3). No carbonate precipitation was predicted for leachates with pH < 5. The EN 12457 leachates (B1 and B2) were oversaturated with respect to azurite ($Cu_3(CO_3)_2(OH)_2$), brochantite ($Cu_4(SO_4)(OH)_6$), malachite ($Cu_2(CO_3)(OH)_2$), tenorite (CuO) and Co_3O_4 (Table 3). Under acidic conditions (pH 4 and 5), all the leachates were undersaturated with respect to the Cu and Co phases. Under alkaline conditions (pH 10), the leachates were oversaturated with brochantite, malachite, tenorite, $Cu(OH)_2$, Co_3O_4 and calcite ($CaCO_3$). Possible Zn-bearing phases (smithsonite $ZnCO_3$, ZnO and $Zn(OH)_2$) yielded negative SI values under slightly acidic or neutral conditions and were not calculated for the leachates with pH > 8. Numerous Fe

oxyhydroxides (HFO), typical secondary phases and metal sorbents [3,14], yielded positive saturation indices under acidic (pH 4–5) and alkaline (pH 9–11) conditions (CEN/TS 14997 leachates), while no HFO were calculated under near neutral conditions due to very low Fe concentration in the leachates. According to the PHREEQC-2 calculation, ferrihydrite ($Fe(OH)_3$), lepidocrocite (FeOOH), maghemite (Fe_2O_3) and also cuprous ferrite ($CuFeO_2$) are the most important Fe-bearing (hydr)oxides predicted to precipitate. Possible Al oxyhydroxides (e.g., diaspore AlOOH, gibbsite $Al(OH)_3$) also yielded positive SI values (Table 3).

4. Discussion

4.1. Effect of sample granulometry on the leaching behaviour

The differences in the leaching behaviour at a specific pH corresponded to heterogeneity in sample granulometry. The effect of reduced grain size on the mobilisation of elements is a familiar phenomenon, since crushing effectively increases the sample specific surface area [1,16,18]. It has been demonstrated that the particle size distribution of waste materials (in addition to their composition) strongly influences the contaminant leachability [4,14,15]. Similarly, during our experiment, increased metal mobility was observed for slag samples with a higher portion of the <0.5 mm fraction. Further ultrasonic removal of dust particles adhering to the surfaces of larger grains (subsample A3) decreased the released concentration even more (Fig. 2).

The pH value of the leaching system is also a key parameter controlling the contaminant mobility [4,5,13]. Our leaching experiments without pH adjustments showed that the granulometry significantly affected the natural pH of the system and created a secondary effect on the metal leachability. Consequently, the pH decreased with decreasing portion of dust particles (including the ultrasonic cleaning effect) and surprisingly, the metal concentrations in the leachates tended to subsequently increase (this effect was the most pronounced for sample A) (Fig. 2). The leaching behaviour of Cu clearly exhibited the strong influence of the pH since the highest Cu concentrations were detected in the most

acidic leachates despite the minimum portion of dust particles. This observation is in sharp contrast to the results of Zandi et al. [18], who reported dramatically lower concentrations for all the studied elements in Pb slag leachates after excluding the <0.5 mm dust fraction from the sample. Nevertheless, it is important to stress that the Pb slag studied by Zandi et al. [18] was produced by alkaline fusion and the leachates had strikingly different pH values (11.90 and 12.35 after dust removal, respectively) compared to our leachates. Slightly acidic natural pH of the material was probably the main factor controlling the leaching process and the leachability of metals. The release of major elements (Ca, Mg, K, Si and S) into solution increased with higher proportion of the fine-grained fraction. In particular, the released concentrations of Ca, Si and S were about 60–70%, 25–35% and 50–60% lower, respectively, after the dust removal for both samples A and B (data not shown). Contrasting leaching behaviour of Cu, Co and Zn was probably related to the presence of newly formed phases. Although higher metal release could be expected in samples with dust fraction, the rapid formation of secondary phases (e.g. oxides and carbonates, Table 3) could possibly attenuate their leaching.

4.2. Implication for testing the hazardous properties of slags using standardised leaching protocols

Except for highly toxic Pb slags produced by the alkaline fusion of old car batteries [18,23], the majority of pyrometallurgical slags from non-ferrous metal smelting are silicate-based materials with a minor proportion of metal-bearing sulphides or intermetallic compounds and during interaction with water they mostly yield steady-state pH values in the circum-neutral range (pH ∼5.5–7.5) [e.g. 14,15,21]. Occasionally, the slag leachates with pH <5 can be found [24]. Furthermore, relatively small amounts of metals can be leached from non-ferrous metallurgical slags under circum-neutral conditions due to efficient mineralogical/geochemical controls (precipitation and sorption to newly formed phases) especially when only coarse-grained fractions were used in the leaching experiments [e.g. 14,16]. A number of studies showed that even when fine-grained slag material is used for the short-term leaching tests, the metal release is still below the acceptable limits. For example, Shanmuganathan et al. [6] recently observed that even after activation of copper slag by crushing/milling, the released metals were below the limits prescribed in the USEPA toxicity characterisation leaching test and similarly low metal leachability has been reported by Ettler et al. [15] for Namibian slags. The data obtained in this study are similar direction and show that, according to batch tests (EN 12457-2), the concentrations of metals released from the studied slag are far below the regulatory levels for hazardous and even non-hazardous waste regardless of whether the fine-grained fraction is included or not (Fig. 2). Additionally, for smelting slags, the effect of the granulometry on the results of standardised EN 12457-2 single-batch leaching tests seems to be marginal, but may influence the pH of the suspension, which can then have a more significant influence on the leaching results (Fig. 2). Nevertheless, the 24-h testing using the EN 12457-2 procedure [9] is definitely too short to describe the long-term behaviour of this kind of material in a given scenario. For more realistic modelling of real-scale slag leaching, either a long-term batch test on the coarse fraction (e.g. 2–5 mm; [14]) or percolation tests [16] could be more suitable for describing the risk related to exposure of slag fragments on dumps.

However, to simulate the practice at numerous smelting sites, the crushing of slag samples to <1 mm (as it is prescribed in the CEN/TS 14997 pH-stat test [12]) can also be relevant. Ettler et al. [15] performed batch leaching tests on granulated and milled Cu–Pb slags from Tsumeb (Namibia) in order to simulate the "worse-case" scenario of their environmental impact. These fine-grained slags are dumped together with mining waste in tailing ponds and represent an important source of wind-blown contamination, which is then deposited in the nearby soil systems [15] (B. Kříbek, personal communication). Similarly, Kříbek et al. [19] observed tiny slag particles in the air and in soils in the vicinity of the Nkana smelter, Copperbelt, Zambia, where the first step of old slag re-processing takes place and slag crushers generate dust, which is subsequently dispersed by wind. Recently, at the same site, Ettler et al. [20] described a number of Cu-bearing phases (e.g. brochantite, $Cu_4(SO_4)(OH)_6$) in the lateritic soil profiles, which can be related to either fly ash or slag wind-blown contamination. Brochantite was predicted by PHREEQC to be a significant Cu-controlling phase in our experiments (Table 3) and was also described as a secondary alteration product on copper smelting slags [21]. Although the studied Cu slag is relatively stable under circum-neutral conditions, our pH-stat leaching results indicate up to 3 orders of magnitude higher release of Cu and Co at pH values between 4 and 5, in particular for slag crushed to <1 mm. This observation may result in an increased mobility of Cu and Co in contact with acidic rainwater usually related to the surroundings of mining and smelting operations in the Copperbelt area. Furthermore, soils adjacent to smelters in the Copperbelt province are quite acidic (pH between 4 and 5; [19,20]) and the leaching properties of fine-grained slag materials can be highly relevant for assessing the slag reactivity in such environmental systems, especially with implications for the vertical mobility of slag-derived contamination in exposed soil profiles.

5. Conclusions

This study points out the importance of sample preparation and pH conditions when assessing the environmental risk related to smelting slag using the leaching tests based on standardised procedures. The contaminant (Cu, Co, Zn) leaching from a copper smelter slag showed a strong dependence on the granulometry and pH. The leaching was generally accelerated by crushing due to the presence of easily soluble dust particles. The highest concentrations were released at pH 4 and 5 with a gradual decrease towards near-neutral conditions and a slight increase at pH 11 or 12. Although the metal levels in the batch leachates were below the EU criteria for non-hazardous materials, the effect of sample preparation on the leaching behaviour was crucial under acidic conditions. The highest metal release was detected for slag crushed to <1 mm at pH 4 (1872 mg Cu/kg). As predicted by the pH-static leaching test, the risk of higher Cu and Co release from tiny wind-blown slag particles should be considered in acidic soil near smelters in the Copperbelt province, Zambia.

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