

**Environmental characteristics of mineral waste
from metallurgy**

Copper-cobalt smelting in the Zambian Copperbelt

Charles University in Prague, Faculty of Science
Institute of Geochemistry, Mineralogy and Mineral Resources



Martina Vítková

**Environmental characteristics of mineral waste
from metallurgy**

Copper-cobalt smelting in the Zambian Copperbelt

**Environmentální charakteristiky minerálních
odpadů z metalurgie**

Zpracování mědi a kobaltu v zambijském Copperbeltu

Ph.D. Thesis



Martina Vítková

Charles University in Prague, Faculty of Science
Institute of Geochemistry, Mineralogy and Mineral Resources

Supervisor: Doc. RNDr. Vojtěch Ettler, Ph.D.

Prague 2012

Preface

The presented thesis is the result of a Ph.D. study carried out at the Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague. A research stay was carried out at the Department of Environmental Engineering, Technical University of Denmark (DTU Environment).

The thesis is divided into 6 chapters followed by Appendices with published papers or a submitted manuscript (I–V) and unpublished results on contaminant bioaccessibility testing (VI). Chapters 1 and 2 provide a general introduction to the work for the reader, Chapters 3–5 introduce the principle topics of the thesis and discuss the main results of the work (both published and unpublished), followed by the conclusions (Chapter 6). Details on the methodology are included in the relevant Appendices so that only the key points referring to the methods used are mentioned and discussed in the main text. Individual journal papers/manuscripts prepared during the course of the study are referred to in the thesis by their Roman numerals.

Acknowledgements

First, I would like to thank my supervisor Vojtěch Ettler for his kind guidance throughout my study, his encouragement, great ideas and never-ending enthusiasm for science. He gave me the opportunity to do interesting research and get valuable experience, both professional and personal. Despite his work load he devoted a lot of his time and energy into our cooperation.

I am also grateful to Jiří Hykš (DHI) for very kind and friendly support during my stay at DTU Environment, for help with the geochemical modelling and many stimulating discussions. Thomas Astrup (DTU Environment) is acknowledged for providing financial conditions for my laboratory work carried out at DTU Environment, for nice collaboration and useful comments to the resulting manuscripts (Appendix II, V).

My special thanks belong to Zdenek Johan for his kind help related to slag mineralogy and for many inspirational consultations.

I would like to thank Bohdan Křibek, who provided us all the samples from the Zambian Copperbelt smelters and also the opportunity to attend the field work in Zambia. I am grateful to the technical staff at the smelter sites for help with the sampling and Tony Gonzáles from the Mufulira smelter for providing dust samples and technological information.

Many people helped with the laboratory work. Ondřej Šebek and Martin Mihaljevič are recognised for huge help with chemical analyses and for useful geochemical consultations. I would like to thank Marie Fayadová for her overall and always kind help in the laboratory, Věra Vonásková and Lenka Jílková for chemical analyses, Jana Škorpíková for help with preparation of the polished sections, Petr Drahotka for XRD analyses, Radek Procházka and Martin Racek for help with SEM analyses, Anna Langrová (Institute of Geology AS CR, v.v.i.) for EPMA, Mariana Klementová (Institute of Inorganic Chemistry, AS CR, v.v.i.) for TEM analyses, Sinh Hy Nguyen (DTU Environment) for chemical analyses, František Veselovský (Czech Geological Survey) for separation of the dust samples, Pavel Vybíral and Jiří Hemerka (Czech Technical University in Prague) for help with separation of the fine dust fraction and Zbyněk Engel for granulometric measurements. Madeleine Štulíková is thanked for revision of the English in the manuscript.

I wish to thank all the people at my home institute and at DTU Environment, who created friendly atmosphere for my study and research.

Special thanks belong to my friends for their enormous support and patience during all the busy days. My last but not least thanks to my brother Petr Vitek for his close support and encouragement during the entire study.

This work was funded by the Czech Science Foundation (GAČR 205/08/0321; GAČR 210/12/1413), the Ministry of Education, Youth and Sports of the Czech Republic (MSM0021620855) and by the student projects of the Grant Agency of Charles University (GAUK 53009; GAUK 644112). Financial support was provided also by University Student Projects No. SVV 261203, SVV 263203 and SVV 265208. This study was carried out within the framework of the IGCP Project No. 594. Mobility Fund of Charles University was used to cover a part of the travel costs related to the research stay at DTU Environment.

Summary

Mineralogical and geochemical characteristics of metallurgical wastes from the Cu-Co smelters situated in the Zambian Copperbelt have been investigated. A number of instrumental analytical methods (XRD, SEM/EDS, EPMA, TEM/EDS) has been used to identify primary and secondary phases in smelter slags and dusts. A set of leaching experiments (CEN/TS 14997 pH-static test, EN 12457 batch test) in combination with geochemical modelling has been performed, with the emphasis on the leaching behaviour of potential contaminants and their release as a function of the pH. The effect of sample preparation on metal leachability from slag was also evaluated, considering the grain size reduction required by the standardised leaching protocols. Environmental and health risk assessments of the dust samples have been performed.

It was shown that the main carriers of metals in the studied slags were Cu sulphides (bornite, digenite, chalcocite), Co sulphides (cobaltpentlandite), Co-bearing intermetallic phases and alloys. Copper and cobalt were detected in major silicates and spinels, substituting for Fe or Mg in their structures, and in glass. The presence of secondary metal-bearing phases observed on the slag surfaces indicated the reactivity of the slags on contact with water/atmosphere. It was reported that in justified cases, high-resolution methods (such as FIB-TEM) need to be employed to verify the element speciation in solid waste materials. Dust from slag crushers (herein *slag dust*), dust from electrostatic precipitator (herein *ESP dust*) and dust from water filters (herein *fly ash*) were also studied. Different solid speciation of metals was observed for the dusts. Minor to trace Cu sulphides of various compositions (Cu(Fe,Co)S) were detected in all the studied dust samples.

The leaching behaviour of the slag and dust was strongly pH-dependent. For the slag, the highest concentrations of Cu, Co and Zn were released at pH 4–5. Based on the PHREEQC calculations, several Cu- and Co-bearing carbonates, hydroxides, oxides or sulphates were suggested to attenuate the metal release under near-neutral conditions. Various slag sample pretreatment (crushing, sieving, cleaning) has resulted in significant differences in contaminant leachability. Greater release of Cu, Co and Zn was reported for samples with a higher portion of fine dust particles. Extensive contaminant leaching was observed for the *ESP dust*, even at the natural pH (~ 4.3) of the dust suspension. About 30–40% of the total Cu, Co and Zn were released at pH 3. Primary chalcantite (CuSO₄·5H₂O) was readily dissolved and secondary Cu sulphates precipitated. The leaching of metals from the *fly ash* was mainly attributed to the dissolution of minor metallic phases and partial dissolution of silicates and/or glass. The ORCHESTRA model suggested CoO and ZnO to control the solubility of Co and Zn, respectively. Sorption on hydrous ferric oxides was assumed to effectively attenuate the release of Pb and Cu from the *fly ash*. Near-equilibrium conditions were achieved in the *fly ash*–water system during the standard testing time of 48 h as only slight changes in leachability were observed after 168 h.

The pH-dependent reactivity of slags and dusts showed high risk of contamination for acidic soils in the Zambian Copperbelt smelting area, particularly during the rainy season. Furthermore, high gastric bioaccessibility of Co, Cu, Pb, Zn and As reported for the smelter dusts indicated severe health risks for local populations in this mining and smelting region.

Abstrakt

Předmětem zkoumání byly metalurgické odpady z Cu-Co hutí z oblasti zambijského Copperbeltu a jejich mineralogické a geochemické charakteristiky. Pro identifikaci primárních a sekundárních fází metalurgických strusek a prachů byla použita řada instrumentálních analytických metod (XRD, SEM/EDS, EPMA, TEM/EDS). Dále byla provedena série loužících experimentů (pH-statický test CEN/TS 14997, vsádkový test EN 12457) v kombinaci s geochemickým modelováním. Testování bylo zaměřeno zejména na loužící charakteristiky potenciálních kontaminantů v závislosti na pH. Byl posouzen také vliv přípravy vzorku na vyluhovatelnost kovů ze strusky s ohledem na zmenšení velikosti částic, které je požadováno ve standardizovaných loužících protokolech. Bylo provedeno posouzení environmentálních a zdravotních rizik vzorků prachu.

Hlavními nositeli kovů ve studovaných struskách byly sulfidy Cu (bornit, digenit, chalkozín), sulfidy Co (kobaltpentlandit), slitiny a intermetalické fáze s Co. Měď a kobalt byly detekovány také v silikátech a spinelech, v jejichž struktuře zastupují Fe nebo Mg, a ve skle. Přítomnost sekundárních fází, které byly pozorovány na povrchu vzorků strusek, ukazuje na reaktivitu strusek při jejich kontaktu s vodou/atmosférou. Výsledky mineralogického studia také ukázaly, že v odůvodněných případech je nezbytné použít metody s vysokým rozlišením (jako je FIB-TEM) pro ověření speciace prvků v daném odpadovém materiálu. Dále byly studovány tři typy prachů: prach z drtičů strusek (zde *struskový prach*), prach z elektrostatického odlučovače (zde *prach z ESP*) a prach z vodního filtru (zde *popílek*). Speciace kovů v pevné fázi se u jednotlivých typů lišila. Minoritní až stopové fáze sulfidů Cu různého složení (Cu(Fe,Co)S) byly zjištěny ve všech vzorcích prachu.

Loužící charakteristiky strusky a prachu prokázaly výraznou závislost na pH. V případě strusky byly nejvyšší koncentrace Cu, Co a Zn uvolněny při pH 4–5. Na základě výpočtů pomocí programu PHREEQC se předpokládá srážení karbonátů, hydroxidů, oxidů či síranů Cu a Co, vedoucí ke snížení vyluhovatelnosti kovů v pseudoneutrálních podmínkách. Různé metody přípravy vzorků strusky (drcení, sítování, čištění) vedly k významným rozdílům v loužení kontaminantů. Větší uvolňování Cu, Co a Zn bylo zaznamenáno u vzorků s vyšším podílem jemných prachových částic. Značně vysoká vyluhovatelnost kontaminantů byla pozorována u *prachu z ESP*, a to i v přirozeném pH (~ 4.3) výluhu tohoto materiálu. Přibližně 30–40% celkového obsahu Cu, Co a Zn se uvolnilo při pH 3. Primární chalkantit (CuSO₄·5H₂O) se snadno rozpouštěl za vzniku sekundárních síranů Cu. Loužení kovů z *popílku* lze vysvětlit zejména rozpouštěním minoritních metalických fází a částečným rozpouštěním silikátů a/nebo skla. Oxidy CoO a ZnO byly podle modelu ORCHESTRA hlavními fázemi řídícími rozpustnost Co a Zn během loužení. Sorpce kovů na oxyhydroxidy Fe se ukázala jako účinný mechanismus snižující uvolňování Pb a Cu z *popílku*. Vzhledem k pouze nepatrným změnám vyluhovatelnosti po 168 hod lze usuzovat, že během standardní doby loužení (48 hod) bylo v systému *popílek*–voda dosaženo podmínek blízkých rovnováze.

Reaktivita strusek a prachů podléhající změnám pH prokázala vysoké riziko kontaminace kyselých půd v hutní oblasti zambijského Copperbeltu, zejména v období dešťů. Vysoká gastrická biodostupnost Co, Cu, Pb, Zn a As zjištěná při testování metalurgických prachů navíc ukázala vážná zdravotní rizika pro místní obyvatele této těžební a hutní oblasti.

Contents

1. Introduction	1
2. Background information	3
2.1 Zambia in context.....	3
2.2 Geology of the Zambian Copperbelt.....	4
2.3 Metallurgy of copper and cobalt.....	4
2.4 Study area & smelting technologies.....	6
2.4.1 <i>Nkana smelter</i>	6
2.4.2 <i>Mufulira smelter</i>	6
2.4.3 <i>Chambishi smelter</i>	7
2.5 Leachability testing of solid waste residues.....	7
3. Characterisation of metallurgical wastes	9
3.1 Introduction.....	9
3.2 Mineralogical investigations.....	10
3.3 Metallurgical slags from the Zambian Copperbelt.....	11
3.4 Metallurgical dusts from the Zambian Copperbelt.....	15
3.5 Solid waste mineralogy – analytical issues.....	19
4. Characterisation of leaching from metallurgical wastes	21
4.1 Introduction.....	21
4.2 Leaching tests.....	22
4.3 Geochemical modelling.....	23
4.4 pH-dependent leaching.....	24
4.5 Influence of the test conditions.....	26
4.5.1 <i>Batch tests without pH control</i>	26
4.5.2 <i>Effect of the pH and sample preparation on slag leaching</i>	26
4.5.3 <i>Effect of pH and time on leaching</i>	28
5. Environmental and health implications	31
5.1 Environmental impacts of metallurgical wastes.....	31
5.2 Health risks.....	33
6. Conclusions	37
References	39

Appendices

List of appendices:

- I. **Vítková M.**, Ettler V., Johan Z., Kříbek B., Šebek O., Mihaljevič M. (2010): Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province, Zambia. *Mineralogical Magazine* 74: 581–600.
- II. **Vítková M.**, Ettler V., Hyks J., Astrup T., Kříbek B. (2011): Leaching of metals from copper smelter flue dust (Mufulira, Zambian Copperbelt). *Applied Geochemistry* 26: S263–S266.
- III. **Vítková M.**, Ettler V., Mihaljevič M., Šebek O. (2011): Effect of sample preparation on contaminant leaching from copper smelting slag. *Journal of Hazardous Materials* 197: 417–423.
- IV. Ettler V., Johan Z., **Vítková M.**, Skála R., Kotrlý M., Habler G., Klementová M. (2012): Reliability of chemical microanalyses for solid waste materials. *Journal of Hazardous Materials* 221–222: 298–302.
- V. **Vítková M.**, Hyks J., Ettler V., Astrup T. (2012): Stability and leaching of cobalt smelter fly ash. *Applied Geochemistry* (revised manuscript submitted).
- VI. Bioaccessibility of smelter dusts (unpublished results)

1. Introduction

The environmental consequences of human activities have become a popular topic in our society. A great many progressive technologies and waste management practices have been developed in order to reduce the impacts of modern industry on natural systems and human health. However, the environmental requirements are not well established in developing countries, such as those in Africa. This study is focused on the Zambian Copperbelt as an example of an area extremely affected by prolonged mining and smelting.

Production of non-ferrous metals represents one of major sources of potentially hazardous materials. During pyrometallurgical processes, solid residues of various compositions and quantities are generated and need to be further treated. Slag (i.e. coarse silicate fragments) and fly ash (i.e. fine dust from flue gas cleaning) are the commonest smelting wastes and have been described in a number of studies (e.g. Ettler et al., 2001, 2005a, 2009; Kierczak et al., 2009; Piatak & Seal, 2010; Skeaff et al., 2011; Sobanska et al., 1999; Williamson et al., 2004). It has been estimated that about 2.2 tons of copper slag is generated for 1 ton of Cu produced (Gorai et al., 2003). Slag is either dumped or utilised in various ways, such as road construction, preparation of cement or recovery of metals (Banda et al., 2002; Gorai et al., 2003). In the past few decades, smelting technologies with highly efficient metal recovery, effective flue gas cleaning systems or recycling of waste materials to recover base metals have been developed (Banda et al., 2002; Ettler et al., 2003; Kaksonen et al., 2011). However, despite attempts to reduce the mass of metallurgical waste, certain amounts of potentially hazardous smelter residues are still dumped or emitted into the environment.

Slags are often considered to be relatively stable smelting waste products, while more soluble forms of metals may be present in the fly ash. However, although they have different chemical and mineralogical characteristics, both types of residues pose a high pollution risk for the environment through potential leaching of metals and metalloids (Doyle et al., 1994; Ettler et al., 2008; Lottermoser, 2002; Pareuil et al., 2010; Parsons et al., 2001; Seignez et al., 2007). Detailed chemical and mineralogical characterisation is essential for understanding the distribution and binding of metals within primary phases and their resistance to weathering. A range of instrumental tools is available to identify the mineralogical composition on a macro- to nano-scale. In particular, structures that are likely to trap the metal/metalloid under the given physical-chemical conditions and stability of metal-bearing phases need to be evaluated (Piantone, 2004).

Laboratory experiments are commonly used to determine the leaching behaviour of solid waste and the release potential of contaminants. Leaching tests are carried out under various conditions to cover the range of parameters that mainly influence the leaching in relation to the purpose of testing (e.g. waste disposal or utilisation, environmental impact assessment). Dissolution/precipitation of solid phases and adsorption/desorption processes are mainly affected by changes in the pH. Therefore, pH-dependent leaching is widely used for basic leaching characterisation of various waste materials, particularly municipal solid waste incineration (MSWI) bottom ash and fly ash or coal fly ash (e.g. Astrup et al., 2006a; Dijkstra et al., 2006; Gitari et al., 2009; Hyks et al., 2007). Considering that significant pH changes are

likely to occur in “full-scale” dump scenarios (i.e. decades to hundreds of years), leaching as a function of the pH may reflect potential long-term behaviour. However, it should be noted that lab-scale experiments can only provide approximate information on full-scale processes and there is no guarantee that equilibrium conditions are attained during short-term testing. For compliance purposes and evaluation of the hazardous properties of waste materials, simple batch leaching test EN 12457 (1999) is conventionally used. However, the obtained results should be treated with care, since their interpretation primarily depends on the given test conditions and specific parameters such as particle size distribution. During sample preparation, i.e. reduction of the grain size as required in the protocol for coarser materials, distinct procedures can be employed, which may have a significant effect on the final results (Zandi et al., 2007).

Comprehensive geochemical knowledge is required to determine the main controlling mechanisms and to assess the environmental stability of solid waste residues. In this context, (i) mineralogical characterisation of the solids before and after leaching (formation of secondary phases), (ii) leaching behaviour of elements as a function of the pH combined with speciation-solubility modelling, and (iii) suitable sample pretreatment provide the necessary data for predictions of the short-term and long-term leaching behaviour.

Extensive mining and smelting activities in the Zambian Copperbelt have resulted in severe environmental pollution of the area. Soil contamination around smelters related to smelter dust emissions and slag deposits has been reported recently (Ettler et al., 2011; Křibek et al., 2010). This thesis provides detailed characterisation of various metallurgical wastes from this area mainly related to their leaching behaviour and subsequent environmental impact assessment.

The aims of the thesis are to:

- (i) characterise the chemical and mineralogical compositions of metallurgical wastes from the Zambian Copperbelt
- (ii) investigate the leaching behaviour of smelter slags and dusts by laboratory experiments and geochemical modelling
- (iii) evaluate the effects of sample handling and the experimental conditions on the release of contaminants
- (iv) assess the environmental and health risks of the studied metallurgical wastes.

For the purpose of this study, the term “slag” is used to denote smelter furnace slag and “dust” generally refers to all types of dust generated in the smelter facility if not specified otherwise. Slags from three smelters, dust from slag crushers (denoted as *slag dust*), dust from an electrostatic precipitator (denoted as *ESP dust*) and dust from water filters (denoted as *fly ash*) were subjected to chemical and mineralogical investigations. Laboratory leaching experiments were performed on most of the studied samples. Environmental and health risk assessments of the dust samples were performed. All the leaching results were coupled with geochemical modelling and predictions.

2. Background information

2.1 Zambia in context

Zambia is a landlocked country in southern Africa lying between latitudes 8 and 18°S and longitudes 20 and 35°E. The neighbouring countries are the Democratic Republic of Congo (DRC) and Tanzania in the north; Malawi and Mozambique in the east; Zimbabwe, Botswana and Namibia in the south and Angola in the west. Zambia is divided into nine provinces and 72 districts and the capital city is Lusaka. The country has an area of 752,612 km² with a population of about 14 million (data of 2011) concentrated mainly around Lusaka in the south-central region and in the Copperbelt Province in the northwest (CSO, 2009; www.state.gov). This province was named after the copper mining district of the Copperbelt, which runs through Zambia and the DRC. Metallurgical wastes from smelters situated in the Zambian part of the Copperbelt (i.e. Copperbelt Province) were studied in this doctoral work.

Climate

Zambia has a tropical climate with three different seasons: (i) a cool dry season from May to August, (ii) a hot dry season in September and October, and (iii) a rainy season from November to April. The wind pattern is dominated by strong south-eastern winds from March to October, while light north-eastern winds prevail from November until February. Tropical thunderstorms typically occur during the rainy season. The highest rainfall is in the north (including the Copperbelt Province) with an annual average ranging from 1100 mm to 1400 mm. The southern parts of the country are drier with rainfall ranging from 600 mm to 1100 mm per year (CSO, 2009; Křibek et al., 2010).

Developing cooperation

Czech-Zambian cooperation has a long tradition. In 1964, Zambia declared independence from the United Kingdom and became a republic. Developing cooperation between Czechoslovakia/ the Czech Republic and Zambia was immediately instituted and has continued over the decades until the present time. A number of contracts from scientific and technical assistance to health care service have been signed. In this context, projects focused on geological and geochemical research in the Zambian Copperbelt followed by assessment of the environmental impacts of mining and smelting activities in this area were carried out. In 2004, Zambia was defined as one of the priority countries in the development cooperation strategy of the Czech Republic (CZDA, 2006) and existing activities were defined to continue until 2017 with the emphasis on education, social and health services (CZDA, 2010). The geochemical research performed in this study follows the cooperation in geosciences and the most recent one was financially supported mainly by the Czech Science Foundation (GAČR 205/08/0321).

2.2 Geology of the Zambian Copperbelt

The Zambian Copperbelt represents one of the world's largest sediment-hosted stratiform Cu and Co deposits. It forms part of the Lufilian Arc, a Pan-African orogenic belt of high geological and economical significance with rich Cu-Co mineralization accumulated in the metasedimentary rocks of the Neoproterozoic Katanga Supergroup (Porada & Berhorst, 2000). Stratigraphically, the Zambian Copperbelt is divided into the Pre-Katanga Basement Complex overlain by the Katanga Supergroup. The Cu-Co mineralization is basically restricted to the lowermost part of the Katanga Supergroup. The host rocks include quartzites, arkoses, shales, arenites and dolomites (McGowan et al., 2006; Porada & Berhorst, 2000). The Zambian Copperbelt ore deposits are characterised by disseminated sulphide minerals with prevalent chalcopyrite (CuFeS_2), pyrite (FeS_2), bornite (Cu_5FeS_4), chalcocite (Cu_2S), and/or carrollite ($\text{Cu}(\text{Co},\text{Ni})_2\text{S}_4$) (Fleischer, 1984; Garlic, 1964; McGowan et al., 2006).

2.3 Metallurgy of copper and cobalt

Copper is conventionally extracted from Cu-Fe sulphide ores through pyrometallurgical processes. The extraction includes (1) comminution of sulphide ore (0.5–2.0% Cu) and isolation of Cu-bearing minerals into a concentrate (20–30% Cu) by flotation, (2) smelting the concentrate to matte (45–75% Cu), (3) converting the matte to blister copper (99% Cu) and refining this blister Cu to ultra-pure Cu. The smelting process may differ depending on the type of furnace used in a particular plant (Davenport et al., 2002).

Copper mining and smelting in the Zambian Copperbelt started in the early 1930s and it is estimated that about 30 Mt of Cu was produced within the 70 years of operation. The ore grades average 3 wt.% Cu and 0.18 wt.% Co in deposits (Kamona & Nyambe, 2002). The ore concentrates are mainly composed of chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) and chalcocite (Cu_2S) (Cutler et al., 2006). The charge contains Al_2O_3 , CaO or MgO and primarily silica (SiO_2) which are either added as a flux or present in the original concentrate (Gorai et al., 2003). Together with coke (as a reductant) and flux(es) (SiO_2) the sulphide concentrates are smelted (1250°C) to produce Cu-rich matte and Fe-rich silicate slag as a by-product. SO_2 -bearing flue gas is also generated. Although a flue gas cleaning system has been introduced in the smelters of the Zambian Copperbelt, significant quantities of SO_2 are still released into the atmosphere. Historically, reverberatory furnaces were used in Zambia, while electric furnaces are often used today. The matte is converted (melted and oxidised by injecting air) to “blister copper” (i.e. molten Cu with SO_2 bubbles or *blisters*) conventionally in Peirce-Smith (PS) converters by removing Fe and S. At this stage, converter slag and SO_2 -containing converter flue gas are generated. Converter slag is recovered by flotation or re-smelted. The metal is further refined in anode furnaces to remove residual SO_2 and produce Cu anodes, which are electro refined to obtain Cu of high purity (Cutler et al., 2006; Davenport et al., 2002; GAA, 2011).

The flue gas consists of N_2 , SO_2 and vaporised metal compounds; small liquid or solid dust particles are transported with the gas. Firstly, the flue gas is cooled by passing through a water-cooled hood and then goes to a settling chamber and waste heat boiler, where coarser

particles (e.g. silica or Cu-sulphides) are mainly trapped. These dusts are returned to the smelting furnace. The gas is further cooled and, as a result, vaporised compounds condense and form fine dust particles, which are collected in the electrostatic precipitator (ESP). Final wet gas cleaning using water quenching and cooling can be applied before the flue gas is sent to a sulphuric acid plant (Davenport et al., 2002; Samuelsson & Björkman, 1998). Dust can be collected in a bag house filter (Samuelsson & Carlsson, 2001).

In the Zambian Copperbelt, cobalt is usually extracted as a by-product of copper smelting. Golder Associates Africa (GAA, 2011) reported the preparation of Co-rich concentrate by isolating Cu concentrate during flotation and further treatment of the Co concentrate through the Roast-Leach-Solvent Extraction/Electro-winning (SX/EW) route. At the present time, methods for effective recovery of metals from discarded materials such as slags have been established. Gorai et al. (2003) and Yucel et al. (1992) reviewed the utilisation of copper slag and recovery of Co and Cu. Metallurgical slags rich in Cu and Co can be treated by a combination of pyrometallurgical and hydrometallurgical practices, i.e. smelting to polymetallic alloy and acid leaching (Acma et al., 1997; Jones et al., 2002; Rudnik et al., 2009).

Solid residues from three smelters situated in the Zambian part of the Copperbelt (Figure 1) were studied. The available technological details for individual facilities are described below in *Chapter 2.4*.

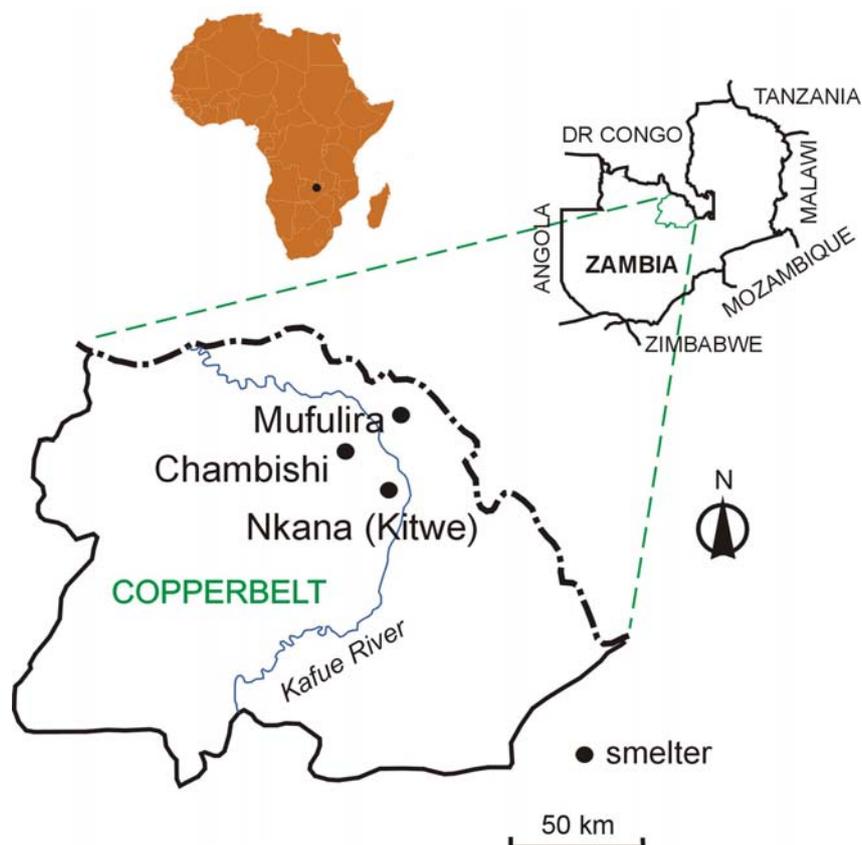


Figure 1 Locations of the smelters in the Copperbelt Province, Zambia.

2.4 Study area & smelting technologies

2.4.1 Nkana smelter

The Nkana smelter located near Kitwe (Figure 1) was commissioned in 1931 (closed in 2009) and was the oldest Cu smelter in the area. The plant consisted of reverberatory furnaces, Peirce-Smith (PS) converters, and blister casting facilities. In 1994, an El Teniente Converter (CT) was installed to upgrade reverberatory furnace matte to white metal (CT end point of 74–77% Cu), prior to conversion in PS converters. The content of Cu in the discarded slag was reduced to <1 wt.% (Cutler et al., 2006). During the course of operations, about 20 Mt of smelting slag was produced and dumped (Jones et al., 2002). A variety of samples ($n = 18$) from the slag dump was studied (Slag I), generally occurring as dark fragments several centimetres in size and with colourful coatings of secondary phases (Figure 2a).

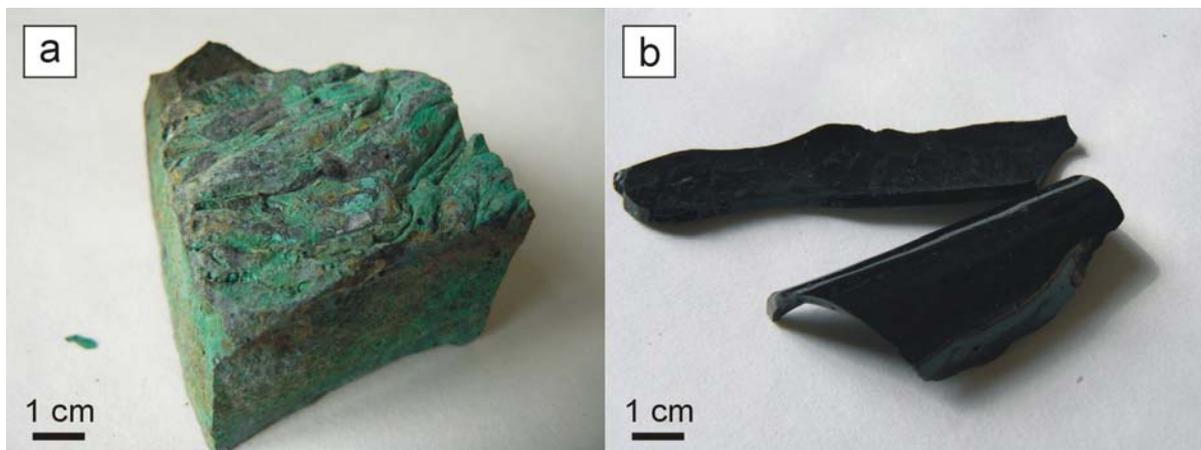


Figure 2 Photographs of slag samples (an example). (a) Nkana slag fragment; (b) vitreous slag from Chambishi.

2.4.2 Mufulira smelter

The Mufulira smelter (for the location, see Figure 1) is now a major processing plant as it treats both Nkana and Mufulira concentrates (GAA, 2011). It was initially commissioned in 1937 with two reverberatory furnaces and four PS converters to produce blister copper; several upgrades including the installation of two anode furnaces followed. The electric furnace was commissioned in 1971 and the reverberatory furnace was put offline in 1978 (Ross & de Vries, 2005). The electric furnace was replaced by an ISASMELT furnace in 2006. The overall smelter upgrade also included the installation of an electrostatic precipitator (ESP), upgrade of the matte settling electric furnace (where slag and matte are separated) and an acid plant, where SO_2 is processed to produce sulphuric acid. Currently, the efficiency of SO_2 capture is about 50%. Upgrading of the facility is still in progress and should be completed by 2015. It is intended mainly to reduce SO_2 and dust emissions (GAA, 2011). Dust from the ESP is conveyed to a feed bin and recycled in the smelting process. About

850,000 tons of concentrate are treated in the smelter per year and 800–1200 tons of slag are produced each day (containing a maximum of 1 wt.% Cu) (T. Gonzáles, Mufulira smelter, personal communication). Slag is tapped and granulated in a high pressure water stream and finally transported to a slag dump (GAA, 2011). In this study, (i) old slag fragments or granulated vitreous slag ($n = 4$; Slag II) and (ii) *ESP dust* were investigated.

2.4.3 Chambishi smelter

The Chambishi smelter was commissioned in 2001 as part of a slag treatment plant designed to recover Co from old Nkana dump slags containing 0.3–2.6 wt.% Co (average grade 0.76 wt.% Co). Prior to re-smelting, the slag is crushed to 15 mm particle size and mixed with fluxes (lime CaO, rutile TiO₂) and a reductant (coal) to prepare the furnace charge. Carbothermic reduction in a direct current (DC) electric arc furnace allows separating desirable non-ferrous metals (Co, Cu) from Fe to produce cobalt-bearing alloy subjected to further hydrometallurgical processing. High operating temperature (1500–1600°C) is used to ensure smelting above the liquidus temperature of the Co-Cu-Fe alloy. Molten slag is tapped (at about 1500°C) into 60-ton slag pots and conveyed to a nearby dump. The alloy (containing 5–14% Co) is tapped, superheated to 1650°C and atomized in a high-pressure water stream to produce fine alloy particles (< 100 μm), which are treated in a leaching plant and finally recovered as Co and Cu by electrowinning (Jones et al., 2002). Acid leaching of the atomized alloy was described in detail by Munnik et al. (2003). The flue gas cleaning system uses water filters to trap the process dust before it enters the atmosphere. The residue is periodically transported to a concrete pool to be partly air-dried and finally conveyed to a slag disposal site. Three main residues were studied: (i) *slag dust* from crushers, (ii) fragments of final vitreous slag ($n = 2$; Slag III; Figure 2b) (ii) *fly ash* from the wet gas cleaning trapped by water filters.

2.5 Leachability testing of solid waste residues

The need for sustainable disposal/utilisation and environmental impact assessment of solid wastes has resulted in the development of leaching test methods worldwide to assess their leaching characteristics (Kosson et al., 2002; van der Sloot et al., 1996). For comparative purposes, harmonisation of the procedures has been established, resulting in international standards (van der Sloot, 2001a). The leaching tests can be applied to almost any material but countless studies have been performed in particular on MSWI residues. Therefore, knowledge of the leaching of these solid residues is referenced frequently in the text of this thesis, because the literature on metallurgical waste leaching is still scarce or not available. Nevertheless, despite great differences in composition, similarities in the leaching behaviour can be found within different types of materials, e.g. MSWI residues, coal incineration residues, stabilised waste, metallurgical waste or contaminated soils and sediments (Cappuyns & Swennen, 2008; Dijkstra et al., 2006; Ettler et al., 2009; Gitari et al., 2009; Hyks et al., 2007; van der Sloot et al., 1996, 2001b; Vítková et al., 2009). The leaching is generally governed by dissolution/precipitation of mineral phases, complexation processes and/or sorption onto reactive surfaces (Astrup et al., 2006a; Ettler et al., 2004, 2008; Dijkstra et al.,

2006; Hyks et al., 2007, 2009a; Meima & Comans, 1998). However, a number of parameters and exposure conditions influence the leaching and they cannot be encompassed by a single “all-purpose” test. Particle size distribution, pH, time, liquid-to-solid (L/S) ratio, chemical speciation, mineral binding, and constituent availability are the parameters that mainly affect the leaching (Al-Abed et al., 2006; Astrup et al., 2006b; Ettler et al., 2008; Fällman, 1997; Hyks et al., 2007; Pareuil et al., 2010; van der Sloot et al., 2001b; Vítková et al., 2009). In this context, it is very important to employ leaching protocols that cover the key factors related to the actual disposal scenarios. Only the most representative conditions are relevant when estimating the release potential and assessing the hazards related to a given waste. On the one hand, underestimation can result in environmental contamination while, on the other hand, overestimation can lead to disposal of materials for beneficial use (Kosson et al., 2002).

In the EU landfill directive (EC 2003), three levels of testing are distinguished in order to assess the suitability of waste for disposal:

- (i) “Basic characterisation” tests for characterisation of waste materials and determination of their short- and long-term leaching behaviour under various conditions. The following leaching tests cover most of the desired factors: pH-dependence test (leaching as a function of the pH; CEN/TS 14997 and CEN/TS 14429), percolation test (leaching as a function of the L/S ratio; CEN/TS 14405) and dynamic test for monolithic materials (surface related leaching; CEN/TS 15863).
- (ii) “Compliance” tests for determining whether the waste complies with a specific behaviour or with specific reference values. European standard EN 12457 is widely used for these purposes.
- (iii) “On-site verification” tests are required before the waste is accepted at the landfill to confirm that the waste material is the same as that previously subjected to laboratory testing. Accordingly, characterisation and compliance batch leaching tests are addressed in this study.

3. Characterisation of metallurgical wastes

3.1 Introduction

As already outlined, solid waste residues with various compositions and characteristics are produced during metallurgical processes. Two types of slag are commonly generated in copper smelters: smelting furnace slag (containing 1–2 wt.% Cu) and converter slag (containing 4–8 wt.% Cu). Converter slag, in which Cu is present mainly as Cu_2O , is conventionally recycled in the smelting furnace (Davenport et al., 2002; Gorai et al., 2003). This study investigated only smelting furnace slag (i.e. tapped from the furnace), generally discarded on a dump as waste material. Copper slag contains various oxides including flux oxide(s), FeO from Fe oxidation and gangue oxides from concentrate. Therefore, SiO_2 (35–40 wt.%), FeO, Fe_2O_3 (30–40 wt.% Fe), Al_2O_3 (≤ 10 wt.%), CaO (≤ 10 wt.%) and/or MgO are the principal slag constituents with small amounts of S (typically < 1 wt.%) and Cu (0.5–2.1 wt.%). The chemical composition of copper slag depends on the smelting process, type of furnace and furnace charge (Davenport et al., 2002; Gorai et al., 2003). Although the composition and phase assemblages of smelting slags may differ, the basic characteristics are comparable to slags from other facilities and metallurgical processes. Typically, silicate phases (pyroxene, olivine, melilite), silicate glass, spinels and small metallic and sulphide inclusions can be found in smelter slag. Spinel oxides are the first to crystallise from the melt before silicates and glass finally solidifies from the residual melt and often traps sulphide/metallic droplets (Ettler et al., 2001, 2009; Gorai et al., 2003; Kierczak et al., 2009; Lottermoser, 2002; Piatak et al. 2004; Vítková et al. **I**). No glassy phases were observed by Navarro et al. (2008). Black, dense and hard crystalline products are formed when molten slag is cooled slowly. In contrast, rapid solidification of the slag melt yields a vitreous (granulated) residue (Ettler et al., 2009; Gorai et al., 2003; Piatak & Seal, 2010; Vítková et al. **I**). Moreover, various contents of metals (Cd, Co, Cu, Ni, Pb, Zn) and metalloids (As, Sb) are present in smelter slags (Ettler et al., 2009; Gorai et al., 2003; Lottermoser, 2002; Parsons et al., 2001; Piatak & Seal, 2010; Vítková et al. **I**), either in silicate and oxide structures and glass or as sulphide/metallic inclusions.

Smelter flue gases may contain substantial amounts of dust particles, conventionally called fly ash, flue dust or air-pollution-control (APC) residues. The dust often has a very complex composition including (i) small particles of unreacted feed charge (concentrate or flux) and droplets of matte/slag transported with the process gas (i.e. *mechanically formed dust*), and (ii) volatilised elements from the concentrate (e.g. As, Sb, Bi, Pb, Zn) which condensed during the flue gas cleaning or reacted to form non-volatile compounds (i.e. *chemically formed dust*). Fine-grained particles of chemical dust are easily transported for a longer distance in the flue gas cleaning system compared to coarser-grained particles of the mechanical dust, and thus the fine fraction increases with increasing distance from the furnace (Davenport et al., 2002; Samuelsson & Björkman, 1998; Skeaff et al., 2011). Consequently, different types of dust are produced and trapped within the flue gas cleaning system, which can also be rather plant-specific. Therefore, metallurgical dusts are highly varied in composition and other parameters, such as particle size. However, they basically concentrate

large amounts of potentially hazardous elements, which can be present in readily soluble forms (Ettler et al., 2005a; Skeaff et al., 2011; Vítková et al., 2009, **II**; Williamson et al., 2004). Moreover, fine dust particles (< 10 µm) can be inhaled and may cause severe health problems (Twining et al., 2005; Uzu et al., 2011; Williamson et al., 2004). The bioaccessibility of contaminants from the metallurgical dust will be discussed in *Chapter 5.2*.

3.2 Mineralogical investigations

A number of tools are available to provide information about the mineralogical composition on a macro- to nano-scale. Box 1 briefly summarises the methods that were employed for mineralogical investigation of the studied slags and/or dusts and that are commonly used for characterisation of these types of residues (Ettler et al., 2001, 2005a, 2009; Kierczak et al., 2009; Piatak & Seal, 2010; Skeaff et al., 2011; Sobanska et al., 1999). Also, it is demonstrated that a combination of methods is usually necessary to identify the mineralogical composition of solid waste residues. X-ray diffraction analysis (XRD) is conventionally used to determine the main crystalline phases. However, the anomalous composition of metallurgical residues often requires detailed investigations and spot chemical analyses to identify the phases, which form solid solutions or are present in low-crystalline forms. Electron microanalytical techniques (Box 1) were used to determine the distribution of potential contaminants within the phases and their substitutions in mineral structures. Scanning electron microscopy coupled with energy dispersion spectrometry (SEM/EDS) and electron probe microanalysis (EPMA) are conventionally used for these investigations. It should be noted here that sample preparation also plays a key role in mineralogical investigations as coarser slag fragments and fine dust particles are treated differently (see methodology in Appendices **I–V** for details). Basically, polished thin sections were prepared for slag analyses, while polished sections of dust samples embedded in epoxy resin were made. A polished surface allows performance of quantitative analyses (SEM/EDS, EPMA), while only qualitative EDS information can be achieved on rough surfaces (e.g. powder samples fixed on a conductive tape). Thermochemical data is frequently lacking for new phases formed during the smelting process due to the anomalous element content. Therefore, mineralogical identification is based on knowledge of the natural mineral phases and mineral names are used for their artificial analogues.

Box 1 Overview of methods for the mineralogical investigation of metallurgical wastes used in this study (description based on Lee, 2010; Potts et al., 1995).

X-ray diffraction analysis (XRD): Basic and widely used method for identification of crystalline phases in bulk (often multi-phase) samples. Phases present in low abundances may not be detectable by XRD. In this study, XRD was used to identify major primary and secondary phases in all the studied samples. Qualitative (or semi-quantitative) analysis was performed using X'Pert HighScore software.

Optical microscopy: This method uses visible light and a system of lenses to study small samples on a micro-scale directly by eye. It yielded the first microscopic observations in transmitted and/or reflected light of samples prepared as polished thin sections (slag) or polished sections (dust) embedded in epoxy resin.

Scanning electron microscopy (SEM): This analytical method uses an electron beam to image a sample in a raster scan pattern using (i) a detector of secondary electrons (SE) to study the sample surface topography and (ii) a detector of back-scattered electrons (BSE) to observe differences in the relative atomic weights of individual entities and study mineral phase relationships and the distribution of elements. The energy dispersive spectrometer (EDS) provides information about the elemental composition of individual particles or phases, or over larger sections through mapping. Polished (thin) sections or, to a lesser extent, powder samples can be investigated. Qualitative, semi-quantitative or quantitative analyses were performed on both crystalline and amorphous specimens.

Electron probe microanalysis (EPMA): Analytical method used to determine the chemical composition of small volumes of solid specimens. Similar to SEM, the measurements are based on the interaction of an electron beam with a polished sample and the emitted characteristic X-rays are detected. Quantitative microanalyses of both crystalline and amorphous specimens were performed. Further calculations were used to determine the individual phase compositions and possible substitutions of elements in the crystal structure.

Transmission electron microscopy (TEM): Analytical method whereby an electron beam is transmitted through a very thin sample to provide imaging at high resolution to study discrete particles on a nano-scale. Energy dispersive analysis (EDS) or selected area electron diffraction (SAED) of the individual particles provides information about the elemental composition and crystallinity, respectively. Several dust samples were successfully studied by TEM. Additionally, focused ion beam (FIB) foils from a slag sample were prepared for TEM investigation to visualise/analyse nano-sized objects within the specimen.

3.3 Metallurgical slags from the Zambian Copperbelt

Wide range of slag samples from the Zambian Copperbelt was studied and described in detail by Vítková et al. (I). Generally, the major slag constituents were as follows SiO₂ (16–60 wt.%), FeO (5.6–30 wt.%), CaO (3.2–22 wt.%), Fe₂O₃ (0.7–19 wt.%) and Al₂O₃ (3.9–13 wt.%) and significant concentrations of Cu (up to 35 wt.%), Co (up to 2.4 wt.%), and As (up to 3650 ppm) were determined (Table 1). Large differences in the chemical composition were found for samples collected at the dump site of the Nkana smelter (Slag I), which reflects the

variations in smelter technology and feed charge over time. Nevertheless, the mean values corresponded well to the results of Jones et al. (2002), who documented about 43 wt.% SiO₂, 20 wt.% total Fe, 8 wt.% Al₂O₃, 8 wt.% CaO, 3 wt.% MgO, 3 wt.% K₂O, and 0.6 wt.% S on an average for the feed slag (i.e. Nkana dump slag) at Chambishi.

Table 1 Statistical summary of chemical compositions of the studied slags (full data in Vítková et al. **I**).

Type*	Slag I			Slag II			Slag III		
	min	max	median	min	max	median	min	max	median
SiO ₂ (wt.%)	15.53	60.18	41.67	36.88	43.98	40.66	48.24	51.38	49.81
TiO ₂	0.35	0.75	0.54	0.43	0.65	0.57	0.58	0.63	0.61
Al ₂ O ₃	3.90	12.60	7.51	5.09	6.03	5.65	9.66	11.03	10.34
Fe ₂ O ₃	0.68	18.79	5.68	5.87	8.74	7.05	1.43	1.76	1.60
FeO	5.60	29.52	16.97	18.40	27.50	21.76	11.30	15.12	13.21
MgO	0.64	6.45	3.23	2.25	3.08	2.75	4.75	6.37	5.56
CaO	3.18	21.87	12.44	12.91	18.03	16.11	13.65	14.29	13.97
K ₂ O	1.13	4.83	2.36	1.84	2.57	2.23	2.73	3.06	2.89
S _{tot}	0.05	2.62	0.16	0.08	0.55	0.27	0.17	0.24	0.21
Cr (mg/kg)	65	7510	244	243	380	290	853	883	868
Cu	2870	353580	10035	4625	9349	6436	2050	3724	2887
Co	922	24104	8193	346	2716	1261	2178	2414	2296
Ni	12	935	23	9.0	46	21	5.5	8.2	6.9
Pb	<1.5	1134	21	11	26	21	<1.5	39	20
Zn	44	2287	247	180	496	308	80	123	101
Ba	246	1297	473	346	445	380	667	731	699
Sr	155	443	300	341	467	419	370	392	381
Mo	61	422	183	95	145	114	30	36	33
As	603	3642	865	627	750	672	621	1191	906
Bi	0.5	1695	5.5	2.4	5.6	3.6	<0.1	0.2	0.1

*Slag I, Nkana; Slag II, Mufulira; Slag III, Chambishi

Representative slag textures and phase associations are shown in Figure 3 (optical microscope images); more detailed SEM images are given elsewhere (Vítková et al. **I**). The commonest phases of the studied slags are listed in Table 2. The results of Vítková et al. (**I**) are in good accordance with the mineralogical characterisation reported for other smelting slags (e.g. Ettler et al., 2001; Kierczak et al., 2009; Piatak & Seal, 2010). Complex phase associations with predominant silicates (Ca-Fe pyroxenes of diopside-hedenbergite series, olivine mainly of fayalite-forsterite series), leucite, ubiquitous glass and commonly observed spinels (magnetite, Cr-spinel) were identified in Nkana and/or Mufulira slags (types I and II). Sulphides and/or metallic alloys occurred as inclusions of various forms and sizes (< 1 µm up to 500 µm) trapped within the silicate and/or glassy matrix (Fig. 3b, c). The Chambishi slags (type III) were composed of silicate glass with trapped sulphide/metallic inclusions. Metallic droplets were observed also for Pb-Zn slags from the Czech Republic (Ettler et al., 2001), Ni slags from Poland (Kierczak et al., 2009) and Zn slags from Illinois (Piatak & Seal, 2010); despite their minor to trace contents they are susceptible to weathering. Important substitutions of metals, particularly Co, for Fe (or Mg) in the silicate or oxide structures were

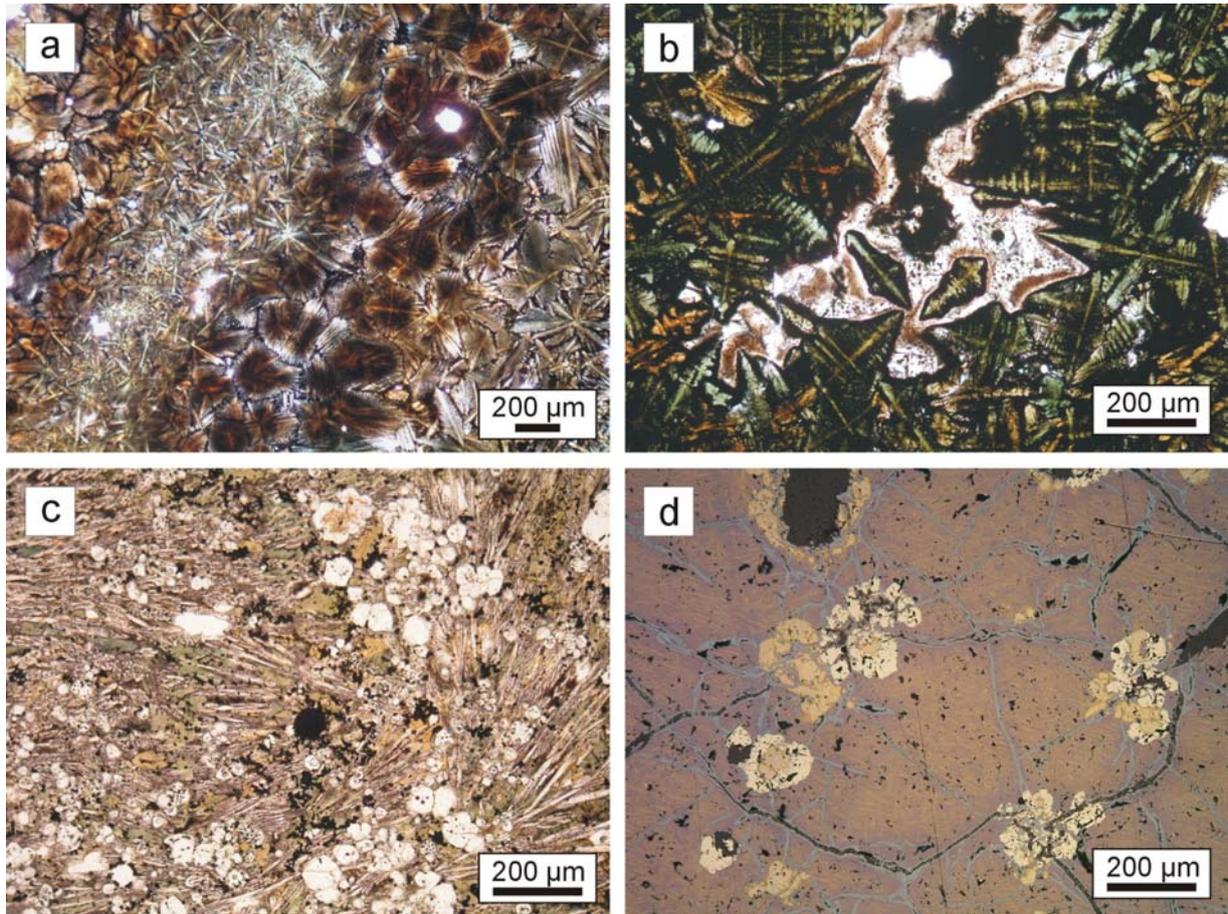


Figure 3 Optical microscope images showing characteristic phases and textures in Zambian slags. (a) Star-shaped pyroxene crystals (transmitted, plan polarised light, Slag I); (b) Green herring-bone or skeletal pyroxenes embedded in transparent to brownish glass and minute opaque sulphide/metallic inclusions trapped within the glass (transmitted, plan polarised light, Slag II); (c) Black sulphide prills in the silicate slag matrix composed of anhedral leucite (white), lath-like olivines (white prisms) and pyroxene (yellow to green) (transmitted, plan polarised light, Slag I); (d) Bornite (brown-violet) with lighter lamellae of Cu-Fe sulphide solid solution, with digenite filling the fractures (grayish) and larger crystals of troilite (beige) and Co-sulphide (bright yellow) (reflected light, Slag I).

detected. According to EPMA, up to 1.8 wt.% CoO and low concentrations of Cu and Zn were present in the pyroxene structure; even up to 7.15 wt.% CoO, but only 0.19 wt.% CuO and 0.44 wt.% ZnO were observed in olivines and finally, up to 5.12 wt.% CoO, 4.11 wt.% CuO and 0.99 wt.% ZnO were detected in the spinel structure. In contrast, elevated concentrations of Zn were found in silicates and spinels from slags at many other smelting sites (e.g. Ettler et al., 2001, 2009; Lottermoser, 2002; Piatak & Seal, 2010; Piatak et al., 2004). High concentrations of Cu and Co (with a maximum of 6.90 wt.% and 0.91 wt.%, respectively) were observed locally in the interstitial glass, while up to 2.54 wt.% CuO and 0.48 wt.% CoO were detected for the Chambishi vitreous slag. Silicate glass highly enriched in Pb, Zn, Cu, and As was also observed by Ettler et al. (2009) in slags from Tsumeb (Namibia). Sulphides and metallic alloys represented the main metal-bearing phases, most commonly observed as Cu-Fe sulphides, namely bornite and digenite or a solid solution

between digenite and chalcocite (Table 2). Galena (PbS) was observed only locally. Similarly, various Cu or Cu-Fe sulphides, galena and other metallic phases were reported by Ettler et al. (2009) and Piatak et al. (2004) in slags from other smelting sites. Finally, Co-bearing phases mainly represented by cobaltpentlandite ((Co,Ni,Fe)₉S₈) and various metallic alloys were determined. The identification of Co-bearing phases and Co substitutions in mineral structures provides new information for characterisation of the metallurgical slag.

Table 2 Major and minor phases determined in the studied slags using EPMA and XRD (source: Vítková et al. **I**).

Group	Name	Composition
Silicates	Diopside-hedenbergite s.s.	Ca(Fe,Mg)Si ₂ O ₆
	Fayalite-forsterite s.s.	(Fe,Mg) ₂ SiO ₄
	Kirchsteinite-monticellite s.s.	Ca(Fe,Mg)SiO ₄
	Leucite	KAlSi ₂ O ₆
	Quartz	SiO ₂
Oxides	Magnetite	Fe ₃ O ₄
	Cr-spinel	Fe ²⁺ (Cr,Al,Fe ³⁺) ₂ O ₄
Sulphides	Bornite	Cu ₅ FeS ₄
	Digenite	Cu ₉ S ₅
	Chalcocite	Cu ₂ S
	Troilite	FeS
	Co-pentlandite	Co ₉ S ₈
	Co ₄ S ₃	Co ₄ S ₃
	CoS	CoS
Others	Copper	Cu
	Alloys	(Fe, Co, As, Cu, Ni)
	Intermetallic compounds	(Fe,Co) ₂ As
Silicate glass		

s.s. = solid solution

Vítková et al. (**I**) often observed secondary phases on the Nkana slag surfaces (Figure 2a), occurring as coatings or stains and represented by sulphates, carbonates and oxides. Typically, green formations of brochantite (Cu₄SO₄(OH)₆) associated with malachite (Cu₂(CO₃)(OH)₂) were observed. Brochantite was also identified by Piatak et al. (2004) on Cu slag from Vermont, USA. Globular pink sphaerocobaltite (CoCO₃) was determined and was often associated with the fibres of calcite (CaCO₃). A reddish coating of hematite (Fe₂O₃) was observed locally. The presence of Fe oxides was also reported by Bril et al. (2008) or Piatak & Seal (2010) on the slag surfaces at the other smelting sites. Lottermoser (2005) detected elevated concentrations of potential contaminants (As, Cd, Co, Cu, Pb, Zn) on the surface precipitates on slags from Rio Tinto (Spain), indicating substitution in the structure of secondary phases, the presence of efflorescence salts or sorption of metals onto hydrous ferric oxides (HFO) (Lottermoser, 2005). A number of factors affect the formation of alteration products, e.g. the age of the slag, bulk slag composition and phase associations. The weathering features indicate the slag reactivity on contact with water and the atmosphere, and thus potential release of metals and metalloids into the environment.

3.4 Metallurgical dusts from the Zambian Copperbelt

Three smelter dust samples of different origin were investigated in this study. Characterisations of the *ESP dust* (Vítková et al. **II**) and *fly ash* (Vítková et al. **V**) are presented together with unpublished results for the *slag dust*. Table 3 clearly shows variances in their bulk chemical composition and high concentrations of metals and metalloids contained in the dusts. Slag dust (D1) mainly consisted of Si (191 g/kg), Fe (178 g/kg), Ca (65 g/kg) and Al (39 g/kg), which corresponds well to the average composition of the Nkana slags (Vítková et al. **I**). Moreover, the dust was highly enriched in Cu (32 g/kg) and Co (8.9 g/kg). Major constituents of the fly ash (D2) were C (111 g/kg), Si (108 g/kg), Fe (87 g/kg), Ca (80 g/kg), Mg (44 g/kg), K (39 g/kg), Al (26 g/kg), and S (35 g/kg) with high contents of Cu (41 g/kg), Zn (21 g/kg), Co (4 g/kg), and Pb (8.4 g/kg). In contrast, the ESP dust (D3) was mainly composed of Cu (273 g/kg), Fe (194 g/kg), and S (85 g/kg); elevated concentrations of As, Bi, Pb, and Zn were observed (Table 3). Similarly, Samuelsson & Carlsson (2001) showed that Cu and Fe are the principal constituents of ESP copper dust from Sweden enriched in Pb (3 wt.%), Zn (6–12 wt.%) and As (1–2 wt.%). This was not the case for the ESP copper dust studied by Samuelsson & Björkman (1998), who documented < 1 wt.% Fe and < 1 wt.% Cu but high levels of Pb (> 40 wt.%), Zn (< 10 wt.%) and As (< 10 wt.%).

Table 3 Chemical composition of the dust samples studied.

g/kg	D1	D2	D3	mg/kg	D1	D2	D3
Si	191	108	43	As	65	523	2786
Ti	2.7	1.5	0.5	Ba	659	327	113
Al	39	26	10	Bi	45	836	15035
Fe	178	87	194	Cd	<1.1	20	195
Mn	0.8	1.5	0.2	Co	8943	4061	992
Mg	15	44	4.8	Cr	487	227	52
Ca	65	80	11	Cu	32240	40983	272745
Na	0.9	1.8	2.1	Mo	41	49	1150
K	19	39	6.6	Ni	70	39	576
P	1.2	1.4	0.2	Pb	144	8424	2156
C _{tot}	16	111	1.4	Sr	334	332	57
S _{tot}	10	35	85	Zn	279	21478	2137

D1, slag dust (Chambishi); D2, fly ash (Chambishi; Vítková et al. **V**); D3, ESP dust (Mufulira; Vítková et al. **II**)

The results of granulometric measurements (using LALLS, low angle laser light-scattering method) also indicated different origins of the samples (Table 4). Dust generated during slag crushing contained relatively larger particles compared to dust trapped by ESP or filter fly ash, both formed during high-temperature processes. Almost 99% of the particles of D2 and 100% of the particles of D3 had a grain size below 80 µm, while this corresponded to only 73.5% for D1 (Table 4). The particle size fraction below 10 µm is considered to be respirable and thus potentially hazardous for human health. Samuelsson & Björkman (1998) found approximately 90% particles < 10 µm for the ESP copper dust and as much as 94% particles < 2 µm was reported by Ettler et al. (2005a) for lead smelter dust collected at the bag-type

filter stage. The latter is assumed to have a severe impact on the environment and humans considering the content of fines and high Pb concentration (43 wt.%) (Ettler et al., 2005a). The < 10 µm fraction yielded 25%, 36.6%, and 50.5% for D1, D2, and D3, respectively (Table 4). The bioaccessibility of the dusts related to health risk is discussed in *Chapter 5.2*.

Table 4 Granulometry of the studied dust samples.

µm	D1 %	D2 %	D3 %
< 1	3.6	2	4.8
1 – 5	12.2	15.3	23
5 – 10	9.2	19.3	22.7
10 – 20	12.8	28.4	27.5
20 – 30	7.7	15.6	12.6
30 – 50	12	13	8
50 – 80	16	4.9	1.4
80 – 200	26.5	1.5	0

A combination of XRD, SEM/EDS and TEM/EDS analytical methods was used for mineralogical characterisation of the smelter dusts (Table 5; Vítková et al. **II**, **V**). In addition, the heavy mineral fraction of D2 and D3 was obtained in order to identify minor to trace metallic phases after removing the matrix. For these purposes, heavy liquid separation using specifically the Clerici solution (bulk density of 4.05 g/cm³) and/or 1,1,2,2-tetrabromoethane (bulk density of 2.96 g/cm³) were applied to samples D2 and D3, respectively.

The composition of slag dust D1 generally corresponded to silicate slags (Vítková et al. **I**) as no high-temperature processes participated in the dust generation, but only crushing. Ca-Fe clinopyroxenes, fayalite, quartz, CuFe₂O₄ and/or magnetite were mainly determined in the sample. In addition, minor to trace copper sulphides (e.g. chalcocite, chalcopyrite or non-stoichiometric Cu(Fe,Co)S) and traces of cobalt sulphides and elemental Cu were observed by SEM (Figure 4a, b). Metallic sulphates and sulphides were determined as principle phases in lead smelter emissions by Sobanska et al. (1999) and metallic sulphates prevailed in copper smelter stack particulates studied by Skeaff et al. (2011). In contrast, calcite, clinopyroxenes (corresponding best to augite (Ca(Fe,Mg)Si₂O₆)), and quartz dominated in the fly ash D2 (Vítková et al. **V**). The calcite is derived from lime added as a flux in the smelting process (Jones et al., 2002). Zinc sulphide was also suggested by XRD but mixed Cu-Zn sulphides were often determined by TEM (Figure 5a). Minor to trace copper sulphides of various compositions, mainly observed as non-stoichiometric Cu-Fe sulphides with traces of Zn and/or Co were determined by SEM (Figure 4c). Elemental Cu and Fe-Cu-Co alloys were also detected. Furthermore, a significant portion of the amorphous/glassy fraction occurred in the sample and the enrichment of Cu, Co and Zn in silicates and silicate glass was determined both by TEM and SEM (Vítková et al. **V**). The presence of CuO, PbO or ZnO incorporated in silicate glass was also detected by Skeaff et al. (2011). According to XRD results, chalcantite and (Cu-bearing) iron oxides, i.e. magnetite or CuFe₂O₄ and delafossite

Table 5 Phases occurring in the dust samples^a as determined using XRD, SEM/EDS and/or TEM/EDS.

Name	Formula	D1	D2	D3
Clinopyroxene ^b	Ca(Fe,Mg)Si ₂ O ₆	***	***	–
Fayalite	Fe ₂ SiO ₄	***	–	–
Leucite	KAlSi ₂ O ₆	–	*	–
Quartz	SiO ₂	***	***	*
Calcite	CaCO ₃	–	***	*
Chalcanthite	CuSO ₄ ·5H ₂ O	–	–	***
Gypsum	CaSO ₄ ·2H ₂ O	–	–	*
Magnetite	Fe ₃ O ₄	**	**	***
Rutile	TiO ₂	–	*	–
Copper iron oxide	CuFe ₂ O ₄	***	–	**
Delafossite	CuFeO ₂	–	–	***
Pyrite	FeS ₂	*	–	–
Zinc sulphide ^c	ZnS	–	**	–
Cu sulphides ^d	Cu(Fe,Co)S	**	**	*
Co-pentlandite	Co ₉ S ₈	*	–	–
Copper	Cu	*	**	–
Alloys	Fe-Cu-Co-(As)	–	*	*
Silicate glass		**	***	***

^a Relative abundance: *** dominant or common phases, ** minor phases, * trace phases, – not determined

^b D1 – clinopyroxenes corresponding to diopside-hedenbergite, D2 – clinopyroxenes corresponding to augite

^c ZnS suggested by XRD, possible substitution with Cu suggested by SEM/EDS and TEM/EDS

^d non-stoichiometric compounds of various compositions; traces of chalcocite Cu₂S, chalcopyrite CuFeS₂, bornite Cu₅FeS₄ or digenite Cu₉S₅ were detected by SEM/EDS or TEM/EDS

(CuFeO₂) represented the main phases in the ESP dust D3 (Vítková et al. **II**). The TEM investigations confirmed the presence of Ca and/or Cu-Ca sulphates and delafossite (Figure 5b). Trace Cu sulphides were determined by TEM and mainly mixed Cu-Fe sulphides were detected by SEM (Figure 4d). Samuelsson & Carlsson (2001) obtained similar results for the ESP copper dust from Sweden consisting mainly of Fe- and Cu-oxides, possibly Fe₃O₄, CuO and CuFe₂O₄ or (Cu,Zn)Fe₂O₄ solid solution. Moreover, vaporised contaminants condensed as sulphates and/or oxides, e.g. PbSO₄, CuSO₄ or ZnSO₄ (Samuelsson & Carlsson, 2001). The leaching characteristics and stability of the ESP dust and fly ash are discussed in *Chapter 4*.

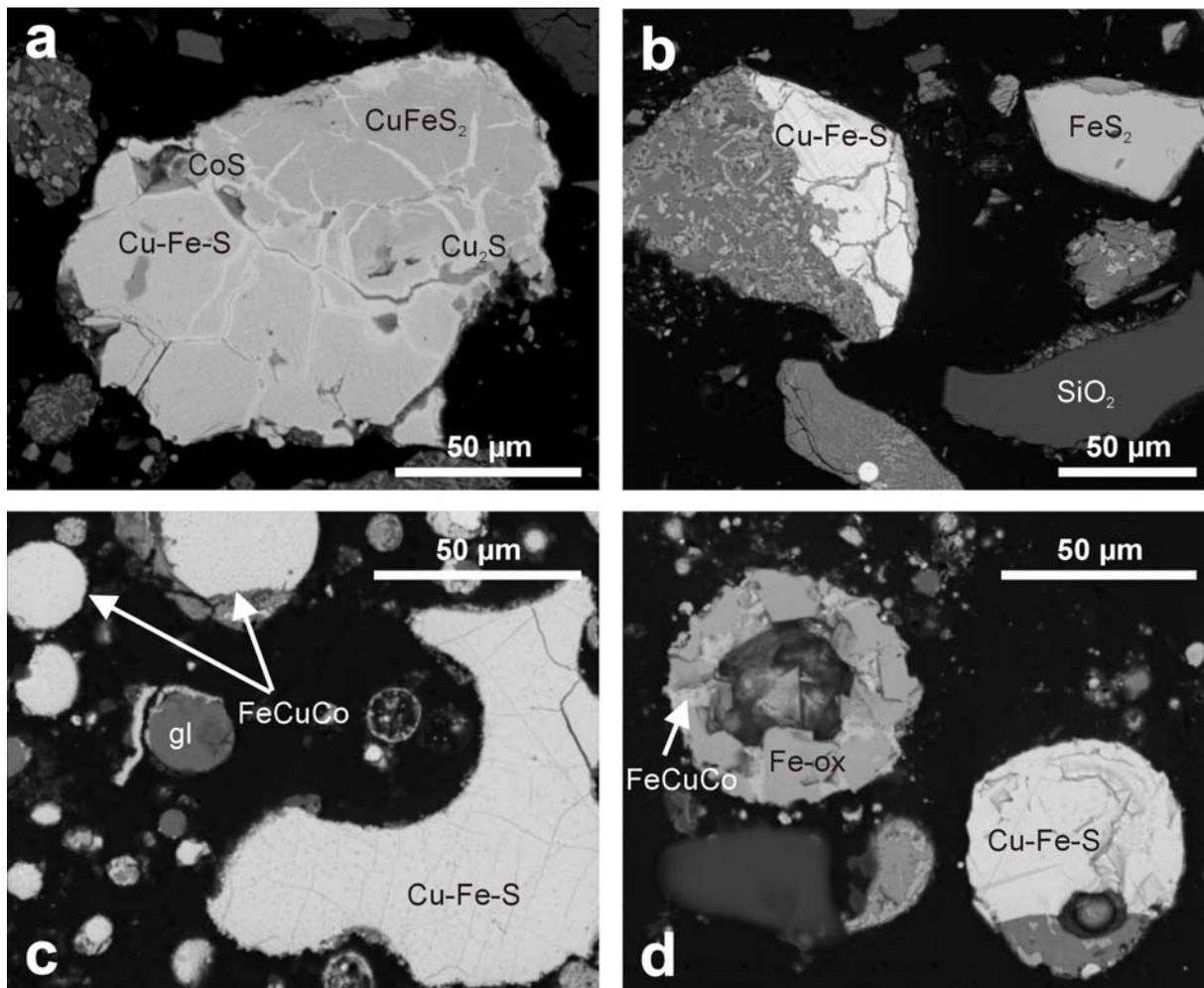


Figure 4 SEM images of metallic phases from the studied dust samples in backscattered electrons. (a) and (b) slag dust D1, (c) fly ash D2 (heavy mineral fraction), (d) ESP dust D3. Abbreviations: Cu-Fe-S – non-stoichiometric Cu-Fe sulphide, CoS – Co-sulphide $(\text{Co,Fe,Ni})_9\text{S}_8$, CuFeS_2 – chalcopyrite, Cu_2S – chalcocite, SiO_2 – quartz, FeS_2 – pyrite, gl – glass, FeCuCo – alloy, Fe-ox – Fe oxide

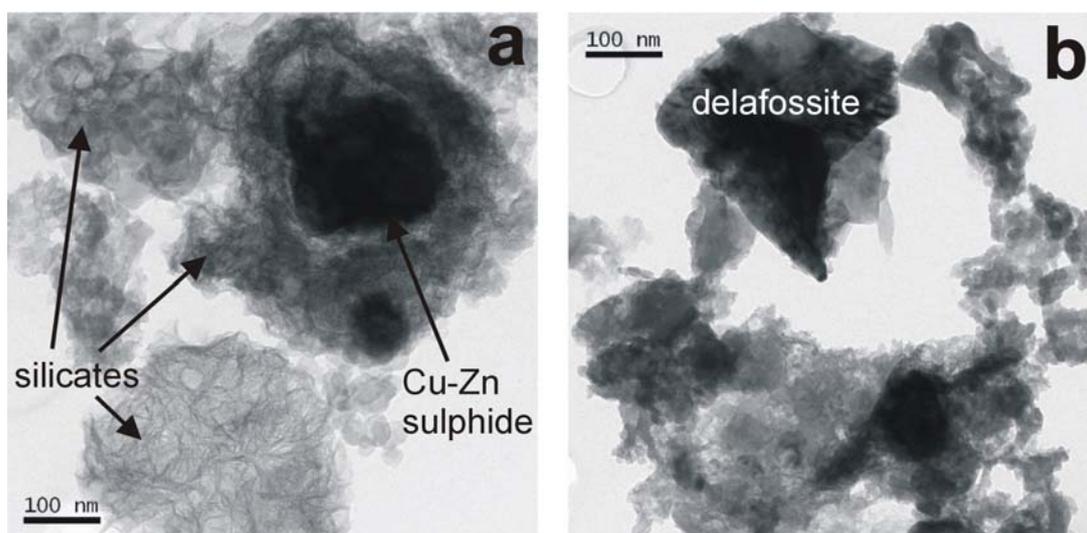


Figure 5 TEM images of selected phases identified in dust samples D2 (a) and D3 (b).

3.5 Solid waste mineralogy – analytical issues

Despite the range of analytical methods for mineralogical investigations, identification of the phases still remains a substantial challenge on the scale of micro-/nanoparticles. As outlined previously, SEM/EDS and EPMA are often used to determine the chemical composition of phases in solid waste materials. However, these methods do not allow detection of nanophases that may occur in the matrix and their composition is therefore considered to be part of the crystal structure of the main phase. This inevitably leads to misinterpretation of the analytical data. During the mineralogical study of the Zambian slags (Vítková et al. **I**), several spot analyses indicated the presence of potassium in clinopyroxenes (Cpx). Considering that the potassium ion is basically too large to enter the Cpx structure at ambient pressures, the EMPA results seemed to be improbable but true. In order to verify this, a more detailed study was performed using modern analytical instruments with much higher spatial resolution (Ettler et al. **IV**). The focused ion beam (FIB) technique was applied to prepare thin foils (90–160 nm thick and 13 μm x 9 μm in size) of the desired area for further TEM analysis. The FIB-TEM investigation revealed the presence of leucite (KAlSi_2O_6) closely associated with Cpx lamellae and finally refuted our hypothesis of potassium-rich Cpx in smelter slag. Variable sizes of leucite inclusions (X0–X00 nm) and intergrowths with Cpx were detected by TEM, while a homogeneous-like matrix was observed on SEM images. As a result, the K concentrations in leucite were erroneously attributed to the Cpx composition. Either small grain size of leucite particles or their position directly below the sample surface might have “masked” their presence during SEM observations. The beam size of EPMA is generally close to 1 μm and the volume of the analysed material usually ranges around several μm^3 (Potts et al., 1995) so a mixture of nano-sized solids and the main phase could be detected.

These results are highly important for the determination of solid speciation of potentially hazardous metals and metalloids. The substitutions of metals for major cations in the crystalline phases and in glass as well as the presence of metallic droplets in glass have been reported in many studies (e.g. Ettler et al., 2001; Kierczak et al., 2009; Piatak et al., 2004; Seignez et al., 2007; Vítková et al. **I**). However, the elevated metal concentrations often observed in glass may correspond either to the actual glass composition or to the admixtures of metallic nanophases. Therefore, the EPMA results should be treated carefully and the verification of their reliability might be necessary. Consequently, the role of nanoparticles in the weathering processes and in environmental impact assessment of solid waste materials should be further evaluated.

4. Characterisation of leaching from metallurgical wastes

4.1 Introduction

Metallurgical wastes exposed to weathering, i.e. upon contact with water and the atmosphere, show different leaching characteristics related to their composition and other factors outlined in *Chapter 2.5*. The stability of mineral phases and thus the leaching behaviour depends strictly on the Eh-pH conditions. Although metallurgical solid residues yield various compositions (as was shown in *Chapter 3*), some general patterns of stability have been derived from the leaching of smelter slags (Ettler et al., 2001, 2003; Parsons et al., 2001; Piatak & Seal, 2010; Piatak et al., 2004). Sulphides and intermetallic compounds are highly reactive under oxidising conditions and thus represent a potential source of contaminants. Silicate glass, even though often considered insoluble, is metastable and commonly more soluble than crystalline silicates with similar composition. Alteration of the glass results in the release of metals either from metallic inclusions trapped within the glassy matrix or directly from glass. Spinel-type oxides are assumed to be most resistant to leaching/weathering. Consequently, the release of metals contained in silicate and oxide forms is rather limited, while metals from glass or metallic sulphides are liberated easily. However, the dissolution rate of individual phases must be taken into account when assessing the environmental impacts since a number of factors influence the leaching kinetics (e.g. Eh, pH, formation of secondary phases). Oxidation of metallic sulphides results in sulphate ion mobilisation, often followed by precipitation of secondary sulphates (Bril et al., 2008; Ettler et al., 2003; Lottermoser, 2005; Navarro et al., 2008; Parsons et al., 2001; Vítková et al. **III**). Furthermore, carbonates formed under neutral to slightly alkaline conditions represent an important attenuation mechanism controlling the mobility of potential contaminants (Bril et al., 2008; Ettler et al., 2003, 2004, 2008; Parsons et al., 2001; Vítková et al., 2009, **III**). In addition, secondary HFO commonly precipitate under oxidising conditions and sorption of metals and metalloids onto HFO surfaces controls the contaminant release (Ettler et al., 2003; Parsons et al., 2001; Vítková et al. **V**). Nevertheless, stability of weathering features is very variable and during rainy periods the soluble metal-bearing secondary phases may release potential contaminants into the environment.

The influence of the pH on the leaching has been studied and large amounts of pH-dependent leaching data have been obtained mostly for MSWI residues. As a result, differences and similarities in the leaching behaviour were identified and three main groups of elements can be distinguished according to their predominant leaching mechanisms (e.g. Astrup et al., 2006a; Dijkstra et al., 2006, 2009; Dzombak & Morel, 1990; Eighmy et al., 1995; Hjelmar, 1996; Hyks et al., 2009b; Meima et al., 1999): (i) availability-controlled elements, (ii) solubility-controlled elements, and (iii) sorption- or complexation-controlled elements. The release of availability-controlled elements is limited only by the presence (i.e. “availability”) of their source compounds (e.g. NaCl), which are readily soluble. Thus, they dissolve rapidly during the leaching and their concentrations in the solution are more or less independent of the pH. The leaching of solubility-controlled elements is limited by the solubility of the mineral phases (e.g. gypsum controls the leachability of Ca). Here, different

leaching behaviour can be observed as a function of the pH. For a single controlling phase whose solubility is not affected by changes in the pH, no differences in concentration are observed within the pH range. In contrast, metals often exhibit a U- or V-shaped leaching trend (i.e. high release at both low and high pH levels with a minimum under near-neutral conditions) as a result of several controlling phases within the pH range or pH-dependent solubility of the controlling phases. Moreover, typically metals (e.g. Cd, Cu, Pb) are controlled by sorption onto reactive surfaces, such as hydrous ferric oxides (HFO) and/or hydrous aluminium oxides (HAIO), and complexation with dissolved organic matter (DOC). A combination of solubility and sorption/complexation-controlling mechanisms usually occurs for metals. The results reported by Vítková et al. (2009, **II**, **V**) indicate that pH-dependent leaching from metallurgical wastes has similar behaviour.

4.2 Leaching tests

Specific sample preparation (e.g. crushing or sieving) and fixed testing conditions (e.g. time, L/S ratio) are used in standardised leaching protocols. There is a simple reason for this, the need for comparison of the results either with other materials or with regulatory limit values. However, experimental conditions and parameters should be addressed especially with respect to the actual leaching scenarios.

The liquid-to-solid ratio, an important parameter often associated with time, should be explained here. The L/S ratio of a laboratory leaching system corresponds to the volume of deionised water in contact with a given mass of solid residue and can be further related to a disposal leaching scenario with rainwater infiltrating into a landfill body. As a result of residue-water interaction, changes in the pH occur over time and thus the leaching behaviour is significantly affected. Accordingly, pH-dependent experiments at fixed L/S ratios are often performed to evaluate the leaching characteristics at specific pH values. However, the relevant pH values that best describe the real-scale situation need to be selected carefully considering that the pH evolution depends on time and L/S ratio (Astrup et al., 2006b; Quina et al., 2011). The relationship between the L/S ratio (L/kg) scale and time scale can be expressed by the following equation (Hjelmar, 1990):

$$t = L/S \cdot \rho \cdot H/I$$

where t is the time after the first leachate appears at the bottom of the residue layer (years), ρ is the average dry bulk density of the deposited residue (kg/L), H is the height of the disposal site (m), and I is the net infiltration rate (m/year). Assuming that the annual net infiltration is 0.2 m/year, with a height of 10 m and residue bulk density is 1 kg/L, then the leaching time (years) corresponds approximately to 50 multiplied by the L/S ratio. Thus, it requires about 500 years to reach an L/S ratio of 10 for such a disposal site. This example illustrates the potential leaching scenario from a long-term perspective.

This thesis is mostly concerned with characterisation of the pH dependence test with continuous pH control (i.e. pH-static test CEN/TS 14997) and the compliance batch test (EN 12457-2). The experimental protocols are described briefly in Box 2.

Box 2 Overview of leaching experimental protocols used in this study.

pH-static test (CEN/TS 14997): One-stage batch test with liquid-to-solid (L/S) ratio of 10 L/kg and standard testing time of 48 hours performed on granular materials with particle size < 1 mm; the material may be crushed prior to the leaching experiment. A mass of dry solid material is placed in glass or high-density polyethylene (HDPE) bottles and mixed with deionised water. The suspension is either stirred or agitated. The pH is adjusted and continuously computer-controlled at pre-defined values in separate reactors. At least 8 pH values (including the natural pH of the material) in the range of pH 4–12 are required. The amounts of acid (HNO₃) or base (NaOH) needed to cover the pH range can be derived from the results of a preliminary titration. For the purposes of this study, selected slag and dust samples were subjected to pH-static leaching following both a standard experimental protocol and modified testing conditions. Slag crushed to grain sizes of < 5 mm and < 1 mm and the effects of the presence/absence of dust particles were investigated in the range of pH 4–12 (see Vítková et al. **III** for details). The grain sizes of the dust samples were all below 1 mm. The ESP dust was tested in the range of pH 3–7 with a step of 0.5 pH (Vítková et al. **II**) and the fly ash was subjected to 24-h, 48-h and 168-h leaching in the range of pH 5–12 (Vítková et al. **V**). After the experiments, the pH, Eh and specific conductivity were measured and filtered leachate samples were taken for further analyses.

Batch test (EN 12457-2): One-stage batch test with L/S ratio of 10 L/kg and standard testing time of 24 hours performed on granular materials with particle size < 4 mm; the material can be crushed prior to the leaching experiment. No pH control is employed. For the purposes of this study, slag crushed to < 4 mm was used and the effects of dust removal were also studied (see Vítková et al. **III** for details). A given mass of dry solid material was placed in HDPE bottles and mixed with deionised water. The bottles with suspensions were closed (HDPE caps) and continuously agitated at 80–100 rpm using a horizontal shaker for a period of 24 hours. After the experiments, the pH, Eh and specific conductivity were measured and filtered leachate samples were taken for further analyses.

4.3 Geochemical modelling

The geochemical modelling framework is a useful tool for leaching behaviour investigations and predictions, as it provides information about (i) possible solubility-controlling phases, (ii) possible sorption onto Fe, Mn, and Al oxyhydroxides, and (iii) complexation with dissolved organic matter (Dijkstra et al., 2009; Dzombak & Morel, 1990; Meima & Comans, 1998). However, detailed mineralogical study is often required to obtain relevant results on the release mechanisms. As described in *Chapter 3*, identification of the phases might be rather difficult due to the complexity of the waste materials. Furthermore, the parameters of these “artificial” phases needed for geochemical calculations are often not available. Therefore, it is necessary to work carefully with the modelled data to avoid misinterpretation.

In this study, the PHREEQC geochemical speciation-solubility code (Parkhurst & Appelo, 1999) was generally used to determine the speciation of the elements and the degree of leachate saturation with respect to the mineral phases (Vítková et al. **II**, **III**). Precipitation

of secondary phases was also predicted. The leaching of *fly ash* (Vítková et al. **V**) was coupled to the ORCHESTRA modelling framework (Meeussen, 2003), commonly used for MSWI residues. The “multisurface” modelling approach (Dijkstra et al., 2009) was employed.

4.4 pH-dependent leaching

pH-dependent leaching has been reported in many studies (e.g. Al-Abed et al., 2006; Astrup et al., 2006a; Brunori et al., 2001; Cappuyns & Swennen, 2008; Dijkstra et al., 2006; Gitari et al., 2009; Hyks et al., 2007; Vítková et al., 2009, **II**, **III**, **V**) as it provides essential information about the leaching behaviour of a given material under various environmental conditions. The pH is a key controlling parameter and the leachability of most constituents depends strongly on the pH. In addition, information about acid and base neutralisation capacities (ANC and BNC) is provided; this yields a measure of the resistance of a material to externally imposed changes in the pH. Consequently, pH-dependence tests can provide insight into long-term changes in the leaching behaviour as the natural pH tends to change with time when the buffering capacity of the material is depleted (van der Sloot, 2001a; 2002). This property is mainly addressed in the pH-dependence test CEN/TS 14429 (2003) with initial addition of pre-defined amounts of acid/base to reach the desired end pH value. Leaching with continuous pH control, i.e. pH-static test CEN/TS 14997 (2006), requires separate batch reactors with electrodes that are computer-connected and the pH and titration are controlled automatically over the entire test period. Alternatively, continuous manual control and titration can be employed and was used successfully by Vítková et al. (2009; **III**). In any case, manual addition of a strong acid/base is often necessary to adjust the predefined pH values in the initial stage of the test, depending on the *natural pH* (i.e. pH obtained when the material is in contact with deionised water without acid/base addition) and neutralisation capacity of the material.

The set of pH values used for the pH-static test should reflect real-life conditions and the neutralisation capacity of a given residue. In this context, the range of pH 3–7 was selected for leachability testing of the ESP dust from the Mufulira smelter by Vítková et al. (**II**). The natural pH of the dust yielded ~ 4.3, which is a much lower value than that of the MSWI fly ash (Astrup et al., 2006b; Gitari et al., 2009; Hyks et al., 2009b; Quina et al., 2011) or smelter fly ash studied by Vítková et al. (2009; **V**). This can be explained by dissolution of sulphates, namely chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Vítková et al. **II**), which introduces H^+ ions into solution, thereby decreasing the leachate pH. Similarly, Skeaff et al. (2011) reported dissolution of CuSO_4 and ZnSO_4 present in smelter stack particulates, resulting in the final pH < 4. These observations are in sharp contrast to those of Astrup et al. (2006b), who studied pH variations as a function of the L/S ratio on MSWI fly ash (natural pH > 11). They found that the residues exhibited alkaline conditions (pH > 7) for L/S ratios up 2000 L/kg corresponding to about 100 000 years for a typical landfill scenario. High alkalinity (i.e. neutralisation capacity) is mostly associated with high contents of Ca and minerals like portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3) or ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) in MSWI residues. Calcite determined in the fly ash from the Chambishi cobalt smelter also affected the natural pH of the leachate, yielding ~ 9.5 (Vítková et al. **V**).

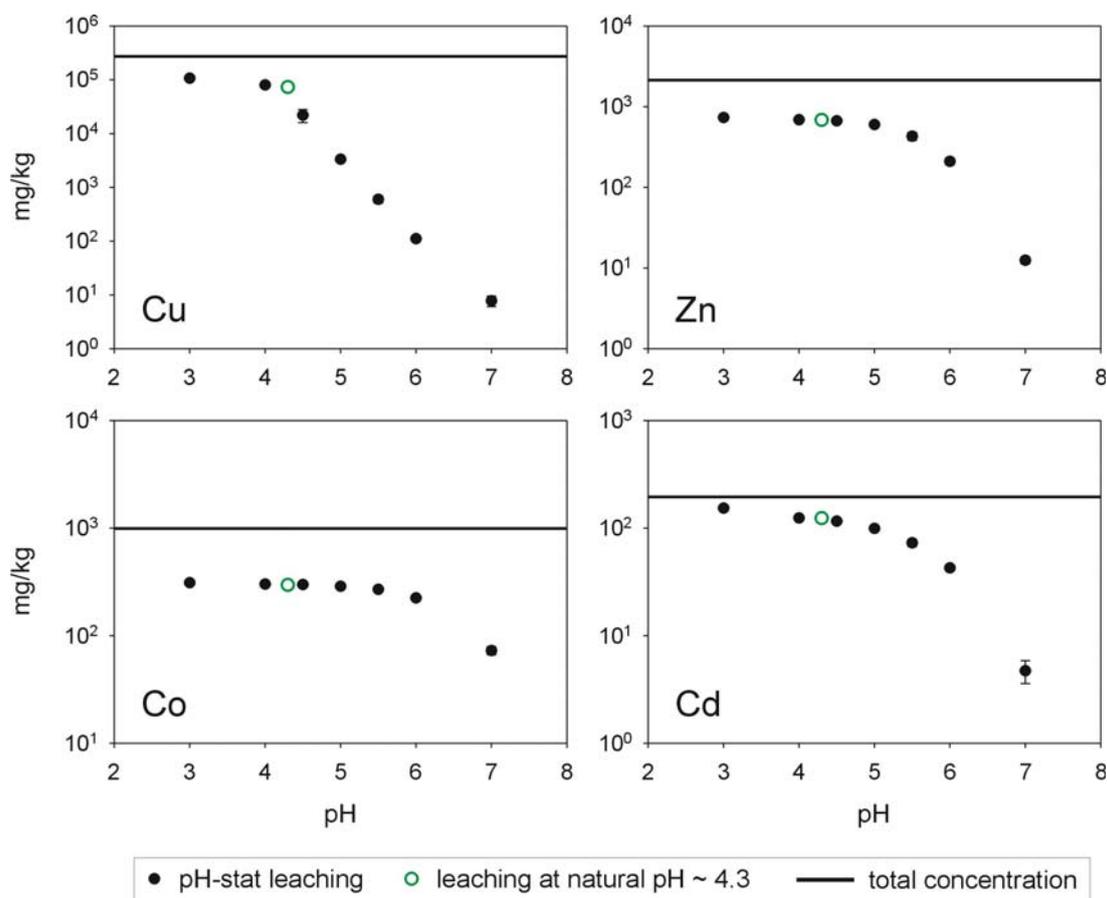


Figure 6 Leaching of Co, Cu, Cd and Zn from the ESP dust (Mufulira) as a function of the pH; total concentrations of the individual metals are plotted to illustrate the leachable fraction; symbols with vertical bars represent the mean and standard deviation of the measurements (source: Vítková et al. **II**).

In accordance with the general leaching trends of metals, the highest release of metals from the ESP dust from the Mufulira smelter was observed under acidic conditions (pH 3–4.5) with gradual decrease towards pH 7 (Vítková et al. **II**, Figure 6). About 80% of the total Cd and 30–40% of the Cu, Zn, and Co were released at pH 3, as illustrated in Figure 6. Significant concentrations of metals were also detected at natural pH, yielding 73.5 g Cu/kg, 686 mg Zn/kg, 297 mg Co/kg and 124 mg Cd/kg (Vítková et al. **II**). These extractable amounts pose a high risk for environmental contamination. The leachability of Cu from the ESP dust was mainly controlled by readily soluble chalcantite and hydrated Cu sulphates precipitated at pH 4–7. Formation of antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$) and brochantite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6$) thus resulted in a rapid concentration decrease for Cu in this pH range. Chalcantite was observed as a secondary weathering product on a slag dump in Spain (Navarro et al., 2008) or in Cu-Co chemical leaching plant waste in Zambia (Sracek et al., 2010) but is highly soluble during rainy periods. The adsorption of metals onto HFO was suggested to attenuate metal leachability from the ESP dust (Vítková et al. **II**). Magnetite (Fe_3O_4) and delafossite (CuFeO_2) were found to be relatively stable during leaching (Vítková et al. **II**), which confirms the fact that spinel-type oxides are the most resistant to weathering.

4.5 Influence of the test conditions

4.5.1 Batch tests without pH control

Simple batch leaching without pH control is often used for material classification in compliance with legislative requirements. Particularly European standard EN 12457 with L/S = 2 (part 1) or L/S = 10 (part 2) is currently used to evaluate materials according to waste acceptance criteria for landfills (EC 2003) and has the status of a Czech Standard. Based on the results compared to the limit values, the waste is classified as inert, non-hazardous or hazardous. However, this type of test describes only short-term leaching at the natural pH of the material without considering the long-term changes (see also the L/S concept in *Chapter 4.2*). Therefore, the differences between the compliance batch tests and characterisation leaching tests should be further evaluated. Thus, a comparison of the EN 12457 standard with other leaching test results or with modified experimental conditions is often presented to understand the leaching behaviour more in detail (Brunori et al., 2001; Ettler et al., 2009; Pareuil et al., 2010; Quina et al., 2011; Vítková et al. **III**).

4.5.2 Effect of the pH and sample preparation on slag leaching

Size reduction is generally performed to accelerate attainment of equilibrium conditions in batch tests, but much slower weathering rates are usually observed in slag dumps (Parsons et al., 2001). For example, sample crushing to < 4 mm is required in the EN 12457-2 standard (Box 2) if the initial particle size exceeds this limit; milling must be avoided. Nevertheless, significant differences in the leachability results may occur depending on sample preparation techniques. Zandi et al. (2007) clearly show how crucial such sample pretreatment could be when assessing the hazardous properties of metallurgical slag. In this context, due to the initial rapid dissolution of fines and increased reactive surface generated during crushing (Pareuil et al., 2010; Fällman, 1997), the release potential may be greatly overestimated during short-term laboratory experiments. On the other hand, dust removal may lead to false classification of the waste material (Zandi et al., 2007) and thus underestimation of the environmental risks of fine-grained slag particles dispersed in the smelter surroundings. Larger slag fragments are often observed on dumps (Ettler et al., 2003, 2009, Vítková et al. **I**); however, granulated slag disposal or fine particles escaping from slag treatment plants (e.g. crushers) also need to be considered (Vítková et al. **III**). Therefore, knowledge of the actual disposal scenario is necessary for evaluation of the hazardous properties of solid waste materials.

Vítková et al. (**III**) subjected copper smelter slag to a set of leaching experiments in order to investigate the effects of fine dust particles on the leaching results. Slag fragments (up to 7 cm in size) were crushed to < 5 mm (A1), < 4 mm (B1) and < 1 mm (C1). Subsamples A2 and B2 were obtained by discarding the dust fraction < 0.5 mm from A1 and B1, respectively. Finally, subsample A3 was obtained by dust removal from A1 and additional ultrasonic cleaning to remove fines adhering to coarser slag particles. The leaching behaviour of Cu and Co as function of the pH and the effects of particle size distribution are illustrated in Figure 7.

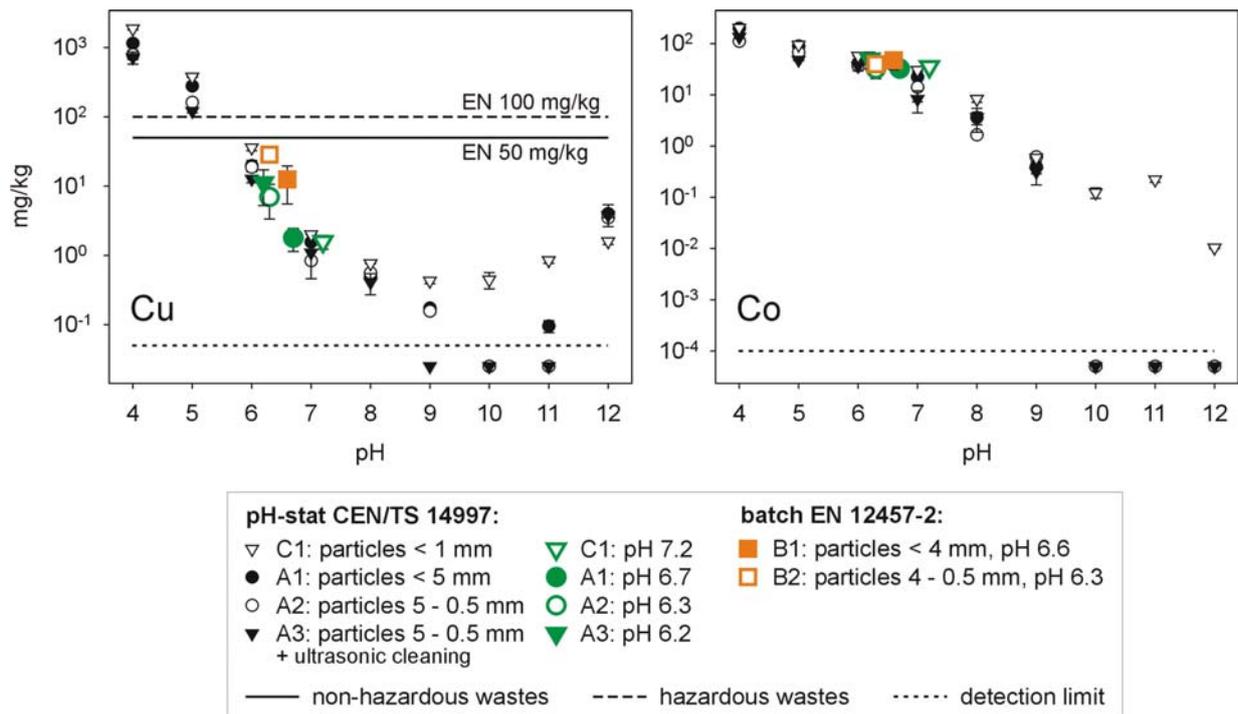


Figure 7 Leaching of Cu and Co from slag as a function of pH and/or particle size distribution and comparison with regulatory concentration limits for non-hazardous and hazardous waste (EC, 2003). The results of 48-h pH-static (CEN/TS 14997) leaching experiments including leaching at natural pH (green symbols) and of 24-h batch (EN 12457-2) experiments (orange symbols) are illustrated; symbols with vertical bars represent the mean and standard deviation of the measurements (source: Vítková et al. **III**).

Increased metal mobility was observed for samples with a higher proportion of dust (< 0.5 mm) fraction. Ultrasonic removal (A3) of the remaining dust particles decreased the concentrations even more (Figure 7). Mechanical activation of slags by milling has been applied in some studies (Ettler et al., 2009; Shanmuganathan et al., 2008) to simulate natural the weathering process in long-term and rather “worst-case” leaching scenario for granulated slags. As a consequence of milling, increased surface area, oxidation and phase structure alteration may occur and result in enhanced dissolution kinetics during leaching (Tkáčová and Baláž, 1996). Nevertheless, low metal concentrations were observed for milled slags studied by Ettler et al. (2009) under near neutral conditions using the EN 12457 standard. Similarly, Vítková et al. (**III**) showed that the metal concentrations in leachates without pH control (i.e. pH 6.2–7.2, Figure 7) were all below the EU limits for non-hazardous waste. Also, Shanmuganathan et al. (2008) reported that, although the metal release increased after mechanical activation and with a decrease in the pH, all the concentrations were within the limit values prescribed for the toxicity characteristic leaching procedure (TCLP; USEPA, 1994). The pH-static leaching performed by Vítková et al. (**III**) provides detailed insight into the leaching characteristics of potential contaminants in different environments. Particularly, the high release of metals under acidic conditions (Figure 7) can describe the slag reactivity in acidic soils (pH 4–5) adjacent to smelters in the surveyed Copperbelt area. Enhanced release of potential contaminants is generally observed under acidic conditions (pH < 6) for both coarser sized and fine-grained slag samples (Ettler et al., 2003, 2009; Pareuil et al., 2010;

Piatak & Seal, 2010; Vítková et al. **III**). In contrast, relatively high stability of slag even at pH 3 was recently reported by Lima & Bernardez (2011). However, the risk of high Cu and Co leachability from fine slag particles (Vítková et al. **III**) should be considered with respect to acidic soils near the Copperbelt smelters. The weathering of larger slag fragments on the dumps as well as fine slag particles dispersed near the slag re-processing plants (i.e. crushers) or granulated slag disposal are relevant scenarios in smelting sites in Africa (Ettler et al., 2009; Kříbek et al., 2010).

4.5.3 Effect of pH and time on leaching

Equilibrium conditions are assumed at the end of batch leaching experiments. Nevertheless, the dissolution/precipitation kinetics for some phases are much slower and non-equilibrium conditions may be obtained for some elements during the standard testing period. The following time-dependent leaching patterns have been previously distinguished for MSWI bottom ash (Dijkstra et al., 2006; Kirby & Rimstidt, 1994): (i) complete dissolution of a readily soluble phase, (ii) partial dissolution of a phase until equilibrium is reached, (iii) slow dissolution of a phase that does not reach equilibrium or steady state during the experiment (slow concentration increase), (iv) rapid dissolution of a phase until it is exhausted, followed by slower dissolution of a less soluble phase, and (v) concentration decrease. The role of newly formed phases and sorption processes should be taken into account. Moreover, the release of an element may display different time trends in different pH ranges (Dijkstra et al., 2006). Similar concentration changes with time and often mixed patterns (concentration increase followed by a decrease or vice versa) were observed for metallurgical solid wastes (Ettler et al., 2003, 2008; Parsons et al., 2001).

A number of analytical and geochemical tools for identification of the relevant mineral phases and mechanisms controlling the leaching behaviour of potential contaminants and the high importance of pH-dependent leaching data for basic characterisation of solid waste residues have already been discussed. Vítková et al. (**V**) studied the leaching behaviour of fly ash generated as a by-product during re-smelting of Cu-Co slags. In addition to calcite, mainly silicates and silicate glass were determined (Table 5, sample D2). The leachability of Ca, Mg, K, Fe, Al, and Si indicated partial dissolution of silicates and amorphous fractions, which are usually considered rather stable during short-term leaching experiments (Skeaff et al., 2011) due to their slow dissolution kinetics. However, acidic conditions ($\text{pH} \leq 5$) may enhance silicate solubility (Gitari et al., 2009). As a result of long-term glass alteration, the formation of clay minerals was reported on weathered MSWI ash (Zevenbergen et al., 1998). Similarly, illite was predicted to control the solubility of K, Mg, Al, and Si in the cobalt smelter fly ash studied by Vítková et al. (**V**). Moreover, transformation of poorly crystalline silicates and glass was assumed to partly control the leachability of metals considering the enrichment of Co, Cu and Zn in silicates and glass (Vítková et al. **V**). The highest release of Co, Cu, Pb and Zn was observed at pH 5, generally with the lowest concentrations leached at pH 9–11, and slightly increased leachability at pH 12 (Figure 8). The release patterns were similar for 24-h, 48-h and 168-h test. Sulphides and alloys represented the main metal carriers in the fly ash and thus their dissolution/oxidation lead to increased leachability of metals (Figure 8). A significant proportional decrease of metallic Cu, particularly at pH 5, was

determined during SEM observations as well as from the XRD patterns for the heavy mineral fraction (Vítková et al. V). In contrast, soluble metallic salts were typically observed to influence the leaching of smelter dusts investigated by Vítková et al. (2009; II) or Skeaff et al. (2011). Vítková et al. (2009) showed that quantitative analysis of phase transformations as a function of pH based on the diffraction data is an effective tool for understanding the contaminant leaching behaviour in smelter fly ash. However, this was not applicable for the cobalt fly ash from Chambishi as the content of metals in sulphides and silicates could not be fully quantified. Furthermore, a high portion of amorphous fraction enriched with metals was present in the sample (Vítková et al. V).

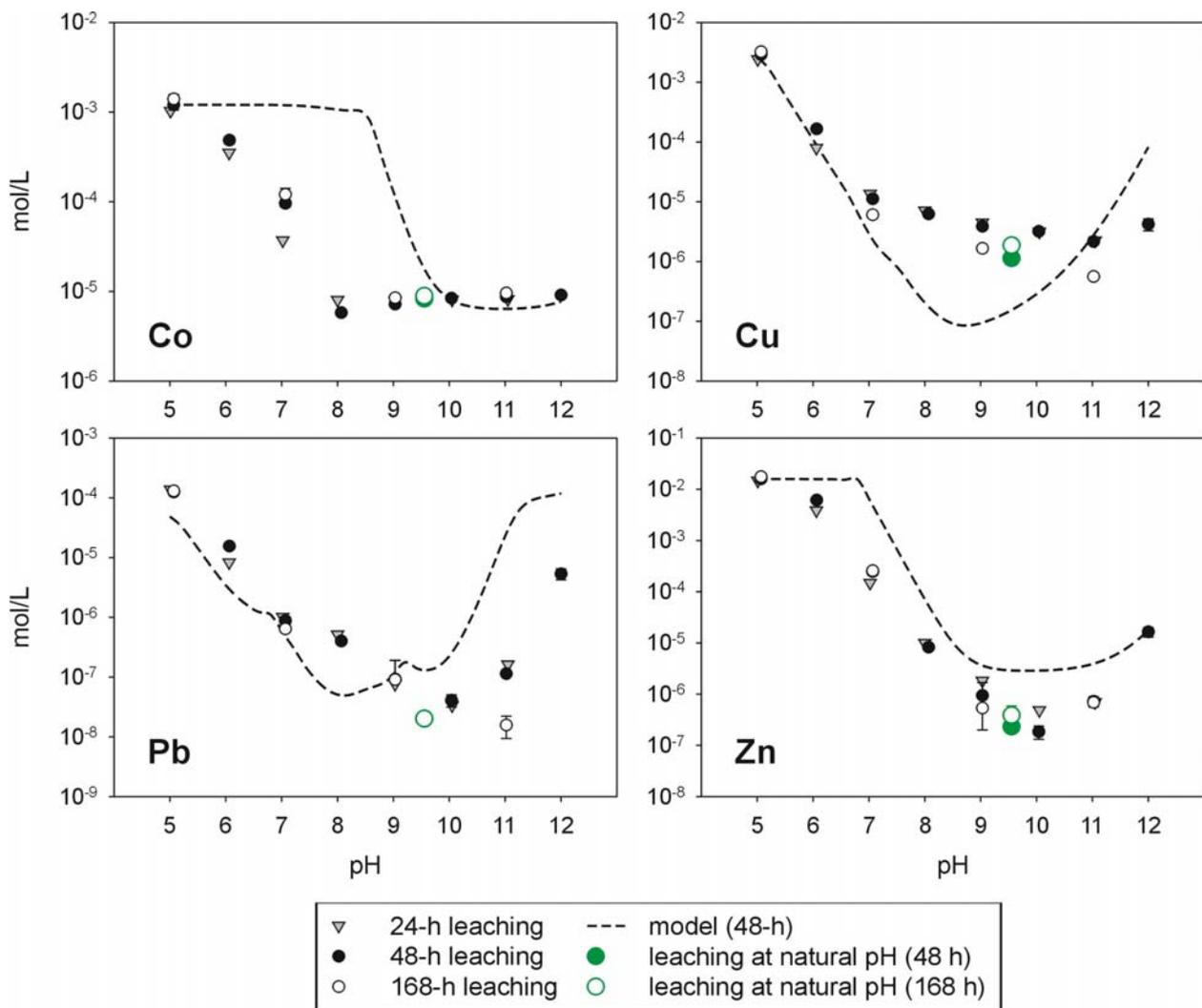


Figure 8 Leaching of Co, Cu, Pb and Zn from the fly ash (Chambishi) as a function of pH and time combined with the ORCHESTRA model prediction; symbols with vertical bars represent mean and standard deviation of the measurements (source: Vítková et al. V).

A combination of solubility and sorption-controlling mechanisms was predicted for Cu, Co, Pb and Zn using the ORCHESTRA model. Although they were not detected analytically, mainly CoO and zincite (ZnO) were suggested to control the leachability of Co and Zn from the cobalt fly ash, respectively. Zincite is highly soluble, particularly under acidic conditions (Bril et al., 2008). The release of Cu (Figure 8) was attributed to the solubility of secondary brochantite and malachite, which were also typically observed as weathering products on the Cu-Co slag surfaces (Vítková et al. **I**). Precipitation of HFO and sorption of metals onto the HFO surface were predicted to control the leaching of Cu and Pb, which corresponds well to other studies (Al-Abed et al., 2006; Meima & Comans, 1998). The prolonged time period of 168 h for the pH-static test did not exhibit any dramatic changes in the metal leachability (Figure 8). In some cases, the released concentrations increased slightly with time; however lower levels of Cu and Pb were observed at $\text{pH} > 7$ after 168 h, most likely due to surface complexation to HFO (Vítková et al. **V**).

5. Environmental and health implications

5.1 Environmental impacts of metallurgical wastes

Mining and smelting of non-ferrous metals pose a high pollution risk for natural systems, which has been reported in numerous studies (e.g. Beavington et al., 2004; Cappuyns et al., 2002; Ettler et al., 2005b, 2011; Křibek et al., 2010; Liu et al., 2010; Martley et al., 2004; Udachin et al., 2003). Dust fallout from smelters, mine tailings as well as slag dumps are typical point sources of soil contamination, also documented in the Copperbelt Province in Zambia (Ettler et al., 2011; Křibek et al., 2010). Elevated concentrations of As, Co, Cu, Pb, and Zn were determined in topsoils near the Nkana smelter, indicating the highest contamination north-west of the smelter (Ettler et al., 2011), which corresponds to prevailing wind direction in the area (see also *Chapter 2.1*). Similar spatial distribution was observed by Křibek et al. (2010) at other mining/smelting sites in the Copperbelt Province with a definite increase in metal contents in soils in the vicinity of the smelters. Copper was found to be the most critical contaminant due to its extremely high concentrations in the topsoil and high mobility in the soil profile (Ettler et al., 2011).

The properties of tropical soils are distinct from those of temperate soils and thus the predictions of metal mobility/bioavailability established for temperate soil types are not applicable in the tropics (Rieuwerts, 2007). Tropical soils are typically characterised by low pH, low-activity clays dominated by kaolinite, low organic matter contents and high levels of Fe oxides (Rieuwerts, 2007). Oxisols represent the main soil type in the Copperbelt area with pH generally < 5 with decreasing values in deeper horizons (Ettler et al., 2011; Křibek et al., 2010). In this context, the reactivity of slags and dusts investigated by Vítková et al. (**II**, **III**, **V**) showed high potential risk of soil contamination due to high leachability of metals under acidic conditions, further enhanced by the increased surface area of the residues (Vítková et al. **III**). Nevertheless, considering the above-mentioned soil properties, the influence of pH on the metal release in tropical soils may not be, by itself, as significant as for temperate soils (Rieuwerts, 2007). Křibek et al. (2010) showed that the correlation between the metal contents and the pH was observed only for Zn in topsoils, while several metals including Co and Cu were significantly correlated with the pH in the subsurface soil. On the other hand, the metals may be effectively attenuated by sorption onto Fe oxides (Rieuwerts, 2007).

Based on the natural attenuation processes observed in the Copperbelt (i.e. sorption of metals to HFO, formation of secondary sulphates, dissolution of carbonates) and considering the tropical climate in the area, sustainable disposal of the fly ash residue from the Chambishi smelter has been suggested (Vítková et al. **V**). The PHREEQC model calculations were used to predict the mobility of metals after mixing the fly ash with local Oxisol (composition derived from Ettler et al., 2011). The model showed that, if the pH is controlled by calcite addition, the presence of hematite can effectively reduce the metal mobility through adsorption (Vítková et al. **V**). Although a wide range of stabilisation methods for fly ashes have been discussed in the literature, the local solutions and on-site available stabilisation media should be primarily used with respect to the conditions found in developing countries such as Zambia.

Laboratory pot experiments were performed by Petrářová (2011) to investigate the release of contaminants from copper smelter dust into soil water and soil. Experimental bags with (i) fly ash from Chambishi (D2, *Chapter 3.4*) and (ii) ESP dust from Mufulira (D3, *Chapter 3.4*) were placed in pots with Oxisol and irrigated with deionised water. Samples of pore water were taken at different time intervals over 504 h. The released concentrations of Cu and Co exhibited an increase within 48 h (sample D2) and 216 h (sample D3), followed by a moderate decrease. The maximum concentrations of Zn were leached over 24 h and 144 h for samples D2 and D3, respectively. The leaching of Co, Cu and Zn was correlated with changes in the pH. Enhanced mobility of metals was observed in D3 samples, most likely due to the lower pH of the soil water (minimum pH 4.01). Chalcantite, the major primary phase of D3, was completely dissolved during the experiments and secondary antlerite precipitated. The dust composition after the experiment was in good agreement with the phase transformations reported by Vítková et al. (II). It was found that the mobile Co fraction in soils corresponded to 5–5.8% and 10–11% for samples D2 and D3, respectively (Petrářová, 2011). Similarly, Ettler et al. (2011) showed that about 3–4% Co was bound in the exchangeable fraction in the uppermost soil horizons of the Oxisols in the vicinity of the Nkana smelter. About 40% mobile Cu in soil was determined for sample D2 and as much as 64–78% in sample D3 (Petrářová, 2011). This is in accordance with the results observed in soils heavily polluted with Cu, where high Cu mobility was observed (Ettler et al., 2011; Křibek et al., 2010). Zinc exhibited poor binding to the soil fraction, indicating that Zn was preferably released into soil water (Petrářová, 2011).

Enhanced leaching of potential contaminants from soils and metallurgical residues may occur during precipitation events (Bril et al., 2008; Křibek et al., 2010; Navarro et al., 2008). Moreover, the dissolution of secondary sulphates may release metals and SO_4^{2-} into the environment and lower the pH, which further affects the contaminant leaching (Bril et al., 2008; Ettler et al., 2009; Navarro et al., 2008; Piatak et al., 2004). Slags and slag-like particles have traditionally been considered relatively stable materials, resistant to weathering due to the presence of low-solubility silicates, oxides and glass. However, it has been shown that potential contaminants incorporated in these compounds may be released into the environment, particularly under acidic conditions (Navarro et al., 2008; Parsons et al., 2001; Vítková et al. III, V). In addition, although sulphides and metallic phases are minor slag components, they are of concern due to their significant reactivity and high potential release of metals (Piatak & Seal, 2010).

5.2 Health risks

An effective flue gas cleaning system has been developed and installed in modern metallurgical plants to reduce the amount of dust emitted into the atmosphere. Despite the improvements in technology and thus air quality related to these operations, a certain amount of metallic particles still can escape into the environment (Beavington et al., 2004; Williamson et al., 2004). In relation to human exposure to contaminants in polluted areas, a number of laboratory methods have been developed to investigate the bioaccessibility/bioavailability of metals from wastes or contaminated soils (e.g. Julien et al., 2011; Oomen et al., 2002; Ruby et al., 1996; Twining et al., 2005). A severe health risk for humans exposed to metallic contaminants and As was reported in the Copperbelt mining and smelting district (Banza et al., 2009; Ettler et al., 2012). Smelter emissions are among the pollution sources that pose high health risks for populations living or working near the operations. However, health studies related to smelting activities are rare in this area (Banza et al., 2009; Ettler et al., 2012). In this context, smelter dusts from the Zambian Copperbelt (samples D1–D3, see *Chapter 3.4*) were subjected to laboratory experiments to investigate the oral (ingestion) and/or respiratory bioaccessibility of metals and As from these solid wastes.

It is known that dusts from smelting or combustion processes are enriched in a number of toxic elements, which are highly concentrated in smaller particles relative to the larger fraction (Campbell et al., 1978; Smith et al., 1979). Fine particles also have higher mobility in the atmosphere and higher solubility rates due to their larger surface area. All these aspects are important for bioaccessibility studies. A significant proportion of metallurgical dust has a size range that can be inhaled and deposited in the lungs. Particles < 10 µm were selected as a nominally respirable fraction. Moreover, it was assumed that dust may be partly ingested when it enters the body during breathing. Once the material enters the human body and comes into contact with biological fluids, there is a higher risk of dissolution and thus contaminant release and absorption. Determination of the contaminant solubility in simulated gastric and/or lung fluids provides better estimation of the potential toxicity of the dust than the total concentrations of these contaminants (Julien et al., 2011; Twining et al., 2005).

Laboratory *in vitro* methods provide important data about the rate and/or extent of contaminant dissolution in an extracting agent that resembles human tissue fluid. The fraction of a given contaminant which is released from the solid matrix into biological fluids and becomes available for absorption is referred to as the *bioaccessibility*. The *bioavailable fraction* can be defined as the amount of contaminant that is transferred to the circulatory system (Ruby et al., 1996; Semple et al., 2004; USEPA, 2007).

In this study, the bioaccessibility of Co, Cu, Pb, Zn and As was studied using simulated lung/gastric fluids (see Box 3 for details). The nominal < 10 µm fraction (denoted as FD1–FD2) of the dust samples was obtained by using a Bahco centrifugal separator. The size distributions of the separated fine fraction were determined using a laser diffraction particle size analyser. The bulk chemistry was determined after dissolution in mineral acids and/or sintering (see Vítková et al. V for details). The chemical composition of the separated dust is given in Appendix VI. The majority of the fractionated dust had a size of less than 10 µm, yielding 81.5%, 79% and 93.5% for samples FD1, FD2 and FD3, respectively (Appendix VI).

The range of dust particles was larger than the fraction that is likely to be inhaled and enter the pulmonary system, which could underestimate the final bioaccessibility in SLF. Nevertheless, most of the particles would be respirable and thus the results provide a valuable estimate of the bioaccessible fraction in the lungs (Twining et al., 2005). The original dust samples D1–D3 (i.e. bulk fraction, Appendix VI) were used for evaluation of the ingestion toxicology. The bioaccessibility (%) was calculated as the fraction present in the biofluid divided by the total concentration of the given element, times 100.

Box 3 Bioaccessibility testing as used in this study.

Leaching in simulated lung fluid (SLF): An *in vitro* method using simulated lung fluid (composition taken from Twining et al., 2005) with L/S ratio of 100 L/kg and performed at 37°C to simulate basal human temperature. Only the nominal < 10 µm fraction was used for testing. A mass of dry dust sample fraction (FD1–FD3) was placed in PP centrifuge tubes and mixed with fresh SLF; the tubes were placed in a laboratory oven (set to 37°C) and agitated occasionally. Each sample was subjected to 2-h, 6-h, 12-h and 24-h leaching, run in triplicate with procedural blanks. During the experiments, the pH was adjusted to 7.4 ± 0.2 using dilute HCl or NaOH (Julien et al., 2011) as necessary. After the experiments, the pH, Eh and specific conductivity were measured. The suspensions were centrifuged, filtered through 0.45 µm and prepared for ICP-MS analysis. CertiPUR[®] reference material was used for quality control of the measurements.

Leaching in simulated gastric fluid (SGF) according to USEPA (2007): An *in vitro* method using simulated gastric fluid (0.4 M glycine adjusted to pH 1.5 with HCl) with L/S ratio of 100 L/kg and performed at 37°C to simulate basal human temperature. The pH is similar to the pH in the stomach of a fasting human being. A mass of dry dust sample (D1–D3) was placed in PP centrifuge tubes and mixed with fresh SGF; the tubes were placed in a laboratory oven (set to 37°C) and agitated occasionally for 2 hours. Each sample was run in triplicate with procedural blanks. The pH was verified during the experiment. After the experiments, the pH, Eh and specific conductivity were measured. The suspensions were centrifuged, filtered through 0.45 µm and prepared for ICP-MS analysis. CertiPUR[®] reference material was used for quality control of the measurements.

The results of the bioaccessible leaching in SLF are reported in Appendix VI. No significant time-dependent patterns of contaminant leachability were observed. The maximum bioaccessibilities of Co, Cu, Zn and As were 0.3–16%, 0.3–2%, 0.4–1.2% and 0.1–2.9%, respectively. These fractions are much lower than the solubilities reported by Twining et al. (2005) for coal fly ash (up to 80% of Zn) or Julien et al. (2011), who tested the release of metals from atmospheric particles using several standard reference materials. In most cases the maximum was reached within the first 2–6 hours, while Zn and As concentrations tended to increase with time for sample FD1. The extraction time represents the residence time of particles in the lungs. Experiments with a duration of a few minutes to several days have previously been performed (Berlinger et al., 2008; Julien et al., 2011; Twining et al., 2005) to

simulate the kinetics of particle removal from the lung environment. Julien et al. (2011) reported rapid dissolution Pb and Zn during the first 30 min to 5 h and a relatively steady state between 24 h and 48 h of the test. The residence time of 24 h was assumed to be an adequate time period as most of the particles are dissolved within this time (Berlinger et al., 2008; Julien et al., 2011).

The bioaccessible fractions of Co, Cu, Pb, Zn and As were all higher than 20% in SGF (Figure 9). The maximum bioaccessibilities of Co, Pb and Zn were observed for sample D2, yielding 80%, 89% and 77%, respectively. Bioaccessible Cu ranged between 42% and 50% for D1–D3 and maximum bioaccessibility of As (83%) was obtained for sample D3. Similarly, high bioaccessibilities of these contaminants related to topsoil ingestion in the smelter areas of the Copperbelt have recently been reported by Ettler et al. (2012).

The bioaccessible fractions detected in SLF and SGF were significantly different for all the studied dust samples due to different contaminant solubilities in the fluids used. High bioaccessibility values are typically observed for experiments at low pH of about 1.5, which corresponds to fasting gastric pH (Oomen et al., 2002; Ruby et al., 1996). The substantial variation in the leachability of the contaminants from different materials is most likely the result of their different solid speciation (silicates, sulphates, oxides or sulphides) present in the dust. For example, the pH-dependent leaching behaviour reported by Vítková et al. (II) showed that primary chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was readily dissolved and large amounts of Cu were released under acidic conditions. Rapid desorption of Pb from the HFO surfaces and increased Pb bioaccessibility can be assumed in the acidic gastric environment (Ruby et al., 1996). Further evaluation of the risk of inhalation/ingestion of the metallurgical dust needs to be conducted in relation to assumptions connected with inhalation/ingestion rates. However, the first results presented here indicate severe health risk for populations exposed to the smelter dusts.

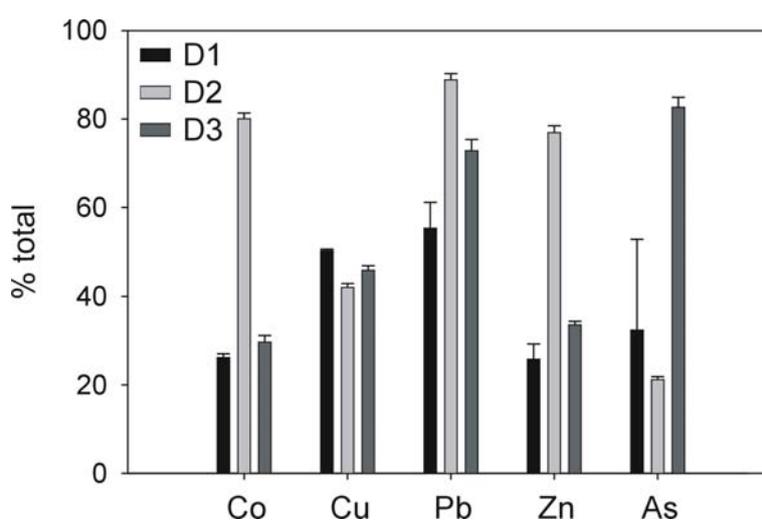


Figure 9 Bioaccessible fractions of Co, Cu, Zn and As leached in simulated gastric fluid; data expressed as % of the total concentrations in the original dust samples, symbols with vertical bars represent the mean and standard deviation of the measurements ($n = 3$).

6. Conclusions

Detailed mineralogical and geochemical characterisations of Cu-Co metallurgical wastes from the smelting area of the Zambian Copperbelt have been performed. The results provide new data on the environmental properties of metallurgical wastes and emphasize the importance of the research conducted in the Zambian Copperbelt to elucidate possible environmental and health risks.

The main findings of this study are given in comparison with the goals that were stated in the Introduction:

(i) Characterise chemical and mineralogical compositions of metallurgical wastes from the Zambian Copperbelt

Determination of the distribution of potential contaminants in the primary phases was the first step in the environmental impact assessment of the metallurgical waste. The slags are enriched in Co and Cu, which are present in various forms. The main metal carriers are sulphides (bornite, digenite, chalcocite, cobaltpentlandite), Co-bearing intermetallic phases and alloys. Elevated concentrations of Co and Cu were detected in major silicates and spinels, substituting for Fe or Mg in their structures, and in glass. The presence of secondary metal-bearing phases, such as malachite, brochantite and sphaerocobaltite, indicates the reactivity of slags exposed to water/atmosphere during weathering on the dumps.

Different solid speciation of metals was observed for the studied dusts. *Slag dust* generally corresponds to the *slag* composition. Chalcantite and delafossite are the predominant Cu-phases in the *ESP dust*. Enrichment of Co, Cu and Zn in the silicates and the glassy fraction was observed for the *fly ash*. Further separation of the heavy mineral fraction of the *fly ash* allowed the identification of minor metallic phases. Minor to trace Cu sulphides of various compositions (Cu(Fe,Co)S) were detected in all the studied dusts.

The problem of reliability of chemical microanalysis using EPMA and SEM has been addressed. Limited spatial resolution of these methods does not allow detection of the nanophases that could occur in the matrix and thus are erroneously considered to be part of the crystal structure of the dominant phase. This implies that, in justified cases, methods with higher resolution (such as FIB-TEM) need to be employed to verify the contaminant speciation in solid waste materials.

(ii) Investigate the leaching behaviour of smelter slags and dusts by laboratory experiments and geochemical modelling

The leaching behaviour of *slags* is strongly pH-dependent with the highest concentrations of Co, Cu and Zn released at pH 4 and 5. Various Cu- and Co-bearing carbonates, hydroxides, oxides or sulphates exhibit close-to-zero saturation indices under near-neutral conditions and are considered to attenuate the metal release.

Extensive contaminant leaching was observed for the *ESP dust*, even at the natural pH (~ 4.3) of the dust. Primary chalcantite is readily dissolved and secondary antlerite and brochantite are formed. Formation of secondary Fe oxides was suggested.

The leaching behaviour of the *fly ash* showed the highest concentrations of Co, Cu, Pb and Zn at pH 5 followed by a decrease towards pH 9–11 and slightly increased concentrations at pH 12. The release of metals is mainly attributed to the dissolution of minor metallic phases and partial dissolution of the silicate or the glassy fraction. ORCHESTRA geochemical modelling was successfully employed for *fly ash* solubility-control predictions. The model suggested that CoO and zincite control the Co and Zn leaching, respectively. Sorption on hydrous ferric oxides was assumed to provide effective attenuation for Pb and Cu release.

(iii) Evaluate the effects of the sample handling and experimental conditions on the release of contaminants

Grain size reduction required by standardised leaching protocols used to evaluate hazardous properties of solid waste materials is a crucial factor that affects the leaching results. Various *slag* sample pretreatment procedures (crushing, sieving, cleaning) have resulted in significant differences in contaminant leachability. Greater release of Cu, Co and Zn was observed for samples with a higher portion of fine dust particles. Although the metal levels at the natural pH were all below the EU criteria for non-hazardous materials, the concentrations of metals at pH 4 dramatically increased in the presence of the fine dust fraction.

Prolonged testing time of 168 h did not result in significant changes in the *fly ash* leachability, indicating that near-equilibrium conditions were achieved in the system during the standard testing time of 48 h.

(iv) Assess the environmental and health risks of the studied metallurgical wastes

The pH-dependent reactivity of slags and dusts investigated in this study showed high risk of contamination for acidic soils in the smelting area of the Copperbelt. Serious environmental impact may occur during the rainy season, when metals from dust-polluted soils are mobilised. Moreover, high bioaccessible fractions of Co, Cu, Pb, Zn and As of the smelter dusts exposed to simulated gastric fluid indicate severe health risks for local populations in the Copperbelt mining and smelting district.

In conclusion, pH-dependent leaching combined with detailed mineralogical investigations and “multisurface” geochemical models were found to be a powerful tool for contaminant leachability prediction. A suitable leaching protocol and relevant testing conditions need to be selected with respect to actual disposal scenarios.

References

- Acma, E., Sesigur, H., Addemir, O., Tekin, A. (1997): Processing of Kure (Turkey) copper slag for the recovery of copper and cobalt and the production of gamma Fe₂O₃. *Trans. Indian Inst. Met.* **50**: 147–151.
- Al-Abed, S.R., Hageman, P.L., Jegadeesan, G., Madhavan, N., Allen, D. (2006): Comparative evaluation of short-term leach tests for heavy metal release from mineral processing waste. *Sci. Total Environ.* **364**: 14–23.
- Astrup, T., Dijkstra, J.J., Comans, R.N.J., van der Sloot, H.A., Christensen, T.H. (2006a): Geochemical modeling of leaching from MSWI air-pollution-control residues. *Environ. Sci. Technol.* **40**: 3551–3557.
- Astrup, T., Jakobsen, R., Christensen, T.H., Hansen, J.B., Hjelmar, O. (2006b): Assessment of long-term pH developments in leachate from waste incineration residues. *Waste Manage. Res.* **24**: 491–502.
- Banda, W., Morgan, N., Eksteen, J.J. (2002): The role of slag modifiers on the selective recovery of cobalt and copper from waste smelter slag. *Miner. Eng.* **15**: 899–907.
- Banza, C.L.N., Nawrot, T.S., Haufroid, V., Decrée, S., De Putter, T., Smolders, E., Kabyla, B.I., Luboya, O.N., Ilunga, A.N., Mutombo, A.M., Nemery, B. (2009): High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. *Environ. Res.* **109**: 745–752.
- Beavington, F., Cawse, P.A., Wakenshaw, A. (2004): Comparative studies of atmospheric trace elements: improvements in air quality near a copper smelter. *Sci. Total Environ.* **332**: 39–49.
- Berlinger, B., Ellingsen, D.G., Náray, M., Záray, G., Thomassen, Y. (2008): A study of the bio-accessibility of welding fumes. *J. Environ. Monit.* **10**: 1448–1453.
- Bril, H., Zainoun, K., Puziewicz, J., Courtin-Nomade, A., Vanaecker, M., Bollinger, J.C. (2008): Secondary phases from the alteration of a pile of zinc-smelting slags as indicators of environmental conditions: an example from Świętochłowice, Upper Silesia, Poland. *Can. Mineral.* **46**: 1235–248.
- Brunori, C., Balzamo, S., Morabito, R. (2001): Comparison between different leaching tests for the evaluation of metal release from fly ash. *Fresenius J. Anal. Chem.* **371**: 843–848.
- Campbell, J.A., Laul, J.C., Nielson, K.K., Smith, R.D. (1978): Separation and chemical characterization of finely-sized fly-ash particles. *Anal. Chem.* **50**: 1032–1040.
- Cappuyns, V., Swennen, R. (2008): The application of pHstat leaching tests to assess the pH dependent release of trace metals from soils, sediments and waste materials. *J. Hazard. Mater.* **158**: 185–195.
- Cappuyns, V., Van Herreweghe, S., Swennen, R., Ottenburgs, R., Deckers, J. (2002): Arsenic pollution at the industrial site of Reppel-Bocholt (north Belgium). *Sci. Total Environ.* **295**: 217–240.
- CEN/TS 14405 (2004): Characterization of waste – Leaching behaviour tests – Up-flow percolation test (under specified conditions). CEN, Brussels, Belgium.
- CEN/TS 14429 (2003): Characterization of waste – Leaching behaviour tests – Influence of pH on leaching with initial acid/base addition. CEN, Brussels, Belgium.

- CEN/TS 14997 (2006): Characterization of waste – Leaching behaviour tests – Influence of pH on leaching with continuous pH-control. CEN, Brussels, Belgium.
- CEN/TS 15863: Characterization of waste - Leaching behaviour test for basic characterisation - Dynamic Monolithic Leaching Test with periodic leachant renewal under fixed test conditions (Standard in development).
- CSO, Central Statistical Office (CSO), Ministry of Health (MOH), Tropical Diseases Research Centre (TDRC), University of Zambia, Macro International Inc. (2009): Zambia Demographic and Health Survey 2007. CSO and Macro International Inc., Calverton, Maryland, USA, 482 pp.
- Cutler, C.J., Natarajan, M., Mponda, E., Eksteen, J.J. (2006): Phasing out reveratory furnace operations at KCM Nkana. In: *Southern African Pyrometallurgy 2006* (R.T. Jones, editor). South African Institute of Mining and Metallurgy, Johannesburg, March 5–8, 2006, pp. 251–264.
- CZDA, Czech Development Agency (2006): Program rozvojové spolupráce mezi Českou republikou a Zambií na období 2006–2010 (in Czech). (<http://www.czda.cz/cra/projekty/zambie.htm>, accessed on July 11th, 2012)
- CZDA, Czech Development Agency (2010): The development cooperation strategy of the Czech Republic 2010–2017. (<http://www.czda.cz/czda/where-we-work.htm?lang=en>, accessed on July 11th, 2012)
- Davenport, W.G., King, M., Schlesinger, M., Biswas, A.K. (2002): Extractive metallurgy of copper, 4th Edition. Pergamon Press, 452 pp.
- Dijkstra, J.J., van der Sloot, H.A., Comans, R.N.J. (2006): The leaching of major and trace elements from MSWI bottom ash as a function of pH and time. *Appl. Geochem.* **21**: 335–351.
- Dijkstra, J.J., Meeussen, J.C.L, Comans, R.N.J. (2009): Evaluation of a generic multisurface sorption model for inorganic soil contaminants. *Environ. Sci. Technol.* **43**: 6196–6201.
- Doyle, T.A., Davis, A., Runnells, D.D. (1994): Predicting the environmental stability of treated copper smelter flue dust. *Appl. Geochem.* **9**: 337–350.
- Dzombak, D.A., Morel, F.M.M. (1990): Surface complexation modeling: hydrous ferric oxides. John Wiley & Sons, Inc., New York, USA.
- EC (2003): Council Decision 2003/33/EC 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. Commun.* L11, 27–49.
- Eighmy, T.T., Eusden, J.D., Krzanowski, J.E., Domingo, D.S., Stämpfli, D., Martin, J.R., Erickson, P.M. (1995): Comprehensive approach towards understanding element speciation and leaching behavior in municipal solid waste electrostatic precipitator ash. *Environ. Sci. Technol.* **29**: 629–646.
- EN 12457 (1999): Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges, parts 1–4. CEN, Brussels, Belgium.
- Ettler, V., Legendre, O., Bodéan, F., Touray, J.C. (2001): Primary phases and natural weathering of old lead-zinc pyrometallurgical slag from Příbram, Czech Republic. *Can. Mineral.* **39**: 873–888.

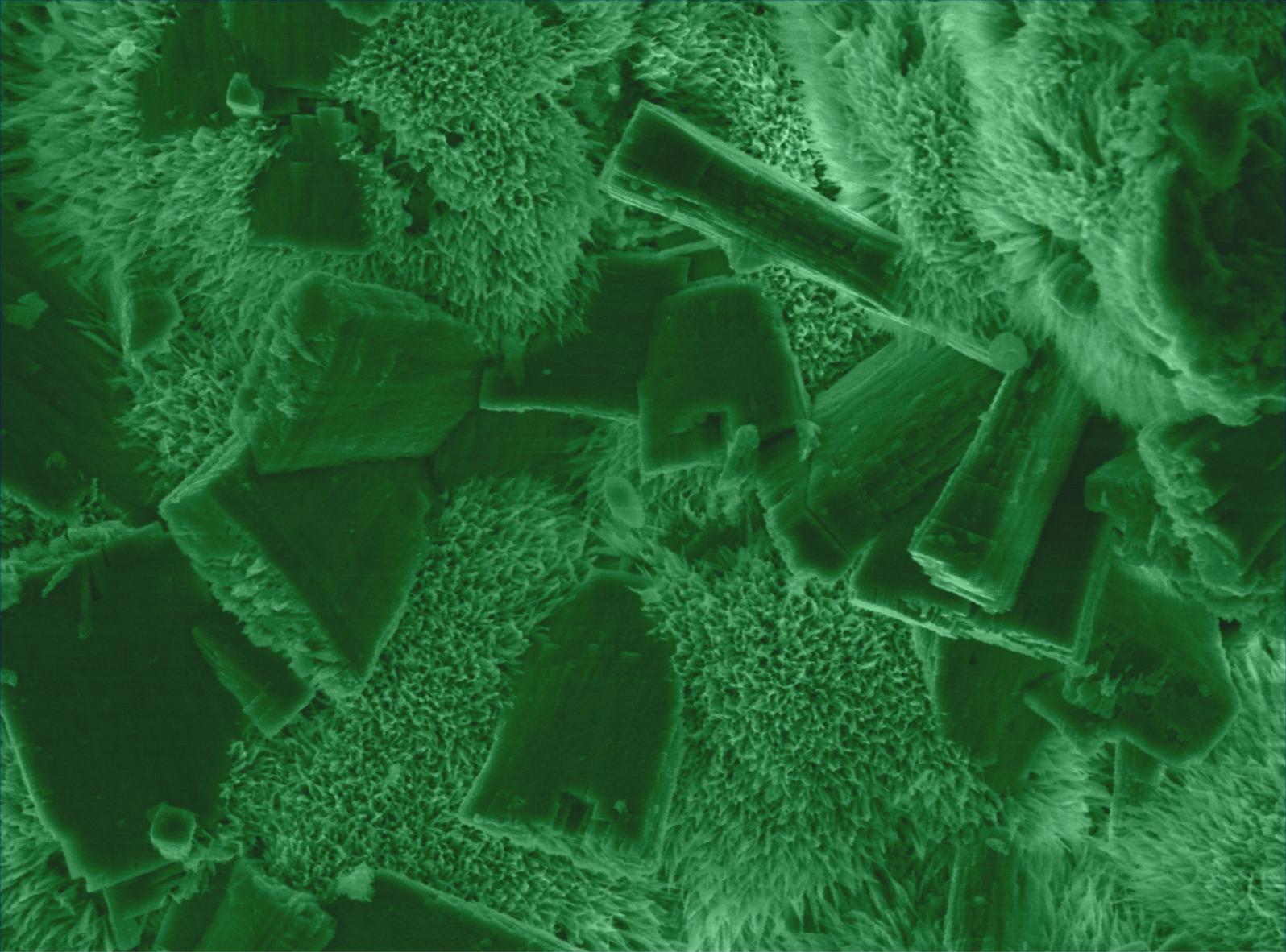
- Ettler, V., Piantone, P., Touray, J.C. (2003): Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental results and long-term assessment. *Mineral. Mag.* **67**: 1269–1283.
- Ettler, V., Komárková, M., Jehlička, J., Coufal, P., Hradil, D., Machovič, V., Delorme, F. (2004): Leaching of lead metallurgical slag in citric solutions—implications for disposal and weathering in soil environments. *Chemosphere* **57**: 567–577.
- Ettler, V., Johan, Z., Baronnet, A., Jankovský, F., Gilles, C., Mihaljevič, M., Šebek, O., Strnad, L., Bezdička, P. (2005a): Mineralogy of air-pollution-control residues from a secondary lead smelter: Environmental implications. *Environ. Sci. Technol.* **39**: 9309–9316.
- Ettler, V., Vaněk, A., Mihaljevič, M., Bezdička, P. (2005b): Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. *Chemosphere* **58**: 1449–1459.
- Ettler, V., Šebek, O., Grygar, T., Klementová, M., Bezdička, P., Slavíková, H. (2008): Controls on metal leaching from secondary Pb smelter air-pollution-control residues. *Environ. Sci. Technol.* **42**: 7878–7884.
- 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.
- Ettler, V., Mihaljevič, M., Kříbek, B., Majer, V., Šebek, O. (2011): Tracing the spatial distribution and mobility of metal/metalloid contaminants in Oxisols in the vicinity of the Nkana copper smelter, Copperbelt province, Zambia. *Geoderma* **164**: 73–84.
- Ettler, V., Kříbek, B., Majer, V., Knésl, I., Mihaljevič, M. (2012): Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). *J. Geochem. Explor.* **113**: 68–75.
- Fällman, A.M. (1997): Performance and design of the availability test for measurement of potentially leachable amounts from waste materials. *Environ. Sci. Technol.* **31**: 735–744.
- Fleischer, V.D. (1984): Discovery, geology and genesis of copper-cobalt mineralisation at Chambishi Southeast prospect, Zambia. *Precambrian Res.* **25**: 119–133.
- GAA, Golder Associates Africa (Pty) Ltd (2011): Independent technical reports: Mopani report. Glencore International plc, Switzerland.
- Garlic, W.G. (1964): Association of mineralization and algal reef structures on Northern Rhodesian copper-belt, Katanga, and Australia. *Econ. Geol.* **59**: 416–427.
- Gitari, W.M., Fatoba, O.O., Petrik, L.F., Vadapalli, V.R.K. (2009): Leaching characteristics of selected South African fly ashes: Effect of pH on the release of major and trace species. *J. Environ. Sci. Health. Part A* **44**: 206–220.
- Gorai, B., Jana, R.K., Premchand (2003): Characteristics and utilisation of copper slag – a review. *Resour. Conserv. Recycl.* **39**: 299–313.
- Hjelmar, O. (1990): Leachate from land disposal of coal fly ash. *Waste Manage. Res.* **8**: 429–449.
- Hjelmar, O. (1996): Disposal strategies for municipal solid waste incineration residues. *J. Hazard. Mater.* **47**: 345–368.

- Hyks, J., Astrup, T., Christensen, T.H. (2007): Influence of test conditions on solubility controlled leaching predictions from air-pollution-control residues. *Waste Manage. Res.* **25**: 457–466.
- Hyks, J., Astrup, T., Christensen, T.H. (2009a): Leaching from MSWI bottom ash: Evaluation of non-equilibrium in column percolation experiments. *Waste Manage.* **29**: 522–529.
- Hyks, J., Astrup, T., Christensen, T.H. (2009b): Long-term leaching from MSWI air-pollution-control residues: Leaching characterization and modeling. *J. Hazard. Mater.* **162**: 80–91.
- Jones, R.T., Denton, G.M., Reynolds, Q.G., Parker, J.A.L. and 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.* **102**: 5–10.
- Julien, C., Esperanza, P., Bruno, M., Alleman, L.Y. (2011): Development of an in vitro method to estimate lung bioaccessibility of metals from atmospheric particles. *J. Environ. Monit.* **13**: 621–630.
- Kaksonen, A.H., Lavonen, L., Kuusenaho, M., Kolli, A., Nähli, H., Vestola, E., Puhakka, J.A., Tuovinen, O.H. (2011): Bioleaching and recovery of metals from final slag waste of the copper smelting industry. *Miner. Eng.* **24**: 1113–1121.
- Kamona, A.F., Nyambe, I.A. (2002): Geological characteristics and genesis of stratiform sediment-hosted Cu-(Co) deposits, Zambian Copperbelt. In: *Proceedings of 11th IAGOD Quadrennial Symposium and Geocongress*, Miller, R.E. (Ed.), Extended Abstracts. Geological Survey of Namibia, Windhoek, Namibia (CD version).
- Kierczak, J., Néel, C., Puziewicz, J., Bril, H. (2009): The mineralogy and weathering of slag produced by the smelting of lateritic Ni ores, Szklary, Southwestern Poland. *Can. Mineral.* **47**: 557–572.
- Kirby, C.S., Rimstidt, J.D. (1994). Interaction of municipal solid waste ash with water. *Environ. Sci. Technol.* **28**: 443–451.
- Kosson, D.S., van der Sloot, H.A., Sanchez, F., Garrabrants, A.C. (2002): An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Environ. Eng. Sci.* **19**: 159–204.
- Kříbek, B., Majer, V., Veselovský, F., Nyambe, 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.
- Lee, M.R. (2010): Transmission electron microscopy (TEM) of Earth and planetary materials: A review. *Mineral. Mag.* **74**: 1–27.
- Lima de Andrade L.R.P., Bernardez, L.A. (2011): Characterization of the lead smelter slag in Santo Amaro, Bahia, Brazil. *J. Hazard. Mater.* **189**: 692–699.
- Liu, L., Wu, L., Luo, Y., Zhang, C. Jiang, Y., Qiu, X. (2010) The impact of a copper smelter on adjacent soil zinc and cadmium fractions and soil organic carbon. *J. Soils Sediments* **10**: 808–817.
- Lottermoser B.G. (2002): Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia. *Mineral. Mag.* **66**: 475–490.
- Lottermoser B.G. (2005): Evaporative mineral precipitates from a historical smelting slag dump, Río Tinto, Spain. *Neues Jahrbuch für Mineralogie (Abhandlungen)* **181**: 183–190.

- Martley, E., Gulson, B.L., Pfeifer, H.-R. (2004): Metal concentrations in soils around the copper smelter and surrounding industrial complex of Port Kembla, NSW, Australia. *Sci. Total Environ.* **325**: 113–127.
- McGowan, R.R., Roberts, S., Boyce, A.J. (2006): Origin of the Nchanga copper-cobalt deposits of the Zambian Copperbelt. *Miner. Deposita* **40**: 617–638.
- Meeussen, J.C.L. (2003): ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. *Environ. Sci. Technol.* **37**: 1175–1182.
- Meima, J.A., Comans, R.N.J. (1998): Application of surface complexation/precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash. *Environ. Sci. Technol.* **32**: 688–693.
- Meima, J.A., van Zomeren, A., Comans, R.N.J. (1999): Complexation of Cu with dissolved organic carbon in municipal solid waste incinerator bottom ash leachates. *Environ. Sci. Technol.* **33**: 1424–1429.
- Munnik, E., Singh, H., Uys, T., Bellino, M., du Plessis, J., Fraser, K., Harris, G.B. (2003): Development and implementation of a novel pressure leach process for the recovery of cobalt and copper at Chambishi, Zambia. *J. S. Afr. Inst. Min. Metall.* JANUARY/FEBRUARY: 1–10.
- Navarro, A., Cardellach, E., Mendoza, J.L., Corbella, M., Doménech, L.M. (2008): Metal mobilization from base-metal smelting slag dumps in Sierra Almagrera (Almería, Spain). *Appl. Geochem.* **23**: 895–913.
- Oomen, A.G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, C., Schoeters, G., Verstraete, W., Van de Wiele, T., Wragg, J., Rempelberg, C.J.M., Sips, A.J.A.M., Van Wijnen, J.H. (2002): Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. *Environ. Sci. Technol.* **36**: 3326–3334.
- Pareuil, P., Bordas, F., Joussein, E., Bollinger, J.C. (2010): Leaching properties of Mn-slag from the pyrometallurgical recycling of alkaline batteries: standardized leaching tests and influence of operational parameters. *Environ. Technol.* **31**: 1565–1576.
- Parkhurst, D.L., Appelo, C.A.J. (1999): User's Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations. US Geol. Surv. Water Resour. Invest. Rep. No. 99-4259.
- Parsons, M.B., Bird, D.K., Einaudi, M.T., Alpers, C.N. (2001): Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California. *Appl. Geochem.* **16**: 1567–1593.
- Petráňová, V. (2011): Experimental investigation of copper smelter fly ash dissolution in a tropical soil (in Czech). MSc. Thesis. Charles University in Prague, Faculty of Science, Prague, Czech Republic.
- Piantone, P. (2004): Mineralogy and pollutant-trapping mechanisms. *C.R. Geosci.* **336**: 1415–1416.
- Piatak, N.M., Seal II, R.R., Hammarstrom, J.M. (2004): Mineralogical and geochemical controls on the release of trace elements from slag produced by base- and precious-metal smelting at abandoned mine sites. *Appl. Geochem.* **19**: 1039–1064.
- Piatak, N.M., Seal II, R.R. (2010): Mineralogy and the release of trace elements from slag from the Hegeler Zinc smelter, Illinois (USA). *Appl. Geochem.* **25**: 302–320.

- Porada, H., Berhorst, V. (2000): Towards a new understanding of the Neoproterozoic-early palaeozoic Lufilian and northern Zambezi belts in Zambia and the Democratic Republic of Congo. *J. Afr. Earth. Sci.* **30**: 727–771.
- Potts, P.J., Bowles, J.F.W., Reed, S.J.B., Cave, M.R. (1995): Microprobe Techniques in the Earth Sciences. The Mineralogical Society series 6, Chapman & Hall, London, England.
- Quina, M.J., Bordado, J.C.M., Quinta-Ferreira, R.M. (2011): Percolation and batch leaching tests to assess release of inorganic pollutants from municipal solid waste incinerator residues. *Waste Manage.* **31**: 236–245.
- Rieuwerts, J.S. (2007): The mobility and bioavailability of trace metals in tropical soils: a review. *Chem. Speciation Bioavailability* **19**: 75–85.
- Ross, J., de Vries, D. (2005): Mufulira smelter upgrade project – “Industry” smelting on the Zambian Copperbelt. Mopani Copper Mines PLC Internal Report, Kitwe, Zambia, 22 pp.
- Ruby, M.V., Davis, A., Schoof, R., Eberle, S., Sellstone, C.M. (1996): Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Environ. Sci. Technol.* **30**: 422–430.
- Rudnik, E., Burzyńska, L., Gumowska, W. (2009): Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag. *Miner. Eng.* **22**: 88–95.
- Samuelsson, C., Björkman, B. (1998): Dust forming mechanisms in the gas cleaning system after the copper converting process. *Scand. J. Metall.* **27**: 54–63.
- Samuelsson, C., Carlsson, G. (2001): Characterization of copper smelter dusts. *CIM Bull.* **94**: 111–115.
- Seigneur, N., Gauthier, A., Bulteel, D., Buatier, M., Recourt, P., Damidot, D., Potdevin, J.L. (2007): Effect of Pb-rich and Fe-rich entities during alteration of a partially vitrified metallurgical waste. *J. Hazard. Mater.* **149**: 418–431.
- Semple, K.T., Doick, K.J., Jones, K.C., Burauel, P., Craven, A., Harms, H. (2004): Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environ. Sci. Technol.* **38**: 228A–231A.
- Shanmuganathan, P., Lakshminathiraj, P., Srikanth, S., Nachiappan, A.L., Sumathy, A. (2008): Toxicity characterization and long-term stability studies on copper slag from the ISASMELT process. *Resour. Conserv. Recycl.* **52**: 601–611.
- Skeaff, J.M., Thibault, Y., Hardy, D.J. (2011): A new method for the characterisation and quantitative speciation of base metal smelter stack particulates. *Environ. Monit. Assess.* **177**: 165–192.
- Smith, R.D., Campbell, J.A., Nielson, K.K. (1979): Concentration dependence upon particle size of volatilized elements in fly ash. *Environ. Sci. Technol.* **13**: 553–558.
- Sobanska, S., Ricq, N., Laboudigue, A., Guillermo, R., Brémard, C., Laureyns, J., Merlin, J.C., Wignacourt, J.P. (1999): Microchemical investigations of dust emitted by a lead smelter. *Environ. Sci. Technol.* **33**: 1334–1339.
- Sracek, O., Veselovský, F., Křibek, B., Malec, J., Jehlička, J. (2010): Geochemistry, mineralogy and environmental impact of precipitated efflorescent salts at the Kabwe Cu–Co chemical leaching plant in Zambia. *Appl. Geochem.* **25**: 1815–1824.
- Tkáčová, K., Baláž, P. (1996): Reactivity of mechanically activated chalcopyrite. *Int. J. Miner. Process.* **44–45**: 197–208.

- Twining, J., McGlenn, P., Loi, E., Smith, K., Gieré, R. (2005): Risk ranking of bioaccessible metals from fly ash dissolved in simulated lung and gut fluids. *Environ. Sci. Technol.* **39**: 7749–7756.
- Udachin, V., Williamson, B.J., Purvis, O.W., Spiro, B., Dubbin, W., Brooks, S., Coste, B., Herrington, R.J., Mikhailova, I. (2003): Assessment of environmental impacts of active smelter operations and abandoned mines in Karabash, Ural Mountains of Russia. *J. Sustainable Dev.* **11**: 133–142.
- USEPA (1994): Toxicity Characteristic Leaching Procedure (TCLP), Method 1311, Solid Waste Characterization Manual SW-848, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Athens, Georgia, USA (<http://www.epa.gov>).
- USEPA (2007): Estimation of relative bioavailability of lead in soil and soil-like materials using *in vivo* and *in vitro* methods. Office of Solid Waste and Emergency Response, US EPA, Washington. OSWER 9285.7-77.
- Uzu, G., Sauvain, J.-J., Baeza-Squiban, A., Riediker, M., Sánchez Sandoval Hohl, M., Val, S., Tack, K., Denys, S., Pradère, P., Dumat, C. (2011): In vitro assessment of the pulmonary toxicity and gastric availability of lead-rich particles from a lead recycling plant. *Environ. Sci. Technol.* **45**: 7888–7895.
- van der Sloot, H.A., Comans, R.N.J., Hjelmar, O. (1996): Similarities in the leaching behaviour of trace contaminants from waste, stabilized waste, construction materials and soils. *Sci. Total Environ.* **178**: 111–126.
- van der Sloot, H.A. (2001a): European activities on harmonisation of leaching/extraction tests and standardisation in relation to the use of alternative materials in construction. In: *ICMAT International Conference on Materials for Advanced Technologies*, Singapore.
- van der Sloot, H.A., Kosson, D.S., Hjelmar, O. (2001b): Characteristics, treatment and utilization of residues from municipal waste incineration. *Waste Manage.* **21**: 753–765.
- van der Sloot, H.A. (2002): Chapter 7: Harmonisation of leaching/extraction procedures for sludge, compost, soil and sediment analyses. In: *Methodologies for Soil and sediment fractionation studies*, Ed. P. Quevauviller. Royal Society of Chemistry, pp. 142–170.
- Vítková, M., Ettler, V., Šebek, O., Mihaljevič, M., Grygar, T., Rohovec, J. (2009): The pH-dependent leaching of inorganic contaminants from secondary lead smelter fly ash. *J. Hazard. Mater.* **167**: 427–433.
- Williamson, B.J., Udachin, V., Purvis, O.W., Spiro, B., Cressey, G., Jones, G.C. (2004): Characterisation of airborne particulate pollution in the Cu smelter and former mining town of Karabash, South Ural Mountains of Russia. *Environ. Monit. Assess.* **98**: 235–259.
- Yucel, O., Addemir, O., Tekin, A., Nizamoglu, S. (1992): Recovery of cobalt from copper slags. *Miner. Process. Extr. Metall. Rev.* **10**: 99–107.
- Zandi, M., Russell, N.V., Edyvean, R.G.J., Hand, R.J., Ward, F. (2007): Interpretation of standard leaching test BS EN 12457-2: is your sample hazardous or inert? *J. Environ. Monit.* **9**: 1426–1429.
- Zevenbergen, C., Van Reeuwijk, L.P., Bradley, J.P., Comans, R.N.J., Schuiling, R.D. (1998): Weathering of MSWI bottom ash with emphasis on the glassy constituents. *J. Geochem. Explor.* **62**: 293–298.
- www.state.gov/r/pa/ei/bgn/2359.htm (accessed on July 12th, 2012)



Charles University in Prague, Faculty of Science
Institute of Geochemistry, Mineralogy and Mineral Resources
Prague 2012

