Cobalt-bearing copper slags from Luanshya (Zambian Copperbelt): Mineralogy, geochemistry, and potential recovery of critical metals

Vojtěch Ettler [a],[*], Martin Mihaljevič [a], Petr Drahota [a], Bohdan Kříbek [b], Imasiku Nyambe [c], Aleš Vaněk [d], Vít Penížek [d], Ondra Sracek [e], Vendula Natherová [a]

[a] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 00 Prague 2, Czech Republic
[b] Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic
[c] University of Zambia, Geology Department, School of Mines, P. O. Box 32379, Lusaka, Zambia
[d] Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 00 Prague 6, Czech Republic
[e] Department of Geology, Faculty of Science, Palacký University in Olomouc, 17. listopadu 12, 771 46 Olomouc, Czech Republic

ARTICLE INFO

ABSTRACT

Waste materials such as metallurgical slags can be considered as potential resources of valuable elements, including technologically critical metals. Copper slags from Luanshya, the oldest mining and smelting site in the Zambian Copperbelt, produced by smelting local Cu ores in reverberatory furnaces between 1932 and 1999, were deposited on two large dumps in the vicinity of the former ore processing area. The slags exhibit high concentrations of Co (247–5990 ppm, median: 2370 ppm) and Cu (1320–95,300 ppm, median: 8550 ppm). This multi-method mineralogical investigation indicates that the slags are predominantly composed of olivine, clinopyroxene, silicate glass, and spinel-family oxides. Copper-(Fe) sulfides, cobaltpentlandite [$(Co,Fe)_9S_8$], Fe sulfides, and metallic Cu prills embedded in the silicate matrix are the major hosts of Cu and Co. The EU regulatory leaching test (EN 12457-2) indicated that the release of contaminants is relatively low and only Cu slightly exceeded the EU limit values for landfilling of inert waste. The secondary phases (Cu hydroxosulfates, Fe (oxyhydr)oxides) observed on the slag surfaces confirm that the slags undergo a weathering process on the dumps. Kinetic abiotic extraction tests were carried out in 0.5 mol/l sulfuric acid at 25 °C and with a pulp density of 1% to determine the release of metals from the milled Luanshya slags under conditions simulating hydrometallurgical recovery via agitation leaching. The Cu and Co extractability correlated with the bulk concentration of these elements, and the highest extraction yields after 24 h of leaching corresponded to 46% of the total Cu and 67% of the total Co. Despite the dramatic increase in Co prices on the global market, the Co recovery from the Luanshya slags appears to be non-economical due to the high costs of the necessary mechanical and chemical processing of the slag materials and the obtained extracts.

1. Introduction

Copper (Cu) slags may contain many elements considered critical from the technological point of view (Piatak and Ettler, 2021). An example of a critical metal found in elevated concentrations in Cu slags is cobalt (Co), which has been listed in many international lists of strategic and critical minerals (Fortier et al., 2018; European Commission, 2020; Hofstra et al., 2021). Cobalt has traditionally been used to produce superalloys or used in the chemical industry (catalyst, pigment), but currently, it increasingly finds applications in the production of batteries (mainly rechargeable lithium-ion batteries), which

is the leading global use for Co. The majority of Co on the global market (>65%) is produced in the central African Copperbelt, with the Democratic Republic of Congo (DRC) and Zambia being the main producers (Roberts and Gunn, 2014; USGS, 2021).

Apart from Cu slag reprocessing based on comminution and flotation, various chemical and biological treatments have also been tested on metallurgical slags to recover valuable metals (Muravyov et al., 2014; Kaksonen et al., 2017; Potysz et al., 2018; Piatak and Ettler, 2021 and references therein). Despite the efficiency of these extraction methods, they have not yet been implemented on an industrial scale (Piatak and Ettler, 2021). Slags issued from the processing of Cu-Co ores in the DRC

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and Zambia contain elevated concentrations of Co; our previous study devoted to Cu slags from several sites in the Zambian Copperbelt indicated that the Co contents in the Cu slags varied from 720 to 24,104 ppm Co (mean: 8390 ppm, median: 7610, $n = 18$) (Vítková et al., 2010). Between 2001 and 2006, the Chambishi smelter processed old slags originating from the closed Nkana smelter in Kitwe, which were particularly rich in Co (0.3–2.6 wt%, mean: 0.76 wt%) to recover Co via a pyrometallurgical technology (Jones et al., 2002; Vítková et al., 2010; Kapobe et al., 2019). Hydrometallurgical technologies were also tested on Co-rich slags (0.7 wt% Co) from Lubumbashi, the DRC, to recover Co and other base metals (Banza et al., 2002).

This paper follows our broader interest in understanding the environmental impact of mining and smelting activities in the Zambian Copperbelt, where slag dumps have been considered as a source of soil/water pollution and dust formation (Kříbek et al., 2010; Ettler et al., 2014). Our previous research devoted to the detailed mineralogy and geochemistry of slags from the Zambian Copperbelt focused on the Mufulira, Kitwe, and Chambishi sites (Vítková et al., 2010, 2011). However, data for the slags from Luanshya, being the oldest Cu smelting site in the Copperbelt Province, are missing in the scientific literature.

The aim of this article is to fill this knowledge gap and to use a multi-method approach to understand the mineralogy, environmental geochemistry, and potential extraction/recovery of valuable elements from these old Luanshya slags.

2. Study site

The central African Copperbelt is one of the world's greatest sediment-hosted stratiform Cu-Co deposits, totaling 140 Mt. Cu and 6 Mt. Co in the Zambian and Congolese parts of the belt (Cailteux et al., 2005). The Luanshya (previously Roan Antelope) deposit located in the eastern part of the African Copperbelt was discovered in 1902, and when opened in 1928, it was the first commercial Cu mine in the Zambian Copperbelt (Coleman, 1971; Sikamo et al., 2016). The smelter began operation in 1932 with coal-fired reverberatory furnaces and Peirce-Smith converters (Mukherjee et al., 1999).

The peak production at Luanshya was in 1960 with 105,000 tons Cu (Ruffini, 2008). The Cu industry in Zambia was nationalized in 1970, and the Roan Antelope Cu mine became part of Zambia Consolidated Copper Mines (ZCCM) in 1982. The mine was privatized in 1997 and
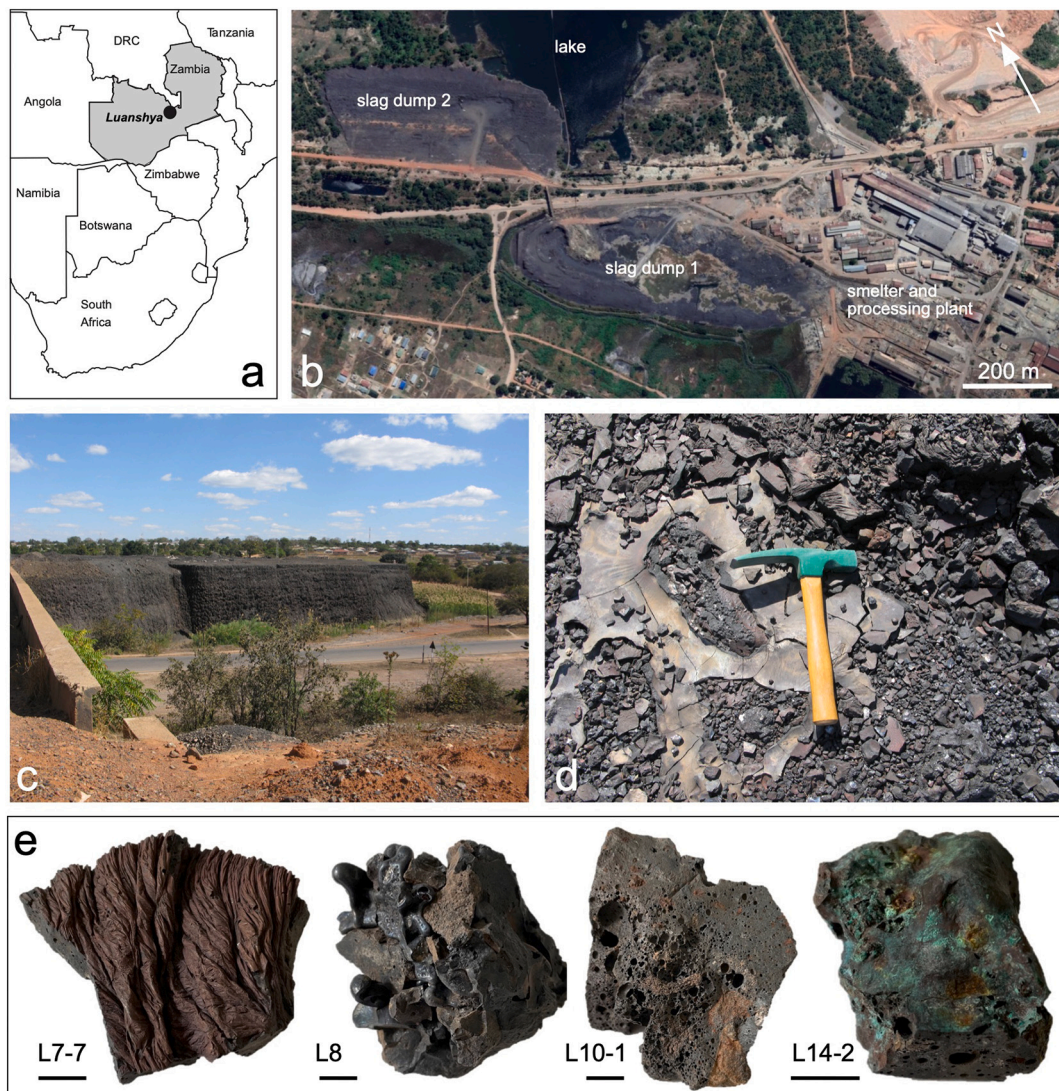
Fig. 1. Slag samples from Luanshya (Zambian Copperbelt). a) Map of southern Africa with the position of Luanshya. b) Aerial photo of the slag dumps and former smelter/processing area in Luanshya (source: 2-D Google Earth). c) View of the southern slag dump formed by pouring the slag melt in layers. d) Slag layers and fragments with lava-flow textures. e) Various slag textures: lava-flow texture (sample L7-7), glassy slag (sample L8), porous slag with vesicles (sample L10-1), and weathered glassy slag with secondary Cu sulfates (sample L14-2). Note the presence of secondary Fe(III) (oxyhydr)oxides on the surface of the slag samples. The scale bar corresponds to 1 cm.

became property of the Roan Antelope Mining Corporation of Zambia (RAMCOZ). Despite the planned upgrade and modernization of the smelter technology designed to increase the production capacity from 42,000 to 60,000 tons Cu anodes per year (Mukherjee et al., 1999; Moskalyk and Alfantazi, 2003), the smelter was finally closed in 1999 (Ruffini, 2008). The owner mismanaged the mining operations, and some of the Luanshya shafts were shut down and flooded (Ruffini, 2008). In 2002, the mine was sold to J & W/Enya and renamed to Luanshya Copper Mine (LCM), but the company failed and closed the operations again in 2008. In 2009, the Chinese-owned company China Nonferrous Metal Mining Group (CNMC) bought 80% of the shares of the LCM, reopened the mines in 2010, and is currently running all the Cu mining operations in the Luanshya area (Mususa, 2010).

Our study focuses on the old slag materials produced between 1932 and 1999, forming two dumps in the vicinity of the former smelter area (Fig. 1). The surface of the two slag dumps was estimated to be ca. 200,000 m^2 (Fig. 1b). Based on the average slag density (3.20 ± 0.41 g/cm^3) and the estimated height of the dumps (ca. 8 m), the amount of the slag has been estimated to be ca. 5.1 ± 0.7 Mt. Other studies (Sracek et al., 2018) and unpublished reports (Kříbek, 2010) indicate that significant mining-related environmental problems are (i) the contamination of the soils (with concentrations exceeding 2200 ppm Cu and 60 ppm Co, especially near the former mine/smelter area) and (ii) the drainage and dust generation in the mining waste disposal sites.

3. Materials and methods

3.1. Sample collection and processing

A total of 21 slag samples were collected from the Luanshya slag dumps in June 2018 (Fig. 1a, b). Parts of the dumps were formed by pouring the slag melt in layers, and slag fragments exhibited lava-flow textures and weathering features, such as the formation of secondary phases on their surfaces (Fig. 1c–e). Representative parts of all the samples were embedded in an epoxy resin and prepared as polished thin sections for the microscopic observations and microanalyses. Aliquots of all samples were pulverized in an agate planetary mill to <50 μm (Retsch PM 400, Germany) and used for the bulk chemistry and phase composition determinations, and for the hydrometallurgical testing. Based on the chemical and mineralogical analysis results (see below), four representative slag samples (L7-8, L8, L10-1, L11-1) were selected for the leaching tests designed to assess the contaminant release; for this leaching procedure, the slag material was crushed using a jaw-crusher to <4 mm.

3.2. Chemical and mineralogical investigations

The determination of the major elements was carried out using a combination of gravimetric, volumetric, and spectrometric analyses as described in Ettler et al. (2009). The contents of the total sulfur (S_{tot}) and total organic carbon (C_{org}) were determined using a combination of ELTRA CS 530 and ELTRA CS 500 TIC analyzers (ELTRA, Germany). For the determination of the trace elements in the slags, we used an acid digestion procedure. A mass of 0.2 g of the sample was dissolved in a closed system (Teflon beakers, Savillex, USA) in a mixture of 10 ml of HF (49% v/v) and 0.5 ml of HClO$_4$ (70% v/v) on a hot plate (130 °C). The mixture was evaporated to dryness, and this procedure was repeated with 5 ml of HF and 0.5 ml of HClO$_4$. The residue was then evaporated to near-dryness, dissolved in 2% HNO$_3$ (v/v), and diluted to 100 ml before the analysis. The digests were analyzed for metals and metalloids (Ag, As, Ba, Bi, Cd, Co, Cr, Cu, Ga, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, V, and Zn) using a combination of inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110, USA) and quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, Thermo-Scientific, iCAP-Q™, Germany). A modified digestion procedure (HNO$_3$, 65% v/v, instead of HClO$_4$) was used when preparing the digests for the

subsequent analysis of Ge by ICP-MS. All the chemicals used during the digestion procedure were reagent-grade (Merck-Sigma-Aldrich, Germany), and deionized water obtained from a Millipore Academic system (Millipore, USA) was used for the dilutions. The quality control/quality assurance (QC/QA) of the bulk digestion procedures and subsequent analyses was performed by the parallel processing of an SU-1b certified reference material (Nickel-Copper-Cobalt Ore, certified by CANMET, Canada) and was found to be satisfactory (Table S1).

The phase compositions of the slags were determined by powder X-ray diffraction analysis (XRD) using a PANalytical X'Pert Pro diffractometer (PANalytical, the Netherlands) equipped with and an X'Celerator detector (analytical conditions: CuKα radiation, 40 kV, 30 mA, 2 theta range of 5–70°, a step of 0.02°, counting time 150 s per step). The diffraction patterns were analyzed by X'Pert High Score Plus 3.0 software coupled with the Crystallography Open Database (COD) (Gražulis et al., 2012). The polished thin sections of the specimens were first examined under a Leica DM LP polarizing microscope (Leica, Germany). A JEOL JXA-8530F (JEOL, Japan) electron probe microanalyzer (EPMA) equipped with a field emission gun source (FEG), energy dispersion spectrometer (EDS; JEOL JED-2300F), and five wave-dispersion spectrometers (WDS) was used for the scanning electron microscopic (SEM) imaging, EDS analyses, and quantitative analyses. The detailed analytical conditions, standards and detection limits used for the EPMA measurements are given in Table S2.

3.3. Leaching test for the environmental assessment

Four slag samples were subjected to a simple batch leaching test used in the European Union (EU) as a regulatory "compliance test", EN 12457-2 (EN 12457, 1999) for classifying waste materials in view of potential landfilling (EU, 1999; EU, 2002; Ettler and Vítková, 2021). The amount of 4 g of slag (fraction <4 mm) was leached in 40 ml of deionized water, corresponding to a liquid/solid (L/S) ratio of 10 l/kg. The leaching test was carried out in duplicate at 20 ± 3 °C, and the reactors were continuously agitated using a horizontal shaker (Heidolph Promax 2020, Germany) for 24 h. Subsequently, the supernatants were filtrated through 0.45 μm filters (disposable Millipore Millex-LCR PTFE membrane filters, USA and Injekt Luer Lock 20 ml syringes, B. Braun, Germany). The pH and Eh values were immediately measured using a WTW Multi 3620 IDS multimeter equipped with a WTW SenTix® 940 pH electrode and SenTix® ORP-T 900 redox electrode, respectively (WTW, Germany). The electrical conductivity (EC) in the leachates was recorded using a Mettler-Toledo Seven2Go conductometer with a Mettler-Toledo InLab® 738 ISM conductivity probe (Mettler-Toledo, Switzerland).

The leachates were analyzed for major cations and trace elements Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Si, Sn, Sr, Tl, V, and Zn by ICP-OES and ICP-MS. The accuracy check (QC/QA) of the measurements was controlled by a parallel analysis of the SRM NIST 1463f certified reference material (Trace elements in water, NIST, USA) (Table S1). The alkalinity in the leachates was measured by back titration (0.05 mol/l HCl) using a Schott TitroLine Easy automatic titrator (Schott Gerätte, Germany). The major anions (Cl$^-$, SO$_4^{2-}$ and NO$_3^-$) were determined by high-performance liquid chromatography (HPLC; Dionex ICS-2000, USA).

3.4. Extraction test for potential recovery of critical metals

For the laboratory hydrometallurgical testing, three representative slag samples were selected: L7-8 (crystalline slag), L10-1 (crystalline slag with vesicles), and L11-1 (glassy slag). On crystalline and glassy Cu slags, Potysz and Kierczak (2019) compared metal extraction efficiencies obtained by various mineral and organic acids (H$_2$SO$_4$, HNO$_3$, HCl, oxalic, citric). A comparison of normality equivalent acids (2 N) indicated that the metal extraction yields were the highest in the HNO$_3$ and HCl extractions for both crystalline and amorphous Cu slags.

However, due to its price and availability, sulfuric acid (H_2SO_4) is considered as the first choice extractant for most hydrometallurgical processes (Binnemans et al., 2020; Potysz and van Hullebusch, 2021 and references therein). Moreover, sulfuric acid is produced in large quantities in sulfuric acid plants in many non-ferrous metals smelters, as it is also the case of a nearby Mufulira smelter equipped with the ISAS-MELT™ smelting technology (Ross and de Vries, 2005; Schlesinger et al., 2011). By varying the sulfuric acid strength and pulp densities, Potysz and Kierczak (2019) demonstrated that the highest metal extraction yields were observed for 0.5 mol/l H_2SO_4 and at 1% pulp density, particularly for the amorphous Cu slags.

Based on these indications, the pulverized samples (<50 μm) were leached in 0.5 mol/l H_2SO_4, and the extraction was performed at a 1% pulp density (L/S = 100 l/kg, i.e., 0.1 g sample into 10 ml of extracting solution). This experimental protocol was modified from Ettler et al. (2020), who used the same approach for the extraction of vanadium and other metals from African slags to simulate the hydrometallurgical recovery via agitation leaching. For each extraction time (1, 6, and 24 h), duplicate reactors were prepared. The suspensions were continuously agitated using a GFL 3018 horizontal shaker (GFL, Germany; 60 rvs/min) at the ambient temperature (25 °C). The samples were then centrifuged at 3000 rpm for 5 min (Hettich UNIVERSAL 320 R centrifuge, Germany) and the extracts were filtrated using the 0.45 μm membrane filters. The pH and Eh values were immediately recorded using a WTW Multi 3620 IDS multimeter. The extracts were diluted and measured for the major and trace elements by ICP-OES (Ag, Cd, Pb, and Sb were systematically below the detection limit for all the extracts). XRD was used to analyze the slag residues obtained after the 24-h extraction to determine the changes in the phase compositions.

3.5. Data treatment

The data were plotted using a combination of Prism 9 (GraphPad, USA) and Graphic for Mac (Picta, USA) software packages. The PHREEQC-3 geochemical code version 3.3 with a Notepad++ 6.6.9 interface (Parkhurst and Appelo, 2013) was used for the speciation-solubility modeling to determine the speciation of contaminants in the leachates and extracts and to calculate the degree of the leachate saturation with respect to potential solubility-controlling phases (saturation index, SI). The default minteq.v4.dat thermodynamic database was used for all the calculations, supplemented with thermodynamic data for some Co minerals (e.g., spherocobaltite, $CoCO_3$) from the llnl.dat database.

Table 1

Basic statistics for the trace element concentrations (ppm) in the slags from Luanshya (Zambian Copperbelt). The full dataset is available in Table S3.

	Min	Max	Mean[a]	Median[a]
Ag	0.5	27	3.65	1.35
Ba	315	1070	538	495
Cd	0.95	6.25	2.71	2.00
Co	247	5990	2696	2370
Cr	7.2	2877	388	213
Cu	1320	95,300	17,835	8550
Ga	16	44	27.5	25.4
Ge	<5	12	7.69	6.23
Mo	39	367	157	149
Ni	15	93	47.5	40.9
Pb	1.2	305	34.5	17.9
Sb	<15	162	61.8	45.7
Sr	125	677	314	268
V	18	324	86	74
Zn	38	2450	256	126

Below detection limit: As <25 ppm, Bi <25 ppm, Se < 40 ppm, Sn < 15 ppm, Tl < 20 ppm.

[a] Calculated for $n = 21$ samples, except for Ge ($n = 8$) and Sb ($n = 13$).

4. Results

4.1. Geochemistry and mineralogy

The Luanshya slags are predominantly composed of Si (27.15–63.25 wt% SiO_2), Fe (4.23–16.81 Fe_2O_3 and 6.05–39.69 wt% FeO), Ca (1.87–23.79 wt% CaO), and Al (3.71–10.50 wt% Al_2O_3) (Table S3). The major trace elements in the slags are Cu (1320–95,300 ppm, mean: 17832, median: 8550) and Co (247–5990 ppm, mean: 2696, median: 2370) (Tables 1 and S3). Other metals and metalloids, including additional critical metals (Ga, Ge, Sb), occur in much lower concentrations (mean values range from ones to hundreds of ppm) (Tables 1 and S3).

The mineralogical composition is rather variable. The combination of the XRD data, optical microscopy, and scanning electron microscopy revealed that the glass is a ubiquitous phase indicating the rapid cooling of the slag melt (Fig. 2, Table S4). Clinopyroxene, olivine, and spinel are also typical phases in most of the studied slags. Clinopyroxene forms fine-grained crystallites (Fig. 2b, c), laths (Fig. 2d), or skeletal crystals (Fig. 3a) embedded in the glass. Olivine generally occurs as skeletal laths (Figs. 2e, 3c, e, f). Spinel commonly forms large blebs several hundreds of μm in size (Fig. 3b) or smaller euhedral crystals (<20 μm in size; Fig. 3c–e). Leucite and melilite are relatively rare within the studied slags with generally large prismatic crystals up to hundreds of μm in size (Fig. 3d). Non-melted residual grains of silicates from the gangue (feldspars, SiO_2 phases) were also found in some samples, indicating that, in some cases, the temperatures in the furnace were not sufficiently high enough to melt the furnace charge completely (Fig. 2a; Table S4).

Sulfides and metallic phases are common in all the studied samples. They form rounded or oval inclusions and blebs of variable size (Figs. 2f, 3b–f). The EPMA indicated that the Cu and Cu-Fe sulfides, such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), digentite (Cu_9S_5), covellite ($Cu_{1+x}S$), bornite (Cu_5FeS_4) or their solid solutions, predominate (Fig. 3; Table S5). Many of these phases were not perfectly stoichiometric (Table S5), and the compositional data plotted in a Cu-Fe-S diagram in comparison with Cu-Fe sulfides from other Copperbelt slags (Vítková et al., 2010) also indicate that these phases formed under non-equilibrium conditions by quenching the melt (Fig. S1). Cobaltpentlandite [$(Co,Fe)_9S_8$] and pyrrhotite ($Fe_{1-x}S$) are less common in the studied slags (Fig. 3e, f), but they are key hosts of Co with 40.40 wt%, and 3.53 wt%, respectively (analyses 2 and 3 in Table S5). Elevated Co concentrations were also detected in chalcopyrite (2.60 wt%) and in the identified Fe-Cu sulfide (2.32 wt%) (analyses 29 and 30 in Table S5). Metallic Cu, forming droplets of variable size, embedded in silicate matrix or sulfides (Fig. 3b, e, f) is an important Cu-bearing phase in the slags.

The compositions of clinopyroxenes are rather variable, ranging from almost pure enstatite ($Mg_2Si_2O_6$) to a diopside ($CaMgSi_2O_6$)-hedenbergite ($CaFeSi_2O_6$) solid solution (Table S6). The EPMA results showed that some Co can substitute for Mg and Fe in the clinopyroxene structure (0.03–0.10 wt% CoO). Copper was only rarely detected in the clinopyroxene (up to 0.04 wt% CuO). Olivine-family phases mainly exhibit compositions in a forsterite (Mg_2SiO_4)-fayalite (Fe_2SiO_4) solid solution with the fayalite end-member accounting for up to 92% (Table S6). Calcium-rich olivines with compositions close to kirschsteinite ($CaFeSiO_4$) were found in sample L13-2 in association with melilite (Fig. 3d; analysis 46 in Table S6). The Co concentrations in the olivines were higher than in the clinopyroxenes, ranging from 0.15 to 0.85 wt% CoO (Table S6). Compared to Co, Cu was found in substantially lower concentrations in the olivines (up to 0.06 wt% CuO) (Table S6). The dominant presence of melilite in one slag sample shows that the slag melt was substantially richer in Ca compared to other slags (Table S6; Fig. 3d). The EPMA data obtained from the melilite and leucite crystals indicated that these phases were not important hosts of Cu and Co (<0.09 wt% CuO or CoO, respectively) (Table S6). Given that the glass occurs in all the studied slag samples, it is a volumetrically important host of Cu and Co with concentrations up to 0.26 wt% CuO
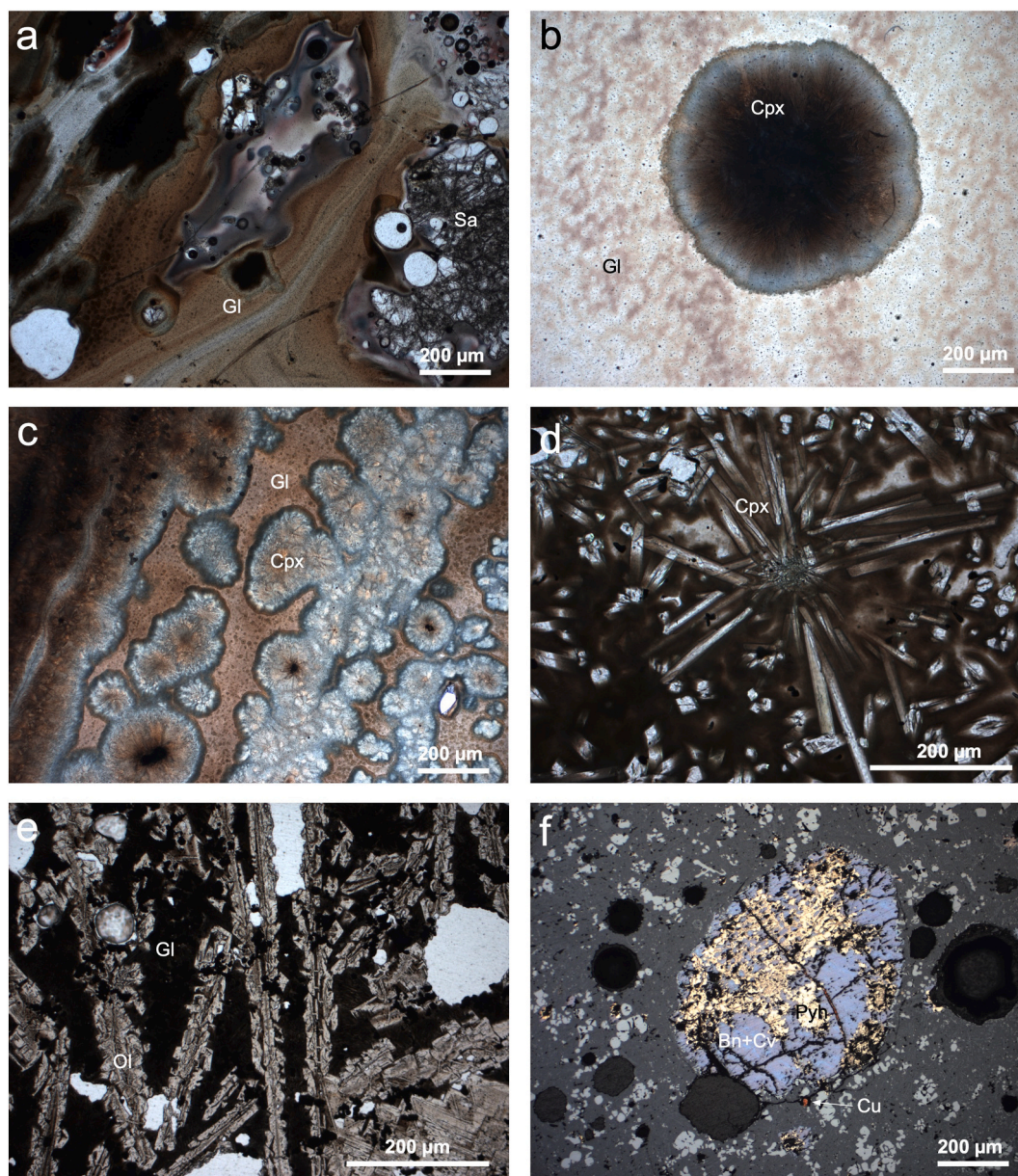
Fig. 2. Textures of the Luanshya slags. a) Melting texture composed of glass (Gl) schlieren with non-melted crystals of sanidine (Sa) (sample L7-1). b) Rounded shape composed of clinopyroxene (Cpx) microcrystallites embedded in the glass containing micrometric inclusions of sulfide/metallic phases (sample L7-2). c) Clinopyroxene micro-crystallites in a glassy matrix (sample L7-3). d) Lath-type and euhedral clinopyroxene crystals (sample L7-7). e) Skeletal olivine (Ol) in glassy matrix (sample L13-1). f) Large sulfide/metallic inclusion composed of bornite (Bn), covellite (Cv), pyrrhotite (Pyh) in association with metallic Cu and embedded in a complex silicate matrix (sample L10-1). Phase abbreviations according to Warr (2021).

and CoO, respectively (Table S7). Spinel-family oxides exhibit considerable variability in their compositions ranging from almost pure magnetite (Fe_3O_4) (analysis 19 in Table S8) to complex spinels with a predominance of Mg-Fe-Al-Cr-rich end-members (analyses 23, 24, 40, and 41 in Table S8). Copper was not detected in many spinels, but some exhibited up to 0.55 wt% CuO. All the analyzed spinels were important hosts of Co with concentrations ranging from 0.02 to 0.97 wt% CoO (Table S8).

4.2. Environmental stability and weathering

The results of the regulatory leaching test EN 12457-2 and comparisons with the EU limit values for inert, non-hazardous, and hazardous waste are reported in Table 2. Except for samples L7-8 and L10-1, where the leached Cu exceeded the limit concentrations values for inert waste

(2 mg/kg), the leachabilities of the other screened contaminants were relatively low. In terms of the waste classification according to the EU legislation, slag samples L7-8 and L10-1 are classified as non-hazardous waste, other samples are classified as inert waste (Table 2). According to the PHREEQC-3 geochemical modeling, the slag leachates are (over) saturated with respect to Fe(III) oxyhydroxides (ferrihydrite, Fe $(OH)_3$(am), SI = -0.29 to 0.65; goethite, FeOOH, SI = 2.41 to 3.35). The secondary formation of Fe(III) oxyhydroxides was macroscopically visible on many slag fragments (Fig. 1e) and, due to their efficient sorption properties, they are likely key phases controlling contaminant leaching from the Luanshya slags. The leachates were all undersaturated with respect to other potential solubility controlling phases, such as Cu hydroxocarbonates (malachite, $Cu_2(CO_3)(OH)_2$; azurite, $Cu_3(CO_3)_2(OH)_2$), Co carbonates (spherocobaltite, $CoCO_3$) and Cu hydroxosulfates (brochantite, $Cu_4(SO_4)(OH)_6$; antlerite, $Cu_3(SO_4)$
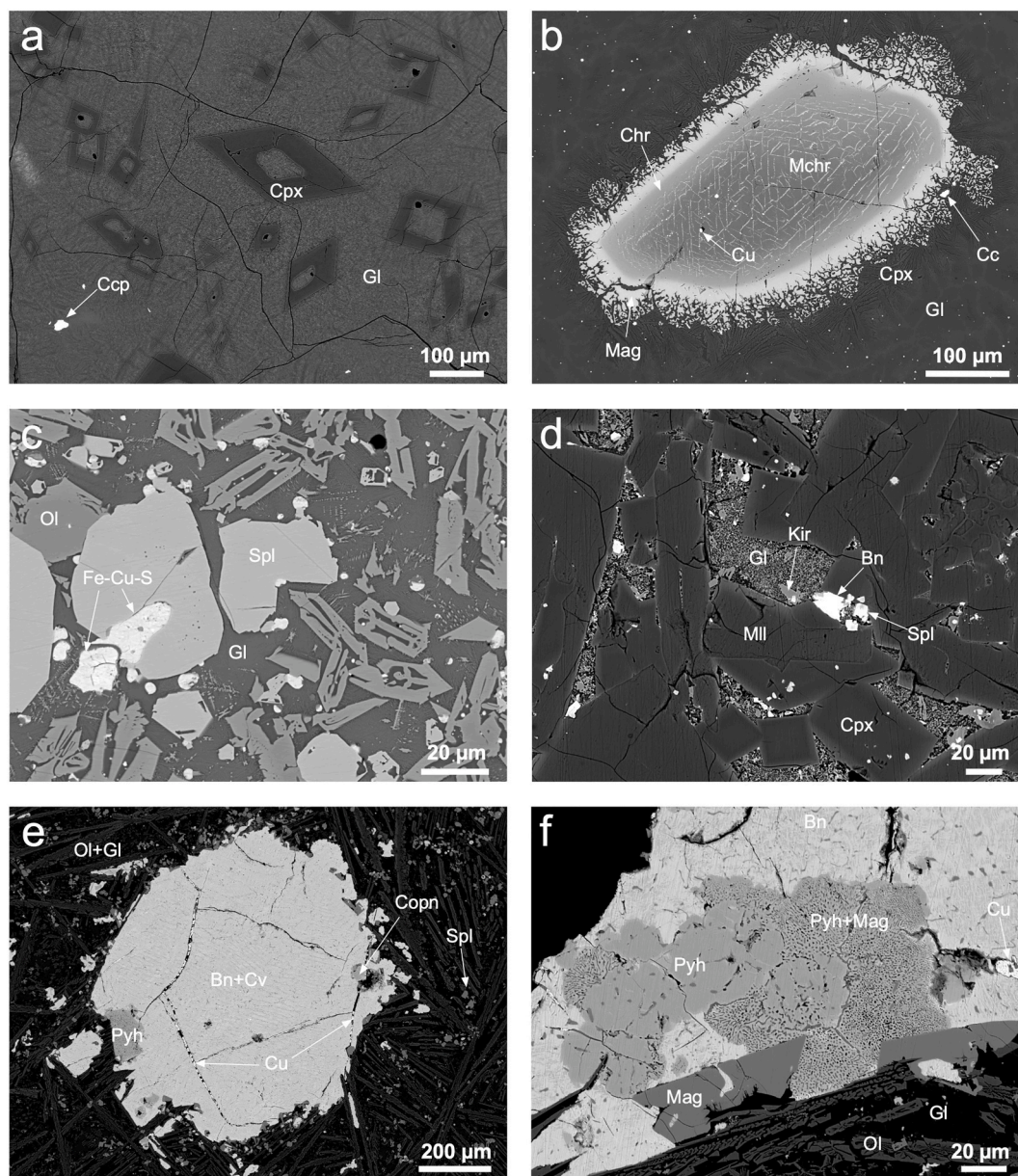
Fig. 3. Scanning electron micrographs in back-scattered electrons (BSE) of the Luanshya slags. a) Skeletal crystals of clinopyroxene (Cpx) embedded in the glass (Gl) with chalcopyrite (Ccp) inclusions (sample L7-7). b) Zoned spinel crystal (magnesiochromite [Mchr] core, chromite [Chr] rim, and magnetite [Mag] dendrites) in silicate matrix composed of glass with clinopyroxene crystallites. Note the presence of the sulfide inclusions (chalcocite, Cc) in the glass and exsolutions of metallic Cu in the spinel (sample L11-1). c) Euhedral spinel crystals and skeletal olivines in a glassy matrix associated with Fe-Cu sulfide inclusions (see analysis 30 in Table S5) (sample L10-1). d) Crystalline slag composed of euhedral melilite (Mll) and clinopyroxene crystals in a glassy matrix with kirschsteinite (Kir), spinel (Spl), and bornite (Bn) (sample L13-2). e) Large sulfide inclusion composed of bornite and covellite (Cv) symplectite, crystals of pyrrhotite (Pyh), cobaltpentlandite (Copn), and metallic Cu in a silicate matrix (sample L7-8). f) Pyrrhotite, magnetite and pyrrhotite-magnetite symplectite embedded in a bornite inclusion (sample LL7-8). Phase abbreviations according to Warr (2021).

(OH)$_4$) as revealed by the PHREEQC-3 calculations. Moreover, the formation of these phases can hardly be accomplished within 24 h of the leaching test used, probably due to relatively low Cu concentrations in the leachates. Nevertheless, the secondary phases of greenish color have been macroscopically documented on many slags from Luanshya (Fig. 1e), and the SEM-EPMA data confirmed that phases precipitating in the vesicles and on the surfaces of the slag fragments have compositions close to Cu hydroxosulfates, such as brochantite and/or antlerite (Fig. S2). These microscopic observations confirm that the Cu hydroxosulfates are direct weathering products formed during the dissolution of the primary Cu-(Fe) sulfides (Fig. S2).

4.3. Potential recovery of Co and other critical metals

The extraction tests were carried out in 0.5 mol/l H$_2$SO$_4$ on three contrasting slag samples having different mineralogy, crystallinity, and content of metallic elements (Cu: 4420–49,900 ppm; Co: 1470–4780 ppm). Within the first 6 h of the experiment, the release kinetics are relatively rapid, then the extractability slows down and almost attains a steady-state (Fig. 4). The extractability of valuable elements in mg/kg is positively correlated with their total concentrations in the original material; the highest Cu leaching was obtained for sample L10-1 (18,612 ± 66 mg/kg), and the highest Co leaching was observed for sample L7-8 (4146 ± 148 mg/kg), whereas the lowest values for both elements

Table 2
Leached concentrations of the selected metal(loid)s (mg/kg; mean values ± standard deviation, $n = 2$), values of the pH and the electrical conductivity (EC, in µS/cm) in the leachates as obtained by the EN 12457-2 leaching test.

Code	As	Ba	Cd	Cu	Cr	Ni	Pb	Sb	Zn	pH	EC
L7-8	ND	0.044 ± 0.0036	0.0004 ± 0.00005	**2.69 ± 1.46**	ND	0.066 ± 0.013	0.001 ± 0.0003	0.0003[a]	0.107 ± 0.006	5.81	22.7
L8	ND	0.030 ± 0.0007	0.0001 ± 0.00005	0.07 ± 0.005	ND	0.003 ± 0.001	ND	0.0004 ± 0.0001	0.012 ± 0.0008	6.69	8.1
L10-1	ND	0.036 ± 0.0143	0.0006[a]	**3.60 ± 0.83**	ND	0.026 ± 0.005	ND	0.0001[a]	0.053 ± 0.004	5.70	13.6
L11-1	ND	0.016 ± 0.0019	0.0001 ± 0.00005	0.64 ± 0.15	ND	0.015 ± 0.003	ND	0.0004 ± 0.0002	0.034 ± 0.0003	6.30	3.3

Limit values[b]	As	Ba	Cd	Cu	Cr	Ni	Pb	Sb	Zn
IW	0.5	20	0.04	2	0.5	0.4	0.5	0.06	4
NHW	2	100	1	50	10	10	10	0.7	50
HW	25	300	5	100	70	40	50	5	200

ND – not detected; detection limits were: As (0.004 mg/kg), Cr (0.003 mg/kg), Pb (0.0001 mg/kg).
[a] Detected only in one replicate.
[b] Limit values for the inert waste (IW), non-hazardous waste (NHW) and hazardous waste (HW) according to the EU (2002) legislation. The values exceeding limits for the IW are indicated in bold.
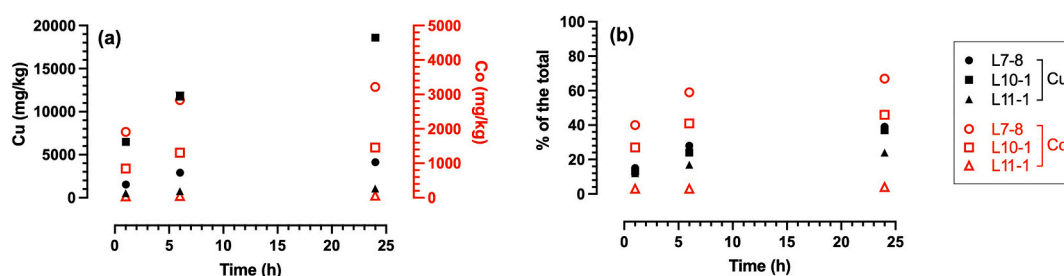
Fig. 4. Extractability of Cu and Co in 0.5 mol/l H_2SO_4 as a function of time expressed as leached concentrations in mg/kg (a) and the percentage of the total content (b) for three slag samples from Luanshya. The small error bars are obscured by the symbols.

corresponded to sample L11-1 (cf. Tables S3 and 3). The highest extraction yields are 46% of the total Cu and 67% of the total Co after 24 h of the experiment (Fig. 4 and Table 3). Other trace elements exhibit relatively low extractabilities in the order of ones to tens of mg/kg, and many of them have not been detected in the extract at all (Ag, Cd, Pb, and Sb). The PHREEQC-3 calculations suggested that barite ($BaSO_4$) and SiO_2 phases of various forms should precipitate from the extracts. The secondary formation of barite during the extraction test (SI in the range

1.18–1.41) may explain the very low extractabilities of Ba from the slags (2–3% of the total) (Table S8). Amorphous SiO_2 and chalcedony exhibited an SI ranging from −0.81 to 0.73 and from 0.00 to 1.51, respectively, indicating that a silica gel can form during the hydrometallurgical acid extraction.

The XRD patterns of slag residues after 24 h of extraction (Fig. S3) show substantial changes in mineralogical compositions. Olivine completely disappears from the samples, whereas clinopyroxene is

Table 3
Extractabilities (mg/kg and % of the total) of selected elements in 0.5 mol/l H_2SO_4 solutions from Luanshya slags as a function of time (mean ± standard deviation).

mg/kg	Time (h)	Ba	Co	Cr	Cu	Mo	Ni	Sr	V	Zn
Sample		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
L7-8	1	9.8 ± 0.3	1912 ± 27	<10	1558 ± 29	10.9 ± 0.4	12.1 ± 0.2	9.2 ± 0.2	<6	97.6 ± 1.2
	6	8.8 ± 0.1	2838 ± 10	10.4 ± 0.2	2935 ± 19	24.3 ± 0.8	18.8 ± 1.0	13.9 ± 0.05	6.1 ± 0.0	149 ± 0.2
	24	9.8 ± 0.6	3217 ± 107	25.3 ± 1.6	4146 ± 148	42.2 ± 0.6	20.9 ± 0.2	18.5 ± 0.7	13.5 ± 0.9	177 ± 9
L10-1	1	6.8 ± 0.2	850 ± 12	18.3 ± 0.1	6509 ± 92	10.8 ± 0.3	14.9 ± 0.7	6.6 ± 0.2	<6	58.8 ± 0.6
	6	7.8 ± 0.2	1308 ± 53	76.3 ± 3.3	11,807 ± 463	24.7 ± 0.0	20.0 ± 0.7	8.7 ± 0.4	6.1 ± 0.1	92.0 ± 3.8
	24	9 ± 0.2	1459 ± 5	176 ± 2.0	18,612 ± 66	38.15 ± 0.6	26.4 ± 2.2	10.4 ± 0.0	12.7 ± 0.3	107 ± 0.6
L11-1	1	11.2 ± 0	42.7 ± 2.0	<10	524 ± 33	3.65 ± 0.3	<10	9.7 ± 0.4	<6	7.4 ± 0.4
	6	8.8 ± 1.5	49.0 ± 0.3	12.5 ± 0.05	768 ± 4	4.40 ± 0.2	<10	10.9 ± 0.2	<6	8.3 ± 0.6
	24	10.4 ± 0.3	58.8 ± 1.9	17.5 ± 0.8	1074 ± 39	5.15 ± 0.4	<10	12.3 ± 0.5	<6	8.8 ± 0.3

%	Time (h)	Ba	Co	Cr	Cu	Mo	Ni	Sr	V	Zn
L7-8	1	2 ± 0.06	40 ± 0.6	<5	15 ± 0.3	5 ± 0.16	25 ± 0.3	3 ± 0.05	<9	48 ± 0.6
	6	2 ± 0.02	59 ± 0.2	5 ± 0.10	28 ± 0.2	11 ± 0.3	39 ± 2.0	5 ± 0.02	9 ± 0.00	73 ± 0.1
	24	2 ± 0.13	67 ± 2.2	13 ± 0.8	39 ± 1.4	19 ± 0.3	44 ± 0.4	7 ± 0.25	19 ± 1.3	87 ± 4.5
L10-1	1	2 ± 0.05	27 ± 0.4	1 ± 0.00	13 ± 0.2	4 ± 0.11	16 ± 0.8	4 ± 0.09	<6	47 ± 0.5
	6	2 ± 0.05	41 ± 1.7	3 ± 0.11	24 ± 0.9	9 ± 0.00	21 ± 0.8	5 ± 0.22	6 ± 0.10	74 ± 3.1
	24	3 ± 0.06	46 ± 0.2	6 ± 0.07	37 ± 0.1	14 ± 0.2	28 ± 2.4	6 ± 0.00	12 ± 0.3	86 ± 0.5
L11-1	1	2 ± 0.00	3 ± 0.14	<1	12 ± 0.8	3 ± 0.21	<48	3 ± 0.11	<6	9 ± 0.51
	6	2 ± 0.05	3 ± 0.13	2 ± 0.10	17 ± 0.9	4 ± 0.30	<48	3 ± 0.14	<6	11 ± 0.4
	24	2 ± 0.05	4 ± 0.13	2 ± 0.10	24 ± 0.9	4 ± 0.30	<48	3 ± 0.14	<6	11 ± 0.4

relatively stable. The dissolution of olivine, being an important Co-bearing phase (Table S6), can also contribute to high Co extraction during our simulated hydrometallurgical process. Rhomboclase [HFe^{3+}(SO$_4$)$_2$·4H$_2$O] and/or szomolnokite (Fe^{2+}SO$_4$·H$_2$O), typically occurring in highly acidic sulfate-rich environments (cf. Ettler et al., 2020), form in the slag residues as the alteration products (Fig. S3).

5. Discussion

The Luanshya slags are composed of phases typical for Cu slags as previously reported from various sites around the world: olivine, clinopyroxene, silicate glass, and spinel-family oxides (Vítková et al., 2010; Kierczak and Pietranik, 2011; Rozendaal and Horn, 2013; Piatak et al., 2015; Potysz et al., 2016; Piatak et al., 2021). However, melilite, a Ca-rich phase crystallizing from Ca-rich melts, is rather typical for air-cooled Pb and/or Zn slags (Ettler et al., 2009; Warchulski et al., 2016) and much less frequent in Cu slags (Kadziolka et al., 2020), was observed only in one sample from Luanshya (sample 13-2 with an anomalous CaO content of 23.8 wt%; Tables S3 and S4). Similarly, leucite was also relatively rare in the Luanshya slags (found only in 5 of 21 samples). However, this phase has been previously found as a minor compound in Cu slag from various sites, including the Zambian Copperbelt and Old Copper Basin in Poland, and indicates that the slag melt was K-rich and Si-undersaturated (Vítková et al., 2010; Kadziolka et al., 2020). The Cu and Co concentrations in the silicates, glass, and oxides in the Luanshya slags are relatively low (<1 wt% CuO or CoO). In contrast, Vítková et al. (2010) reported that Co-bearing Cu slags from other sites in the Zambian Copperbelt exhibit much higher concentrations of these metals in the silicates (e.g., up to 7.15 wt% CoO in the olivines) and oxides (up to 4.11 wt% CuO and 5.12 wt% CoO), which might be related to the processed ore and/or smelting technology used.

The major hosts of Cu and Co in Luanshya slags are sulfides (e.g., bornite, chalcopyrite, covellite, chalcocite, digenite) and metallic Cu (Table S5), which agrees well with other studies devoted to the mineralogical characterization of Cu slags originating from various sites around the world and different Cu smelting technologies (Vítková et al., 2010; Rozendaal and Horn, 2013; Potysz et al., 2016; Jarošíková et al., 2017; Piatak et al., 2021 and references therein). Cobaltpentlandite and Fe-sulfides are typically the most Co-enriched phases in the Cu slags from the Zambian Copperbelt in general (Table S5; Fig. 3e; cf. Vítková et al., 2010). Other phases can also host Co (Tables S6-S8), and especially glass and olivine are volumetrically important in the studied slags. To better understand the modal compositions (% of phases) and deportment of Co and other metals in the slags, it would be helpful to use the mineral liberation analysis (MLA) carried out by an automated scanning electron microscope (autoSEM) (Wang et al., 2015; Gabasiane et al., 2021). However, recent studies devoted to the application of autoSEM on complex slag particles demonstrated that there are several limitations: (i) problems with an adequate database of reference EDS spectra leading to difficulties in the slag phase identification (Pietranik et al., 2018) and (ii) difficulties in setting of the concentration boundaries (e.g., highly variable compositions of the slag glass), which then closely affects the results of the deportment calculations (Tuhý et al., 2020).

The EU regulatory leaching test suggests that all the monitored contaminants are released from the Luanshya slags to a low degree, except for Cu, which exceeded levels for inert waste for two of the four investigated slag samples (Table 2). However, the test duration of 24 h is relatively short to describe the long-term leaching of metal(loid)s from slags in natural environments (Ettler and Vítková, 2021 and references therein). Using 12-year leaching experiments on Pb-Zn slags, Ettler and Johan (2014) demonstrated that contaminants bound in silicates and oxides continue to leach over the long term because of the slow kinetics of their dissolution in an aqueous environment. The actual situation, which also considers the proximity to water bodies, where the slag is partly submerged in water for a substantially more extended period (see

Fig. 1b), should be modeled using other types of leaching experiments such as column tests, flow-through tests, pH-dependent tests, or tests conducted on monolithic samples (Ettler and Vítková, 2021 and references therein). Nevertheless, the formation of secondary phases observed on the surface of the majority of the studied slag samples indicates that these materials underwent intensive weathering (Figs. 1 and S2), which is a typical feature in humid subtropical areas, as also reported on slags from other smelting sites in the Zambian Copperbelt (Vítková et al., 2010).

The elevated concentrations of valuable elements in the Luanshya slags (e.g., Co: up to 5990 ppm, Cu: up to 95,300 ppm) suggest that these materials can be considered as potential resources of these elements. Even though Vítková et al. (2010) reported slightly higher Co concentrations in other slags from the Zambian Copperbelt, the median concentrations in the Luanshya slags (Co: 2370 ppm; Cu: 8550 ppm) are similar or even higher than for the Cu slags from other sites, which have already been tested in view of any potential recovery (Bulut, 2006; Kaksonen et al., 2017; Mikoda et al., 2019; Meshram et al., 2020). The maximum extraction yields obtained after 24 h of extraction in 0.5 mol/l H$_2$SO$_4$ were 46% of the total Cu and 67% of the total Co (Fig. 4 and Table 3). Potysz and Kierczak (2019) found similar Cu extractability (ca. 50% of the total) from amorphous Cu slags leached under identical conditions (0.5 mol/l H$_2$SO$_4$, 1% pulp density, 24 h; Potysz and Kierczak, 2019). A higher yield can be obtained at higher temperatures and higher acid strengths (e.g., Bulut, 2006; Potysz and Kierczak, 2019). However, under such conditions, the problem of silica gel formation acting as a newly formed adsorbent for the leached metals and hindering the extraction efficiency can occur (Potysz and Kierczak, 2019; Potysz and van Hullebusch, 2021). A longer leaching time can also result in the higher extractability of metals (Mikoda et al., 2019), but time frames longer than 48 h can hardly be expected in real-scale hydrometallurgical operations based on agitation leaching.

Given the growing global demand for Co, its recovery from secondary resources provides an alternative stream of supply. These secondary resources include spent catalysts, magnets, superalloys, rechargeable batteries, and mining and metallurgical wastes, which can be processed by pyrometallurgical, (bio)hydrometallurgical, or pyro-hydrometallurgical route (Chandra et al., 2022 and references therein). Cobalt is also a key critical metal potentially recoverable from the Luanshya slags. Its price dramatically increased from $32,000/t in December 2020 to more than $70,500/t at the beginning of 2022 (tradingeconomics.com/commodity/cobalt). Considering a 50% extraction efficiency for Co (Fig. 4 and Table 3), the profit related to extracted Co is estimated to be ~$0.095 per kg of slag. Mikoda et al. (2019) calculated that the Co extracted from Polish slags could correspond to a profit of $0.051 (granulated slags) and $0.124 (shaft furnace slag) per kg of slag, which is in good agreement with our estimates. However, the costs for the mechanical operations (milling/crushing) correspond to $5.5 per kg of treated slag (Potysz et al., 2018), and the additional costs for the chemicals (sulfuric acid) can attain up to $1 per kg of treated slag (Ettler et al., 2020). It is also important to stress that additional chemical and metallurgical processes should be applied to separate the Co from the extracts, which contain other metals and major elements with only limited economic value. Similar to the production of Co from Cu-Co ores via hydrometallurgy, successive processes, such as the solvent extraction of Cu, the step-by-step removal of Fe, Al, Mn, and Zn impurities by precipitation, the pre-final precipitation of Co hydroxide, the redissolution of Co(OH)$_2$, and Co electrowinning should be carried out (Crundwell et al., 2011). All these processes would generate additional costs related to the Co recovery from the slags. As a result, despite the increasing price on the global market and the relatively high Co reserves in the Luanshya slags (a total of about 12 kt of Co as calculated from the median Co concentration), such a recovery operation appears to be currently (beginning of the year 2022) non-economical.

6. Conclusions

Cobalt-bearing Cu slags from Luanshya, the oldest mining and smelting site in the Zambian Copperbelt (smelter operated between 1932 and 1999), are chemically and mineralogically complex waste materials with high concentrations of valuable metals (Cu: up to 95,300 ppm; Co: up to 5990 ppm). The slags are predominantly composed of olivine, clinopyroxene, silicate glass, and spinel-family oxides, but all these phases contain relatively low concentrations of Co and Cu ($<$1 wt % CoO or CuO). The major hosts of Co and Cu are Cu-(Fe) sulfides, cobaltpentlandite, Fe sulfides, and metallic Cu forming droplets and blebs embedded in the silicate matrix. The EU regulatory leaching test EN 12457-2 indicated that relatively low amounts of contaminants are leached from the slags, and only Cu exceeds limits for landfilling of inert waste in several cases. Nevertheless, the occurrence of secondary phases such as Cu hydroxosulfates and Fe (oxyhydr)oxides indicates that the slags undergo weathering processes, and metallic contaminants can be released over the long term. The extraction tests in sulfuric acid designed to simulate the hydrometallurgical processing of slags to recover valuable metals indicated that up to 46% of the total Cu and 67% of the total Co were extracted. However, despite the dramatic increase in the Co prices on the global market in 2021, the Co recovery from Luanshya slags seems to be currently non-economical when considering all the costs related to the mechanical treatment of the materials and the chemical processing and Co separation from the obtained leachates.

CRediT authorship contribution statement

Vojtěch Ettler: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, Visualization, Roles/Writing - original draft, Writing - review & editing.
Martin Mihaljevič: Data curation, Formal analysis, Funding acquisition, Investigation, Project administration, Resources, Writing - review & editing.
Petr Drahota: Formal analysis, Investigation, Writing - review & editing.
Bohdan Kříbek: Investigation, Project administration, Resources, Writing - review & editing.
Imasiku Nyambe: Investigation, Project administration, Resources, Writing - review & editing.
Aleš Vaněk: Investigation, Resources, Writing - review & editing.
Vít Penížek: Investigation, Resources.
Ondra Sracek: Investigation, Resources, Writing - review & editing.
Vendula Natherová: Investigation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2022.106987.

References

Banza, A.N., Gock, E., Kongolo, K., 2002. Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction. Hydrometallurgy 64, 63–69. https://doi.org/10.1016/S0304-386X(02)00138-X.

Binnemans, K., Jones, P.T., Fernández, A.M., Torres, V.M., 2020. Hydrometallurgical processes for the recovery of metals from steel industry by-products: a critical review. J. Sust. Metall. 6, 505–540. https://doi.org/10.1007/s40831-020-00306-2.

Bulut, G., 2006. Recovery of copper and cobalt from ancient slag. Waste Manag. Res. 24, 1–7. https://doi.org/10.1177/0734242X06063350.

Cailteux, J.L.H., Kampunzu, A.B., Larouge, C., Kaputo, A.K., Milesi, J.P., 2005. Genesis of sediment-hosted stratiform copper-cobalt deposits, central African Copperbelt. J. Afr. Earth Sci. 42, 134–158. https://doi.org/10.1016/j.afrearsci.2005.08.001.

Chandra, M., Yu, W., Tian, Q., Guo, X., 2022. Recovery of cobalt from secondary resources: a comprehensive review. Miner. Process Extr. Metall. Rev. https://doi.org/10.1080/08827508.2021.1916927 (in press).

Coleman, F.L., 1971. The Northern Rhodesia Copperbelt, 1899–1962: Technological Development up to the end of the Central African Federation. Manchester University Press, Manchester.

Crundwell, F.K., Moats, M.S., Ramachandran, V., Robinson, T.G., Davenport, W.G., 2011. Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals. Elsevier, Oxford.

EN 12457, 1999. Characterization of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges, Part 2. CEN, Brussels.

Ettler, V., Johan, Z., 2014. 12 years of leaching of contaminants from Pb smelter slags: geochemical/mineralogical controls and slag recycling potential. Appl. Geochem. 40, 97–103. https://doi.org/10.1016/j.apgeochem.2013.11.001.

Ettler, V., Vítková, M., 2021. Slag leaching properties and release of contaminants. In: Piatak, N.M., Ettler, V. (Eds.), Metallurgical Slags: Environmental Geochemistry and Resource Potential. The Royal Society of Chemistry, Cambridge, UK, pp. 151–173. https://doi.org/10.1039/9781839164576-00151.

Ettler, V., Johan, Z., Kříbek, B., Šebek, O., Mihaljevič, M., 2009. Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Appl. Geochem. 24, 1–15. https://doi.org/10.1016/j.apgeochem.2008.10.003.

Ettler, V., Vítková, M., Mihaljevič, M., Šebek, O., Klementová, M., Veselovský, F., Vybíral, P., Kříbek, B., 2014. Dust from Zambian smelters: mineralogy and contaminant bioaccessibility. Environ. Geochem. Health 36, 919–933. https://doi.org/10.1007/s10653-014-9609-4.

Ettler, V., Jarošíková, A., Mihaljevič, M., Kříbek, B., Nyambe, I., Kamona, F., Mapani, B., 2020. Vanadium in slags from smelting of African Pb-Zn vanadate ores: Mineralogy, extractability and potential recovery. J. Geochem. Explor. 218, 106631 https://doi.org/10.1016/j.gexplo.2020.106631.

EU, 1999. Council Directive 99/31/EC of 26 April 1999 on the landfill of waste. Off. J. Eur. Comm. L L182, 1–19.

EU, 2002. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Off. J. Eur. Comm. L 11, 27–49.

European Commission, 2020. Study on the EU's List of Critical Raw Materials. European Commission, Brussels.

Fortier, S.M., Nassar, N.T., Lederer, G.W., Brainard, J., Gambogi, J., McCullough, E.A., 2018. Draft critical mineral list – Summary of methodology and background information – U.S. Geological Survey technical input document in response to Secretarial Order No. 3359. In: U.S. Geological Survey Open-File Report 2018–1021. https://doi.org/10.3133/ofr20181021, 15 pp.

Gabasiane, T.S., Danha, G., Mamvura, T.A., Mashifana, T., Dzinomwa, G., 2021. Characterization of copper slag for beneficiation of iron and copper. Heliyon 7, e06757. https://doi.org/10.1016/j.heliyon.2021.e06757.

Gražulis, S., Daškevič, A., Merkys, A., Chateigner, D., Lutterotti, L., Quirós, M., Serebryanaya, N.R., Moeck, P., Downs, R.T., Le Bail, A., 2012. Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration. Nucleic Acids Res. 40, D420–D427. https://doi.org/10.1093/nar/gkr900.

Hofstra, A., Lisitsin, V., Corriveau, L., Paradis, S., Peter, J., Lauzière, K., Lawley, C., Gadd, M., Pilote, J., Honsberger, I., Bastrakov, E., Champion, D., Czarnota, K., Doublier, M., Huston, D., Raymond, O., VanDerWielen, S., Emsbo, P., Granitto, M., Kreiner, D., 2021. Deposit classification scheme for the Critical Minerals Mapping Initiative Global Geochemical Database. In: U.S. Geological Survey Open-File Report 2021–1049. https://doi.org/10.3133/ofr20211049, 60 pp.

Jarošíková, A., Ettler, V., Mihaljevič, M., Kříbek, B., Mapani, B., 2017. The pH-dependent leaching behavior of slags from various stages of a copper smelting process: Environmental implications. J. Environ. Manag. 187, 178–186. https://doi.org/10.1016/j.envman.2016.11.037.

Jones, R.T., Denton, G.M., Reynolds, Q.G., Parker, J.A.L., van Tonder, G.J.J., 2002. Recovery of cobalt from slag in a DC arc furnace at Chambishi, Zambia. J. S. Afr. Inst. Min. Metall. 101, 5–9.

Kadziolka, K., Pietranik, A., Kierczak, J., Potysz, A., Stolarczyk, T., 2020. Towards better reconstruction of smelting temperatures: methodological review and the case of historical K-rich Cu-slags from the Old Copper Basin, Poland. J. Arch. Sci. 118, 105142. https://doi.org/10.1016/j.jas.2020.105142.

Kaksonen, A.H., Särkijärvi, S., Puhakka, J.A., Peuraniemi, E., Junnikkala, S., Tuovinen, O.H., 2017. Solid phase changes in chemically and biologically leached copper smelter slags. Miner. Eng. 106, 97–101. https://doi.org/10.1016/j.mineng.2016.08.029.

Kapobe, J., Mazala, C., Phiri, R., 2019. Kitwe Black Mountain – is Zambia realizing the true value from it? J. Nat. Appl. Sci. 3, 62–72. https://journals.unza.zm/index.php/JONAS/article/view/462.

Kierczak, J., Pietranik, A., 2011. Mineralogy and composition of historical Cu slags from the Rudawy Janowickie Mountains, southwestern Poland. Can. Mineral. 49, 1281–1296. https://doi.org/10.3749/canmin.49.5.1281.

Křibek, B., 2010. Evaluation of the environmental and human health impacts of ore mining and processing in selected areas of Central and Copperbelt Provinces. In: Report of the Development Project RP/3/2008. Czech Geological Survey, Prague, Czech Republic, pp. 28 + 7 annexes. (in Czech).

Křibek, B., Majer, V., Veselovský, F., Naymbe, I., 2010. Discrimination of lithogenic and anthropogenic sources of metals and sulphur in soils of the central-northern part of the Zambian Copperbelt Mining District: a topsoil vs. subsurface soil concept. J. Geochem. Explor. 104, 69–86. https://doi.org/10.1016/j.gexplo.2009.12.005.

Meshram, P., Prakash, U., Bhagat, L., Abhilash, Zhao, H.B., van Hullebusch, E.D., 2020. Processing of waste copper converter slag using organic acids for extraction of copper, nickel and cobalt. Minerals 10, 290. https://doi.org/10.3390/min10030290.

Mikoda, B., Potysz, A., Kmiecik, E., 2019. Bacterial leaching of critical metal values from polish copper metallurgical slags using Acidithiobacillus thiooxidans. J. Environ. Manag. 236, 436–445. https://doi.org/10.1016/j.jenvman.2019.02.032.

Moskalyk, R.R., Alfantazi, A.M., 2003. Review of copper pyrometallurgical practice: today and tomorrow. Miner. Eng. 16, 893–919. https://doi.org/10.1016/j.mineng.2003.08.002.

Mukherjee, A., Boetsch, C., Luraschi, A., 1999. Modernization of the Luanshya smelter, Zambia. In: George, D.B., Chen, W.J.P., Mackey, P.J., Weddick, A.J. (Eds.), Smelting Operations and Advances, Proceedings of the 4th International Conference of the COPPER 99/COBRE 99, Phoenix, AZ, USA, pp. 1–15.

Muravyov, M.I., Bulaev, A.G., Kondra'eva, T.F., 2014. Complex treatment of mining and metallurgical wastes for recovery of base metals. Miner. Eng. 64, 63–66. https://doi.org/10.1016/j.mineng.2014.04.007.

Mususa, P., 2010. 'Getting by': life on the copperbelt after the privatisation of the Zambia Consolidated Copper Mines. Soc. Dynamics 36, 380–394. https://doi.org/10.1080/02533951003790546.

Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3–A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. In: U.S. Geological Survey Techniques and Methods, Book 6, Chap. A43.

Piatak, N.M., Ettler, V., 2021. Introduction: metallurgical slags – environmental liability or valuable resource? In: Piatak, N.M., Ettler, V. (Eds.), Metallurgical Slags: Environmental Geochemistry and Resource Potential. The Royal Society of Chemistry, Cambridge, UK, pp. 1–13. https://doi.org/10.1039/9781839164576-00001.

Piatak, N.M., Parsons, M.B., Seal II, R.R., 2015. Characteristics and environmental aspects of slag: a review. Appl. Geochem. 57, 236–266. https://doi.org/10.1016/j.apgeochem.2014.04.009.

Piatak, N.M., Ettler, V., Hoppe, D., 2021. Geochemistry and mineralogy of slags. In: Piatak, N.M., Ettler, V. (Eds.), Metallurgical Slags: Environmental Geochemistry and Resource Potential. The Royal Society of Chemistry, Cambridge, UK, pp. 59–124. https://doi.org/10.1039/9781839164576-00059.

Pietranik, A., Kierczak, J., Tyszka, R., Schulz, B., 2018. Understanding heterogeneity of a slag-derived weathered material: the role of automated SEM-EDS analyses. Minerals 8, 513. https://doi.org/10.3390/min8110513.

Potysz, A., Kierczak, J., 2019. Prospective (bio)leaching of historical copper slags as an alternative to their disposal. Minerals 9, 542. https://doi.org/10.3390/min9090542.

Potysz, A., van Hullebusch, E.D., 2021. Secondary metal recovery from slags. In: Piatak, N.M., Ettler, V. (Eds.), Metallurgical Slags: Environmental Geochemistry and Resource Potential. The Royal Society of Chemistry, Cambridge, UK, pp. 268–301. https://doi.org/10.1039/9781839164576-00268.

Potysz, A., Kierczak, J., Fuchs, Y., Grybos, M., Guibaud, G., Lens, P.N.L., van Hullebusch, E.D., 2016. Characterization and pH-dependent leaching behaviour of historical and modern copper slags. J. Geochem. Explor. 160, 1–15. https://doi.org/10.1016/j.gexplo.2015.09.017.

Potysz, A., van Hullebusch, E.D., Kierczak, J., 2018. Perspectives regarding the use of metallurgical slags as secondary metal resources – a review of bioleaching approaches. J. Environ. Manag. 219, 138–152. https://doi.org/10.1016/j.envman.2018.04.083.

Roberts, S., Gunn, G., 2014. Cobalt. In: Gunn, G. (Ed.), Critical Metals Handbook. John Wiley & Sons, Hoboken, New Jersey, USA, pp. 122–149.

Ross, J., de Vries, D., 2005. Mufulira smelter upgrade project – "industry" smelting on the Zambian Copperbelt. available from. In: ISASMELT™ – 2020 Compendium of Technical Papers. Glencore Technology Pty Limited, Brisbane, Australia, pp. 222–242. https://www.isasmelt.com.

Rozendaal, A., Horn, R., 2013. Textural, mineralogical and chemical characteristics of copper reverb furnace smelter slag of the Okiep Copper District, South Africa. Miner. Eng. 52, 184–190. https://doi.org/10.1016/j.mineng.2013.06.020.

Ruffini, A., 2008. Central Africa's copper renaissance. WOMP (World of Mining Professionals). e-journal. www.womp-int.com/story/2008vol2/story024.htm.

Schlesinger, M.E., King, M.J., Sole, K.C., Davenport, W.G.I., 2011. Extractive Metallurgy of Copper, 5th edition. Elsevier, Amsterdam.

Sikamo, J., Mwanza, A., Mweemba, C., 2016. Copper mining in Zambia – history and future. J. South. Afr. Inst. Min. Metall. 116, 491–496. https://doi.org/10.17159/2411-9717/2016/v116n6a1.

Sracek, O., Křibek, B., Mihaljevič, M., Ettler, V., Vaněk, A., Peníz̆ek, V., Filip, J., Veselovský, F., Nyambe, I., 2018. The impact of wetland on neutral mine drainage from mining wastes at Luanshya in the Zambian Copperbelt in the framework of climate change. Environ. Sci. Pollut. Res. 25, 28961–28972. https://doi.org/10.1007/s11356-018-2929-7.

Tuhý, M., Hrstka, T., Ettler, V., 2020. Automated mineralogy for quantification and partitioning of metal(loid)s in particulates from mining/smelting-polluted soils. Environ. Pollut. 266, 115118 https://doi.org/10.1016/j.envpol.2020.115118.

USGS, 2021. Cobalt data sheets. Mineral Commodity Summaries 2021. https://pubs.usgs.gov/periodicals/mcs2021/mcs2021-cobalt.pdf.

Vítková, M., Ettler, V., Johan, Z., Křibek, B., Šebek, O., Mihaljevič, M., 2010. Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province, Zambia. Mineral. Mag. 74, 581–600. https://doi.org/10.1180/minmag.2010.074.4.581.

Vítková, M., Ettler, V., Mihaljevič, M., Šebek, O., 2011. Effect of sample preparation on contaminant leaching from copper smelting slags. J. Hazard. Mater. 197, 417–423. https://doi.org/10.1016/j.jhazmat.2011.09.102.

Wang, X., Geysen, D., Padilla Tinoco, S.V., D'Hoker, N., Van Gerven, T., Blanpain, B., 2015. Characterisation of copper slag in view of metal recovery. Trans. Inst. Min. Metall. Sect. C-Miner. Process. Extr. Metall. 124, 83–87. https://doi.org/10.1179/1743285515Y.0000000004.

Warchulski, R., Gaweda, A., Janeczek, J., Kadziolka-Gawel, M., 2016. Mineralogy and origin of coarse-grained segregations in the pyrometallurgical Zn-Pb slags from Katowice-Welnowiec (Poland). Miner. Petrol. 110, 681–692. https://doi.org/10.1007/s00710-016-0439-1.

Warr, L.N., 2021. IMA-CNMNC approved mineral symbols. Mineral. Mag. 85, 291–320. https://doi.org/10.1180/mgm.2021.43.