# Copper metallurgical slags : mineralogy, bio/weathering processes and metal bioleaching

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# Copper metallurgical slags: mineralogy, bio/weathering processes and metal bioleaching



**PhD Thesis
(2012-2015)
Anna POTYSZ**

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UNIVERSITA DEGLI STUDI DI CASSINO E DEL LAZIO MERIDIONALE
SOL PER NOCTEM
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Institute for Water Education

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# Copper metallurgical slags: mineralogy, bio/weathering processes and metal bioleaching

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Degree of Doctor in Environmental Technology

# Thèse – Tesi di Dottorato – PhD thesis

Anna POTYSZ

COPPER METALLURGICAL SLAGS:
MINERALOGY, BIO/WEATHERING PROCESSES AND METAL BIOLEACHING

Defended on December 10$^{th}$ 2015

In front of the PhD committee

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## ETeCoS³

Erasmus Joint doctorate programme in Environmental Technology for Contaminated Solids, Soils and Sediments (ETeCoS³)

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# List of abbreviations

a.p.f.u.: atoms per formula unit

ARE: artificial root exudates

AS: agitation speed

AS: amorphous slag

Bn: bornite

CS: crystalline slag

d.l.: detection limit

Di: diopside

EDS: energy dispersive system

Fa: fayalite

FA: fulvic acid

Gl: glass

GM: growth medium

GMB: growth medium with bacteria

GS: granulated slag

h: hour

HA: humic acid

HS: historical slag

LS: leaching solution

LS: lead slag

LS: liquid to solid ratio

LT: leaching time

n.a.: not analysed

PD: pulp density

Po: pyrrhotite

PS: particle size

S/L: solid to liquid ratio

SEM: scanning electron microscope

SFS: shaft furnace slag

Sp: sphalerite

T: temperature

UPW: ultrapure water

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# Abstract

# Copper metallurgical slags: mineralogy, bio/weathering processes and metal bioleaching

**Problem statement:** Copper pyrometallurgical slags are inevitable waste by-products of Cu smelting operations. These waste are considered to be important due to their production volume and high residual metal content that are inefficiently recovered during industrial process. Due to the lack of sustainable practices in the past, tremendous volumes of Cu-slags have been disposed in many industrial districts, regardless of the weathering and associated environmental risks. Consequently, there are many areas where slags have been proven to be a source of metallic pollution for the surrounding environment. At the present time, the outstanding contradiction between the sustainable development and environmental pollution encourages to undertake the action regarding this aspect. For this reason, slags are currently being used as supplementary materials for civil engineering purposes (e.g. cement and concrete additives, road bed filling materials, hydraulic construction materials) rather than disposed. Additionally, modern-day management strategies require slags to be thoroughly evaluated with respect to their environmental stability prior undertaking any reuse action.

**Main objectives** were to evaluate environmental stability of Cu‑metallurgical slags resulting from different periods of industrial activities and different smelting technologies. Those included: *historical crystalline slag (HS)* as well as *modern*: s*haft furnace slag (SFS)*, *granulated slag (GS)* and *lead slag (LS)*. Different approaches undertaken in this PhD work considered: i) chemical and mineral phase compositions of slags, ii) leaching susceptibility of slags under exposure to different pH-stat conditions, iii) slags weathering under exposure to organic acids commonly found in soil environment, iv) bacterially (*Pseudomonas aeruginosa*) mediated weathering of slags and v) future application of studied slags for metal recovery by implementing the bioleaching method.

**Crucial results:** The results of the pH-dependent leaching tests showed a higher metal release in strong acidic conditions (pH 2 and 4), whereas leachability at alkaline conditions (pH 10.5) revealed a lower importance for all the slags analyzed. The study considering soil weathering scenario demonstrated that Cu-slags are susceptible to dissolution in the presence of artificial root exudates (ARE), humic (HA) and fulvic acids (FA), whereby ARE were found to have stronger contribution than HA and FA. According to data collected, the different behavior of individual slags is strictly related to their characteristics (chemical and phase composition) reflecting various susceptibilities to dissolution under the investigated conditions. The study considering bio-weathering scenario revealed that *Pseudomonas aeruginosa* considerably

enhances the release of major (Si and Fe) and metallic (Cu, Zn, Pb) elements compared to the effects of abiotic factors, regardless of the slags chemistry and structure. Furthermore, a high gain (up to 90%) of metals (Cu, Zn, Fe) could be credited to bioleaching with *Acidithiobacillus thiooxidans* under laboratory conditions.

**General conclusions:** The environmental stability of slags depends on both, their bulk chemistry and mineralogy. However, mineral phases harbouring the metals are the key players in metal leachability intensity. For, this reason consideration of individual slags behaviour is important for preventing environmental contamination and should be regarded as priority branch of sustainable slag management. Optimization of operating parameters for bioleaching following development of industrial scale technology is an incentive scheme for future management of Cu-metallurgical slags.

# Résumé

# Scories métallurgiques du cuivre: minéralogie, processus de bio/altération et biolessivage métallique

**Énoncé du problème:** Les scories pyrométallurgiques du cuivre sont des sous-produits des opérations de fusion des minerais du cuivre. Ces déchets sont considérés comme importants en raison des volumes générés et également en raison des teneurs residuelles en métaux qui restent élevée à cause d'un processus d'extraction relativement inefficace. En raison de l'absence de pratiques durables dans le passé, d'énormes volumes de scories au Cu ont été entreposés dans de nombreux districts industriels, quelle que soit l'altération et le risque environnemental associé. Par conséquent, il y a de nombreuses zones où les scories se révèlent être une source de pollution métallique pour le milieu environnant. À l'heure actuelle, la contradiction entre le développement durable et la pollution de l'environnement encourage à prendre des mesures en ce qui concerne cet aspect. Pour cette raison, les scories sont actuellement recyclées comme matériaux supplémentaires (remblais) à des fins de génie civil (par exemple, le ciment et adjuvants pour béton, sous-couche routière, matériaux de construction). En outre, les stratégies de gestion des déchets exigent que les scories soient soigneusement étudiées par rapport à leur stabilité dans l'environnement avant d'établir toute action de réutilisation.

**Les principaux objectifs** étaient d'évaluer la stabilité dans l'environnement des scories métallurgiques de Cu résultant de différentes périodes d'activités industrielles et de différentes technologies de fusion. Parmi les scories étudiées, on retrouve: les scories historiques cristallines (SH) ainsi que des scories modernes: scories issues d'un four vertical (SFS), les scories granulaires (GS) et les scories de plomb (LS). Les différentes approches adoptées dans ce travail de thèse ont tenu compte de: i) la composition chimique et de la minéralogie des scories, ii) la sensibilité à la lixiviation des scories exposées sous différentes conditions de pH en mode statique, iii) l'altération des scories exposées aux acides organiques couramment trouvés dans l'environnement des sols, iv ) la bio-altération des scories par les bactéries hétérotrophes (*Pseudomonas aeruginosa*) et v) l'application future de la récupération des métaux provenant des scories étudiées en mettant en œuvre une méthode de bio-lixiviation.

**Résultats importants:** Les résultats des tests de lixiviation dépendant du pH ont montré une libération de métal plus élevée dans des conditions fortement acides (pH 2 et 4), alors que la lixiviation dans des conditions alcalines (pH 10.5) était moins importante pour toutes les scories analysées. L'effet de l'altération par le sol a été démontré, la dissolution des scories est notamment sensible à la présence d'exsudats racinaires artificiels (ERA), d'acides humiques

(AH) et d'acides fulviques (AF), la contribution des ERA étant la plus forte. Selon les données recueillies, la dissolution relative des scories est strictement liée à leurs caractéristiques (composition chimique et minéralogique) en fonction des différentes conditions étudiées. L'étude concernant l'effet de l'altération biologique a révélé que *Pseudomonas aeruginosa* améliore considérablement la libération des éléments majeurs (Si et Fe) et métalliques (Cu, Zn, Pb) par rapport aux effets des facteurs abiotiques, indépendamment de la chimie et de la structure des scories. En outre, une récuperation élevée (jusqu'à 90%) des métaux (Cu, Zn, Fe) pourrait être obtenue grâce à la biolixiviation en présence d'*Acidithiobacillus thiooxidans* dans des conditions de laboratoire.

**Conclusions générales:** La stabilité des scories dans l'environnement dépend à la fois des caractéristiques chimiques et de la minéralogie. Cependant, la nature des phases minérales hébergeant les métaux est le facteur les plus déterminant concernant l'intensité de la lixiviation des métaux. Pour cette raison, l'examen individuel du comportement des scories est important pour prévenir la contamination de l'environnement et cette approche doit être considérée comme une priorité pour la gestion durable des scories. L'optimisation des paramètres de fonctionnement pour la biolixiviation et le développement de cette technologie à l'échelle industrielle pourrait permettre une meilleure gestion (voir l'exploitation) des scories métallurgiques de Cu.

# Sintesi

# Scorie metallurgiche di rame: mineralogia, processi di bio/weathering e bioliscivazione di metalli

**Definizione del problema:** le scorie pirometallurgiche di rame (Cu) sono inevitabili sottoprodotti di scarto derivanti dalle operazioni di fusione del rame. Tali rifiuti sono di notevole importanza dato il loro volume di produzione e l'alto contenuto di metalli residui causato dall'inefficiente recupero del processo industriale stesso. A causa della passata mancanza di strategie di gestione sostenibili, volumi molto elevati di scorie contenenti Cu sono state spesso smaltite in numerosi distretti industriali, a prescindere dai fenomeni di invecchiamento/alterazione e dal rischio ambientale associato. Di conseguenza, in numerose aree le scorie metallurgiche sono state dimostrate essere una fonte di inquinamento metallico per l'ambiente circostante. Al momento attuale, la contraddizione tra lo sviluppo sostenibile e l'inquinamento ambientale incoraggia a intraprendere azioni nei confronti di tali aspetti. A tale scopo, le scorie sono attualmente utilizzate come materiali supplementari per scopi di ingegneria civile (ad esempio, cemento e additivi per calcestruzzo, materiali di riempimento di strade, materiali da costruzione idraulici) piuttosto che smaltiti. Inoltre, le moderne strategie di gestione di tali rifiuti speciali pericolosi, richiedono, prima di intraprendere qualsiasi azione di riutilizzo, una attenta valutatazione in relazione alla loro stabilità ambientale.

**Obiettivo principale** del presente elaborato, è stata la valutazione della stabilità ambientale delle scorie metallurgiche di Cu derivanti da diversi periodi di attività industriali e diverse tecnologie di fusione. Nel dettaglio, sono stati studiati i seguenti tipi di scorie: scorie storiche cristalline (HS) e moderne: scorie da forni verticale (SFS), scorie granulate (GS) e scorie di piombo (LS). I diversi approcci, intrapresi nel corso dell'attività di dottorato, hanno preso in considerazione: i) composizione chimica e fasi minerali delle scorie, ii) suscettibilità delle scorie alla lisciviazione previa esposizione a diverse condizioni statiche di pH, iii) alterazione delle scorie in condizioni di esposizione agli acidi organici che si trovano comunemente nel suolo, iv ) alterazione delle scorie mediata da batteri (*Pseudomonas aeruginosa*) e v) future applicazioni delle scorie sono in fase di studio al fine di ottimizzare il recupero di metalli per bioliscivazione.

**Risultati cruciali:** I risultati delle prove di lisciviazione pH-dipendente hanno mostrato un notevole rilascio di metalli in forti condizioni acide (pH 2 e 4), mentre la lisciviazione in condizioni alcaline (pH 10.5) ha mostrato minore efficacia per tutte le scorie analizzate. Lo studio dell'invecchiamento per effetto delle componenti del suolo ha mostrato come le scorie

di Cu vadano soggette a dissoluzione in presenza di essudati radicali artificiali (ARE), acidi umici (HA) e acidi fulvici (FA). In presenza di ARE con maggiore efficacia rispetto a HA e FA. Dai dati ottenuti, si evince come il diverso comportamento delle scorie sia strettamente legato alle loro caratteristiche (composizione chimica e mineralogica) riflettendo tendenze relativamente diverse alla dissoluzione nelle condizioni indagate. Lo studio dei processi di bioweathering ha mostrato come la presenza *Pseudomonas aeruginosa* favorisca considerevolmente il rilascio di elementi principali (Si e Fe) e metallici (Cu, Zn, Pb) rispetto agli effetti di fattori abiotici, indipendentemente delle charatteristiche chimiche e strutturali delle scorie. Inoltre, un alto recupero (fino al 90%) di metalli (Cu, Zn, Fe) potrebbe essere ottenuto in condizioni di laboratorio sfruttando la bioliscivazione operata da *Acidithiobacillus thiooxidans*.

**Conclusioni generali:** La stabilità ambientale delle scorie dipende, quindi, sia della loro composizione chimica che della loro mineralogia. Tuttavia, le fasi minerali che ospitano i metalli sono gli attori principali che determinano l'intensità della lisciviazione metallica. La valutazione del comportamento individuale delle scorie è imprescindibile per prevenire la contaminazione ambientale e deve pertanto essere considerata una priorità se si vuole ottenere una gestione sostenibile delle scorie. L'ottimizzazione dei parametri di bioliscivazione e il possibile successivo sviluppo di tecnologie a scala industriale potrebbero, infatti, essere un incentivo per una futura gestione sostenibile delle scorie metallurgiche di Cu.

# Samenvatting

# Koper metallurgische sintels: mineralogie, bio/verweringsproces en metaal bio-uitspoeling

**Probleemstelling:** Koper bevattende pyrometallurgische sintels zijn onvermijdbare afval-bijproducten van Cu smeltactiviteiten. Dit afval is belangrijk vanwege het productievolume en het hoge gehalte aan residuële metalen als gevolg van inefficiënte metaalwinning tijdens het industriële proces. Doordat er in het verleden gebrek aan aandacht was voor duurzaamheid werden Cu-sintels in enorme hoeveelheden, en in vele industriële gebieden, weggegooid zonder rekening te houden met factoren als verwering en andere risico's voor het milieu. Hierdoor zijn vele gebieden ontstaan waar sintels een bron van metallische vervuiling vormen voor de omgeving. Omdat milieuvervuiling duurzame ontwikkeling in de weg staat, is er tegenwoordig veel aandacht voor dit probleem. Daarom worden sintels tegenwoordig gebruikt als supplementaire materialen voor civieltechnische doeleinden (b.v. cement en additieven voor beton, vulmateriaal voor wegen, hydrologische constructiematerialen), en worden ze niet meer gedumpt. Voordat hergebruik overwogen kan worden moet tegenwoordig wel de ecologische stabiliteit van sintels grondig worden getest.

**Hoofddoelstellingen:** De evaluatie van de ecologische stabiliteit van Cu-metallurgische sintels, die in verschillende perioden van industriële activiteiten, en met verschillende smelt-technologieën, zijn geproduceerd. De verschillende sintelmonsters waren: historische kristallijne sintels (HS), sintels uit moderne schachtovens (SFS), korrelige sintels (GS) en lood sintels (LS). Dit PhD onderzoek bestond uit de volgende delen: i) bepaling van de chemische- en mineralensamenstelling van sintels, ii) gevoeligheid voor uitloging van sintels bij blootstelling aan verschillende pH condities, iii) verwering van sintels bij blootstelling aan organische zuren die van nature in de bodem aanwezig zijn, iv) verwering veroorzaakt door bacteriën (*Pseudomonas aeruginosa*), v) toekomstig gebruik van de onderzochte sintels voor metaal terugwinning met behulp van biologische uitspoelingsmethodes.

**Belangrijkste resultaten:** De resultaten van de pH-afhankelijke uitspoelingstesten vertoonden een hogere metaaluitloging in sterke zure condities (pH 2 en 4), terwijl de uitloogbaarheid onder alkalische omstandigheden (pH 10.5) minder groot was voor alle geanalyseerde types sintels. Studies van verwerings-scenario's in de bodem lieten zien dat Cu-sintels gemakkelijker kunnen oplossen in de aanwezig van kunstmatige wortelexsudaten (ARE), humuszuren (HA) en fulvozuren (FA). Wij vonden dat dat ARE een sterkere bijdrage leverde dan HA en FA. De data laten zien dat het gedrag van individuele sintels sterk gerelateerd is aan hun eigenschappen (chemische en fase samenstelling), en dat ze, onder de

onderzochte omstandigheden, in verschillende mate gevoelig waren voor uitloging. De bioverweringsstudies lieten zien dat *Pseudomonas aeruginosa* het uitlogen van de meest voorkomende (Si en Fe) en metallische (Cu, Zn, Fe) elementen aanzienlijk vergoot in vergelijking met de effecten van abiotische factoren. Dit was onafhankelijk van de chemische eigenschappen en de structuur van de sintels. Ook bio-uitloging met *Acidithiobacillus thiooxidans* onder laboratorium omstandigheden resulteerde in een flinke verhoging (tot 90%) van de uitloging van metalen (Cu, Zn, Fe).

**Algemene conclusie:** De ecologische stabiliteit van sintels hangt af van hun chemische samenstelling en mineralogie. Toch zijn de metalen bevattende mineraalfasen het belangrijkst voor de mate van metaaluitloogbaarheid. Dit resultaat toont aan dat kennis van het uitloog-gedrag van individuele sintels erg belangrijk is om de aantasting van het milieu te voorkomen, wat de belangrijkste voorwaarde is voor de duurzame verwerking van sintels. Optimalisering van de parameters voor bio-uitloging, gevolgd door de ontwikkeling van deze technologie op industriële schaal, is een stimulans voor het toekomstige beheer van Cu-metallurgische sintels.

# CHAPTER 1

# INTRODUCTION

# 1.1 INTRODUCTION

## 1.1.1 General introduction

Copper has been an essential metal for human civilization beginning from ancient times. Due to several number of applications (from various tools and coins production towards electronic related products) copper has remained indispensable for modern day cultures (Themelis, 1994; Hong et al., 1996; Radetzki, 2009). Consequently, Cu-related mining and pyrometallurgical activities are currently well developed worldwide. Besides benefits gained from copper production, resources depletion, waste by-products generation and pollutant emissions are also associated (Tiller, 1989; Hudson-Edwards et al., 1999; Lottermoser, 2010). Among the wastes generated, metallurgical slags are of particular relevance for dual reasons related to high production volume (approximately 2.2 tones of slags per 1 ton of Cu) and residual concentrations of metals still entrapped in slags during processing (Gorai, 2003). Remaining metals are of main concern as they can be released if slags are weathered, therefore this aspect receives significant attention in recent years.

## 1.1.2 Problem statement

Slags disposal was a common way of management in the past, when these by-products were considered to be inert materials and their life cycle was usually limited into two stages which included production and dumping. As the result, tremendous volumes of waste slags have been disposed in many industrial districts (Fig. 1.1). A long-term exposure of these slags to bio-geochemical weathering led to mobilization of metals and deleterious environmental effects on soils, sediments and waters are being faced nowadays (*e.g.* Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Piatak et al., 2004; Kierczak et al., 2013; Ettler & Johan, 2014). That resulted in implementing strong environmental restrictions concerning disposal and slags management in environmentally friendly manner is of particular attention of sustainable development nowadays.

Waste management strategies require slags to be thoroughly evaluated with respect to their environmental stability prior disposal or recommend other actions in between to be undertaken in the slags life cycle. An appropriate recycling/re-use action should be selected based on slag properties. Metal recovery could be implemented if residual metal concentrations are high enough to be gained, while application for civil engineering is reasonable if slags are found to be stable (Shen & Forssberg, 2003; Mateus et al., 2011; Schmukat et al., 2012; Ettler & Johan, 2014). Therefore, environmental impact assessment must employ characterization of slags with respect to their chemical and mineralogical

composition as well as evaluation of slags susceptibility to release of metals (Ettler et al., 2009; Piatak et al., 2015). Furthermore, an examination of biotic and physico-chemical parameters affecting slags stability is relevant for already existing dumping areas in order to implement preventive operations against contaminants migration as well as to propose perspectives of areas remediation or slags collection and re-use if feasible.
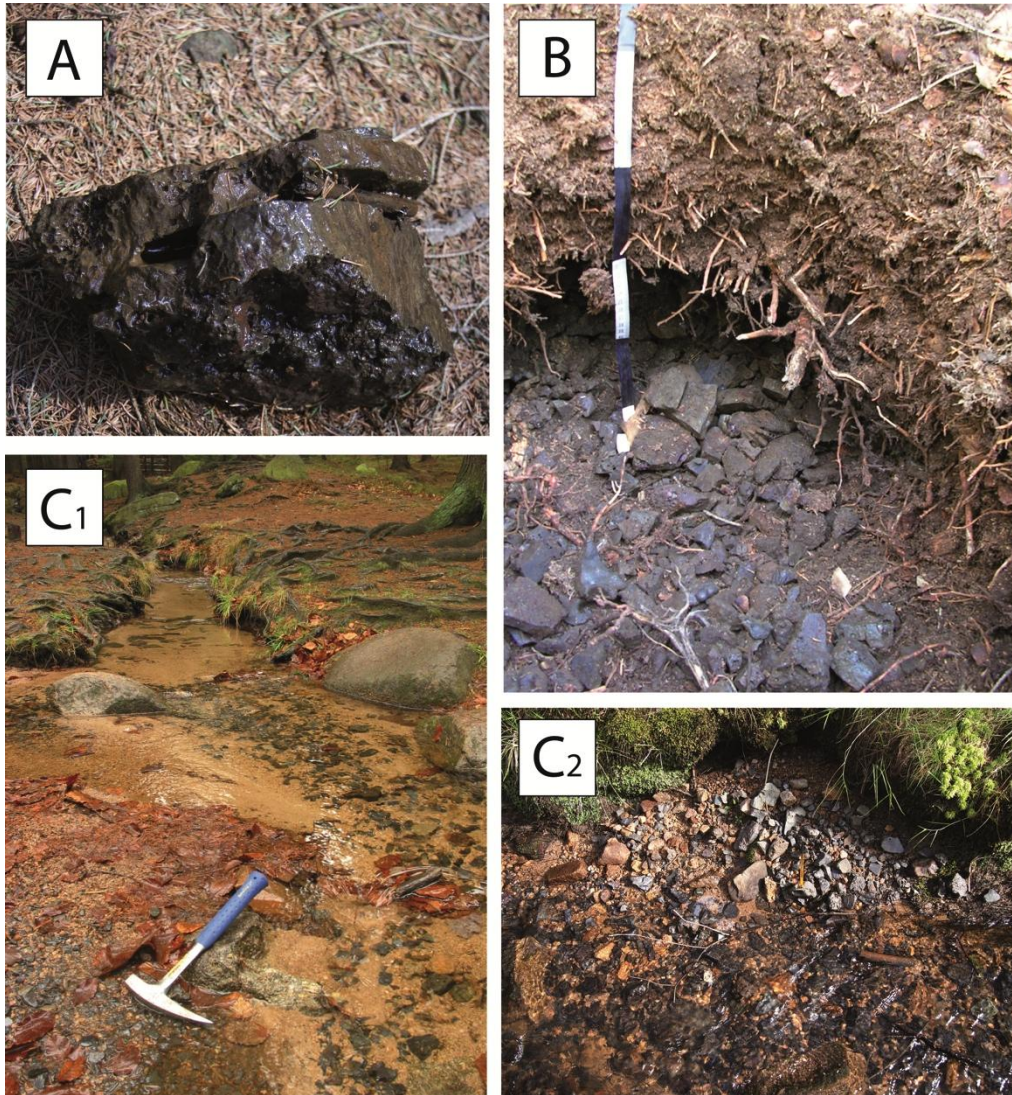


**FIGURE 1.1 An example of historical disposal site (Rudawy Janowickie Mountains, SW Poland) where slags are commonly found on the surface ground (A), in the soil profiles (B) and streams (C$_1$ and C$_2$).**

### 1.1.3 Objectives

The main objective of this research is to evaluate "*Environmental stability of Cu- metallurgical slags and feasibility of reuse Cu-slags as secondary metal resources*"

Specific research objectives include:

1. CHARACTERIZATION OF COPPER SLAGS
   - to determine bulk chemical composition of slags resulting from different periods of industrial activities and different technologies
   - to identify mineral phases present and to determine their chemical composition with special attention given to distribution of metals
   - to specify modal phase composition and to quantify metals accommodated in individual mineral phases

2. EXAMINATION OF SLAGS LEACHING BEHAVIOUR
   - to examine leachability of Cu, Zn and Pb as a function of pH (from 2 to 13)
   - to indicate pH conditions at which slags are stable
   - to evaluate potential of slags to be employed to metal recovery process

3. EXAMINATION OF IMPACT OF VARIOUS ORGANIC ACIDS ON MOBILIZATION OF METALS FROM Cu-SLAGS
   - to compare the effect of humic acid, fulvic acid and artificial root exudates on mobilization of heavy metals from various slags
   - to answer the question which factors disturb slags stability

4. EVALUATION OF BIOWEATHERING PROCESS
   - to examine the role of *Pseudomonas aeruginosa* on the weathering of Cu-slags exhibiting different chemical and structural properties
   - to evaluate whether bacteria enhance bio-weathering process of Cu-slags in a long term perspective
   - to evaluate whether bacteria can sorb mobilized metallic elements released from slags?
   - to observe which mineral phases undergo weathering under exposure to biotic and abiotic conditions

5. FEASIBILITY STUDY OF METALS BIOLEACHING BY MEANS OF *PSEUDOMONAS FLUORESCENS* AND *ACIDITHIOBACILLUS THIOOXIDANS*

- to assess the performance of 2 different bacterial trophic groups as leaching agents
- to reach efficient metals extraction
- to indicate the optimal leaching conditions

An overview of experimental work and methodologies employed are listed in Table 1.1.

## 1.2 STRUCTURE OF THE PhD THESIS

The present PhD thesis is divided into 8 following chapters:

### Chapter 1: Introduction

- Presents overview of PhD thesis including general introduction to the topic, problem statement, research objectives and thesis structure

### Chapter 2: Literature review: Copper slags- current knowledge and fate

- Based on literature assembly, chapter 2 focuses on copper metallurgical slags and presents the aspects related to: copper production, chemical and mineralogical characteristics of slags and their environmental stability, methods aiming at assessing the environmental risk that Cu-slags could pose, different experimental approaches devoted to bio/leaching and bio/recovery of metals from Cu-slags, chemical and biotic parameters playing a superior role in the extraction efficiencies.

### Chapter 3: Materials and methods

- Presents the origin of the samples and gives an overview of technological processes that the samples originate from. This chapter also gathers all the methodologies used in the studies and presents experimental approaches.

### Chapter 4: Characterization and pH-dependent leaching behaviour of historical and modern copper slags

- Comprises geochemical study of copper slags (*historical, shaft furnace, granulated* and *lead slag*) resulting from different industrial periods of copper production as well as various technological processes. This chapter provides a comparison of different slags with respect to their chemistry, mineralogy and pH-dependent leaching behaviour as well as it relates the leaching trends to mineral phase composition of

slags. Additionally, leaching tests give an insight regarding the environmental behaviour of such materials that results in finding an optimal conditions for their management.

**Chapter 5: Metal mobilization from Cu-slags by soil organic acids**

- Demonstrates leachability of metals (Cu, Zn, Pb) under weathering conditions which might be encountered at dumping sites. These include slags (*historical, shaft furnace, granulated* and *lead slag*) exposure to different organic solutions such as artificial root exudates applied as rhizosphere model compounds, humic and fulvic acids used as soil organic matter model. Results are discussed and compared based on literature data.

**Chapter 6: Bacterially-mediated weathering of crystalline and amorphous Cu-slags**

- Presents long-term (112 days) interactions of two different (crystalline and granulated) Cu-slags with *Pseudomonas aeruginosa* employed as environmental proxy of heterotrophic bacteria. Abiotic factors of the weathering are used for comparison purposes. The results of solution chemistry (Si, Fe, Cu, Zn, Pb), excreted microbial by-products, scanning electron microscope observations of altered mineral phases as well as geochemical modeling are presented and discussed.

**Chapter 7: Comparison of Cu, Zn and Fe bioleaching from Cu-metallurgical slags in the presence of *Pseudomonas fluorescens* and *Acidithiobacillus thiooxidans***

- Evaluates possibility of application of microorganisms as leaching agents. Presents data concerning effect of pulp density, particle size and time (1-40 days) on metal (Cu, Zn and Pb) leaching as well as proposes the way of process improvement.

**Chapter 8: General discussion and perspectives**

- Summarizes findings and draws conclusions based on data gained as well as presents future recommendations and further perspectives of the work.

The chapters presenting the research work are preceeded by the preface section that summarizes the results obtained in the previous chapter and justifies the research undertaken in the following chapter.

**Appendix 1** includes supplementary figures.
**Appendix 2** lists papers related to the PhD work, courses, trainings and conferences attended.

**TABLE 1.1 Phases of work, experimental approaches and methodologies applied.**

| EXPERIMENTAL APPROACH | OBJECTIVES | METHODOLOGIES |
|---|---|---|
| **PHASE 1: CHARACTERIZATION OF COPPER SLAGS** | | |
| **EXPERIMENT 1 A:** Bulk chemical composition | • To determine total concentrations of elements | Acid digestion ICP-OES ICP-MS |
| **EXPERIMENT 1 B:** Phase recognition | • To indicate mineral phases present in slags | Optical microscopy XRD SEM |
| **EXPERIMENT 1 C:** Phase chemical composition and quantification of metals accommodated in mineral phases | • To determine distribution metallic elements in particular mineral phases<br>• Modal phase composition | EMPA<br><br>JMicro Vision 1.2.7 software |
| **PHASE 2: PROPERTIES OF THE MATERIALS AND LEACHING BEHAVIOUR** | | |
| **EXPERIMENT 2:** Liquid-solid partitioning as a function of extract pH using parallel batch extraction procedure (US EPA 1313) | • To examine leachability of Cu, Zn and Pb as a function of pH (2-13)<br>• To indicate conditions at which slags display the lowest/highest stability | pH meter ICP-OES |
| **PHASE 3: ENVIRONMENTAL BEHAVIOUR OF SLAGS (*E.G.* SOIL ENVIRONMENT)** | | |
| **EXPERIMENT 3:** Effect of various organic acids (i.e. humic acid, fulvic acid, artificial root exudates) on metals (Cu, Zn, Pb, Cd) leaching from slags. Batch leaching experiments under slags exposure to organic acids (24 h, 48 h, 72 h, 168 h, 960 h) | • To present leaching trends<br>• To indicate the most influential organic solution on metals mobilization | pH meter ICP-MS |
| **PHASE 4: BIO-WEATHERING** | | |
| **EXPERIMENT 4:** Bio-weathering behaviour of two types of Cu-slags with bacteria *Pseudomonas aeruginosa* | • To examine the role of *Pseudomonas aeruginosa* on the weathering of Cu-slags exhibiting different chemical and structural properties | pH meter Spectrophotometer ICP-MS SEM 3D fluorescence |
| **PHASE 5: METAL BIOLEACHING** | | |
| **EXPERIMENT 5:** The feasibility of metals bioleaching from Cu-metallurgical slags by means of *Pseudomonas fluorescens* and *Acidithiobacillus thiooxidans*. | • To investigate the performance of 2 different bacterial trophic groups as leaching agents<br>• To reach efficient metals extraction | pH meter AAS SEM |

## REFERENCES

1.  **Ettler V. & Johan Z. (2014):** *„12 years of leaching of contaminants from Pb smelter slags: geochemical/mineralogical controls and slag recycling potential".* Applied Geochemistry 40, 97-103.

2.  **Ettler V., Johan Z., Křibek B., Šebek O., Michaljevič M. (2009):** *„Mineralogy and environmental stability of slags from Tsumeb smelter, Namibia".* Applied Geochemistry 24 (1), 1-15.

3.  **Ettler V., Piantone P., Touray J.C. (2003):** *„Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long- term assessment".* Mineralogical Magazine 67 (6), 1269-1283.

4.  **Gee C., Ramsey M.H., Maskall J., Thornton I. (1997):** *„Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead".* Journal of Geochemical Exploration 58 (2-3), 249-257.

5.  **Gorai B., Jana R.K., Premchand (2003):** *„Characteristics and utilization of copper slags-a review".* Resources, Conservation and Recycling 39 (4), 299-313.

6.  **Hong S., Candelone J.P., Soutif M. Boutron C.F (1996):** *„A reconstruction of changes in copper production and copper emissions to the atmosphere during the past 7000 years".* Science of The Total Environment 188 (2-3). 183-193.

7.  **Hudson-Edwards K.A., Schell Ch., Macklin M.G. (1999):** *„Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain".* Applied Geochemistry 14 (8), 1015-1030.

8.  **Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Néel C., Ettler V., Mihaljevič M. (2013) :** *„Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland).* Journal of Geochemical Exploration 124, 183-194.

9.  **Lottermoser B.G. (2002)**: *„Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia".* Mineralogical Magazine 66 (4), 475-490.

10. **Lottermoser B.G. (2010)**: „Mine Wastes: Characterization, Treatment and Environmental Impact: [2.1]: Early Historical Observations on Sulfide Oxidation and Acid Mine Drainage, [2.7]: Acid generation prediction". Springer 3rd edition.

11. **Manz M. and Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District, Mexico".* Environmental Pollution 98 (1), 7-13.

12. **Mateus A., Pinto A, Alves L.C., Matos J.X., Figueiras J., Neng N.R. (2011):** *„Roman and modern slag at S. Domingos mine (IPB, Portugal): Compositional features and implications for their long-term stability and potential reuse".* Int. Journal of Environment and Waste Management 8, 133-159.

13. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California".* Applied Geochemistry 16 (14), 1567–1593.

14. **Piatak N.M., Parsons M.B., Seal R.R. (2015):** *„Characteristics and Environmental Aspects of Slags: A review".* Applied Geochemistry

15. **Piatak N.M., Seal 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".* Applied Geochemistry 19, 1039-1064.

16. **Radetzki M. (2009):** *„Seven thousand years in the service of humanity-the history of copper the red metal".* Resources Policy 34, 176-184.

17. **Schmukat A., Duester L., Ecker D., Schmid H., Heil C., Heininger P., Ternes T.A. (2012):** *„Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength".* Journal of Hazardous Materials (227), 257–264.

18. **Shen H. & Forssberg E. (2003):** *„An overview of recovery of metals from slags".* Waste Management 23 (10), 933–949.

19. **Sobanska S., Ledésert B., Deneele D., Laboudigue A. (2000):** *„Alteration in soils of slag particles resulting from lead smelting".* Earth and Planetary Sciences 331 (4), 271-278.

20. **Themelis M.J. (1994):** *„Pyrometallurgy near the end of 20th century".* Industrial Insight 46 (8). 51-57.

21. **Tiller K.G. (1989):** *„Heavy metals in soils and their environmental significance".* Advances in Soil Science 9, 113 142.

# CHAPTER 2

# COPPER METALLURGICAL SLAGS - CURRENT KNOWLEDGE AND FATE: A REVIEW

## ABSTRACT

Cu-slags are a by-product of pyrometallurgical processing and contain elevated concentrations of metallic elements that may be released during weathering. Hence, they may pose environmental risk and thus need to be properly disposed off. On the other hand, the high residual content of metals makes slags interesting as secondary resources for metal recovery. This review presents current knowledge about the chemical and phase composition of Cu-metallurgical slags and discusses environmental issues related to their disposal. Furthermore, it provides an overview of experimental approaches assessing environmental risk as well as recent achievements regarding the leaching and recovery of valuable metals from Cu-slags.

**Keywords:** Cu-slags, weathering, (bio)leaching, metal recovery, sustainable development

## 2.1 INTRODUCTION

Copper (Cu) is an essential metal that has had a relevant importance since early human civilization going backwards as long as 6 000-7 000 years ago (Themelis, 1994; Hong et al., 1996; Radetzki, 2009). Initially, it was used for production of primitive tools, vessels and coins due to its easy stretching and possibility of shape formation. Subsequent discovery of properties such as heat and electric conductivity caused that copper has gained an even more prominent value. Nowadays, copper is considered as one of the most widely produced metals, indispensable for humans and thus essential for the global market. It is used for a variety of applications such as power transmission, building, electronic and related industries (Radetzki, 2009). Expansion of the copper demand has increased its mining and production. In 2012, the world copper mine production reached 16.7 million tons. Smelter and refinery production were maintained at approximate levels of 16.7 and 20.1 million tons, including primary and secondary production (ICSG, 2013). Due to the fact that copper reserves are considered to be non-renewable, undiscovered copper resources receive important attention in mineral supply assessments (Svedberg & Tilton, 2006).

On the other hand, industrial activity related to mining and processing of copper is a reason of growing environmental concern. Considering this industrial activity, it should be noticed that apart from advantages arising from effective production, this industrial sector produces huge amounts of metallurgical wastes (slags) that are classified as "potentially hazardous" (Ettler et al., 2009; Kierczak et al., 2013). Pyrometallurgical processes extract metals from ores, however, depending on the process efficiency some residual amounts of the metals still remain in the waste materials.

Metallurgical wastes are mostly dumped close to the centre of industrial activity, but in case of inappropriate isolation of the disposal site, it may entail serious environmental consequences (Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Piatak et al., 2004; Reuter et al., 2004; Vdović et al., 2006; Ettler et al., 2009; Maweja et al., 2010; Vítková et al., 2010; Piatak & Seal, 2010; Yang et al., 2010; Kierczak et al., 2013; Ettler & Johan, 2014). Biogeochemical weathering and physical erosion of non-protected wastes may mobilize metallic elements. Then, local migration of pollutants and further transfer to large distances make the remediation of polluted areas difficult or in some cases even impossible. That is why appropriate isolation of wastes as well as frequent environmental monitoring of disposal sites are necessary to prevent the deterioration of environmental quality.

The distribution of metallic elements in various phases occurring in metallurgical wastes constitutes an important factor governing mobility of these elements during weathering. The presence of some metal-bearing phases showing relatively high susceptibility to alteration could increase the potential risk of metal mobilization from slags, therefore not only the total

metal concentration, but also the solid speciation (phase composition) should be considered in order to ensure safe disposal (Ettler et al., 2002; Ettler et al., 2005; Ettler et al., 2009; Piatak & Seal, 2010; Kierczak et al., 2013). Another important factor governing stability of disposed slag wastes is the indigenous microorganisms present at the dumping site (Willscher & Bosecker, 2003). The activity of these microbes may contribute to the alteration of slags and mobilization/immobilization of metallic elements. Therefore, this aspect of bioweathering is especially interesting and important for investigations of the alteration of metallurgical slags (Yin et al., 2014, van Hullebusch et al., 2015).

According to current guidelines of waste management, disposal of metallurgical slags is considered as the least favourable method (Lottermoser, 2011). From environmental point of view, pyrometallurgical slags are undesirable materials. Therefore, recent attention given to sustainable waste management has focused on methods allowing reuse of metallurgical wastes instead of their disposal. Reuse of slags as additives for building and construction materials, concretes and abrasive materials has been recently applied (*e.g.* Shi & Qian, 2000; Gorai et al., 2003; Al-Jabri et al., 2006; Moura et al., 2007; Shi et al., 2008; Al-Jabri et al., 2009; Al-Jabri et al., 2011; Najimi et al., 2011). However, application of these materials for engineering purposes can be justified only in the case if prior analysis of the materials proves their inertness. Moreover, (bio)recovery of metals remaining in the wastes is a promising technology for the future (*e.g.* Banza et al., 2002; Altundoǧan et al., 2004; Baghalha et al., 2007; Deng & Ling, 2007; Yang et al., 2010; Vestola et al., 2010; Tshiongo et al., 2010; Kaksonen et al., 2011; Ahmed et al., 2012; Nadirov et al., 2013; Muravyov and Fomchenko, 2013). Besides advantages derived from the recovery of valuable compounds, it is also important that extraction of metals decreases the hazardousness of the metallurgical wastes and consequently allows further reuse or safe disposal. Undoubtedly, (bio)recovery is currently the most desired solution to reuse these kinds of materials. However, it requires advanced development of the process as well as investment outlays. Therefore, metal recovery technologies and adaptation of processing conditions ensuring high recovery efficiencies receive considerable attention.

The main objective of this review paper is to present the current knowledge about metallurgical slags generated during processing of copper including their chemical and phase composition, environmental risk and fate. Special attention is given to gathering information about environmental stability and prediction of the environmental hazard related with these wastes. Additionally, this review paper presents achievements in the field of metal recovery from these waste materials, including comparison of various (bio)leaching and (bio)recovery methods and their efficiency.

## 2.2  MINING AND SMELTING OF COPPER

Copper ores consist mostly of copper sulfides and constitute the initial product for pyrometallurgical processes (Davenport et al., 2002; Alp et al., 2008). The most commonly present copper sulfide minerals in ores are chalcopyrite ($CuFeS_2$), bornite ($Cu_5FeS_4$) and chalcocite ($Cu_2S$). Besides minerals of interest, other sulfide minerals such as *e.g.*, pyrrhotite ($Fe_{(1-X)}S$), sphalerite (($Zn,Fe$)$S$), galena ($PbS$), pyrite ($FeS_2$), magnetite ($Fe^{2+}Fe^{3+}_2O_4$), malachite ($Cu_2CO_3(OH)_2$), azurite ($Cu_3(CO_3)_2(OH)_2$) are also associated with copper ores. Sulfide copper ores contain 0.5-2% of Cu and are a principal raw material for pyrometallurgical production. Copper may also occur in non-sulfide minerals (*e.g.*, carbonates, sulfates and oxides), but generally these minerals contain much lower quantities of copper than sulfides. Therefore, processing of non-sulfide ores is based on hydrometallurgical methods. Pyrometallurgy aims to obtain pure metal during a process including several stages: concentration, smelting and fire/electro-refining allowing to achieve different purities (99.5-99.9%) of copper (Figure 2.1).

Sulfide ore does not easily dissolve in water, therefore in order to improve the extraction efficiency, thermal treatment is used. As copper ores also contain a variety of non-copper bearing minerals, the first step of copper processing involves an enrichment of initial product containing up to 2% of Cu into high-grade concentrate. For this reason, the ore is crushed to fine ground material allowing further separation of grains containing copper from those useless for the process. The next stage includes flotation generating Cu-concentrate for further stages of processing. Subsequently, the copper concentrate is submitted to high temperature smelting under oxygen atmosphere. This treatment leads to the oxidation of sulfur and iron present in the concentrate and allows to obtain Cu-rich molten matte (up to 80%) (Davenport et al., 2002). This stage of the process corresponds to the following chemical reaction:

$$2\ CuFeS_2 + 13/4\ O_2 \rightarrow Cu_2S \times 1/2\ FeS + 3/2\ FeO + 5/2\ SO_2 \qquad \text{Eq. n°1}$$
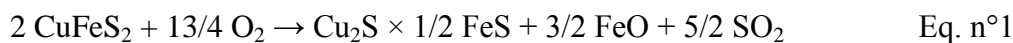
Silica flux addition promotes binding of iron in the slag (U.S. Congress, Office of Technology Assessment, 1988; Davenport et al., 2002; Gorai et al., 2003; Vítková et al., 2010) according to the following chemical reaction:

$$2\ FeO + SiO_2 \rightarrow 2\ FeO \times SiO_2 \qquad \text{Eq. n° 2}$$

Due to the high viscosity of silica at its melting point, oxide fluxes (*e.g.* CaO, $CaCO_3$) are often added. They decrease the viscosity of silica at the melting point by breaking the silica network and consequently promote easier and more efficient metal and silicate separation (Manasse & Mellini, 2002; Piatak & Seal, 2010). High temperatures allow to eliminate sulfur

that is transformed to the off-gas $SO_2$ (Davenport et al., 2002). Copper slags constitute by-products of the smelting stage and are generally formed at the temperatures ranging from 800 to 1300°C.

A further step of Cu production relies on the oxidation of the molten copper matte according to the following chemical reaction:

$$Cu_2S + O_2 \rightarrow 2\ Cu + 2\ SO_2 \hspace{3cm} \text{Eq. n°3}$$

This part of the process allows to obtain impure copper that is subsequently submitted to fire or electrorefining aiming to receive cathode copper with a high level of purity. This stage involves electrochemical dissolution of copper that passes into the electrolyte $CuSO_4$-$H_2SO_4$–$H_2O$ and further electrochemical treatment that leads to the deposition of copper onto the cathode (Davenport et al., 2002) (Figure 2.1).
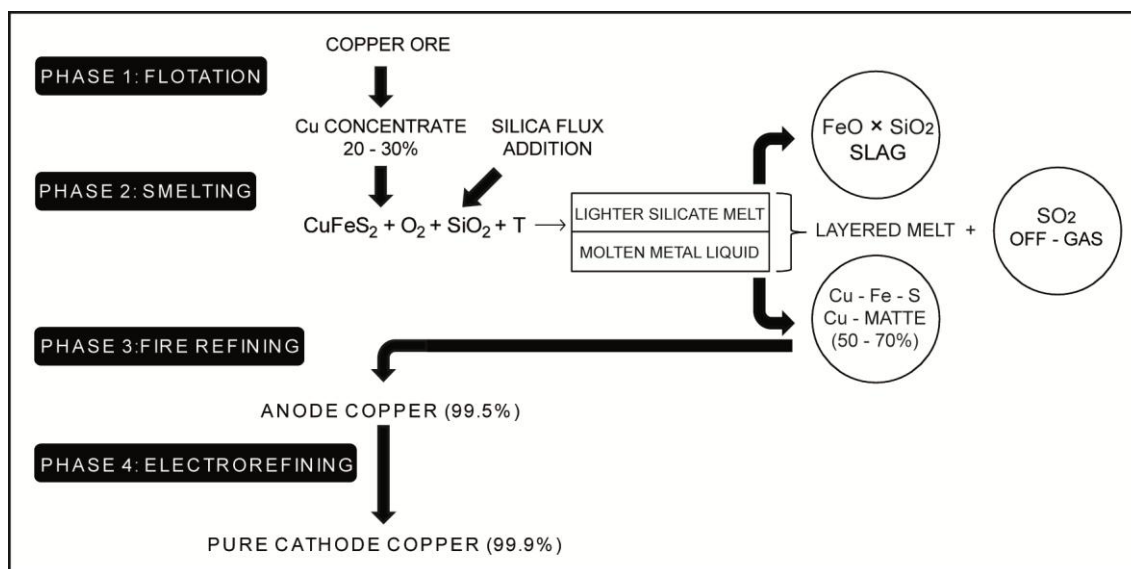


**FIGURE 2.1 Flowsheet of pyrometallurgical copper production from sulfidic ores.**

## 2.3  Cu-METALLURGICAL SLAGS

Ore processing heading towards recovery of valuable metals has been practised since historical times (Themelis, 1994; Radetzki, 2009). Although the fact that smelting technologies have been gradually improving, this industrial sector still generates various kinds of waste materials including waste rocks, ashes, sludges and slags (Piatak et al., 2003; Piatak et al., 2004). Slags are considered as important waste materials, because they are produced in large quantities and additionally contain elevated amounts of metallic elements (Ettler et al., 2001; Piatak et al., 2004; Lottermoser, 2005; Kierczak et al., 2010; Vítková et al., 2010; Ash et al., 2013). Due to the fact that historical technologies were not as efficient as modern ones,

slags originating from former smelting industry are expected to contain higher amounts of metals and other impurities (Lottermoser, 2002). It is also important to notice that current knowledge about the environmental behaviour of metallurgical slags has increased and it is now commonly known that slags can pose environmental risk (Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Ettler et al., 2003; Piatak et al., 2004; Reuter et al., 2004; Ettler et al., 2009; Vítková et al., 2010; Piatak & Seal, 2010; Kierczak et al., 2013; Ettler & Johan, 2014; Piatak et al., 2015).

For this reason, slags are nowadays classified as potentially hazardous materials in contrast to historical times when they were considered as inert for the environment. Thus, in many former industrial areas, these wastes were abandoned without any environmental monitoring. At several sites, research evaluating environmental quality has revealed that slags occurring at disposal sites are not as environmentally stable as previously assumed (Piatak et al., 2004). It is noticed that local pollution of the environment is related to wastes storage concluding that long-term disposal of slags and their exposition to weathering may lead to the mobilization of metallic elements and their transfer to environmental components such as soils, sediments, ground and surface waters (Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Vítková et al., 2010; Kierczak et al., 2013). The studies devoted to environmental aspects of slag disposal have certainly contributed to improvement of knowledge about the stability of these wastes. Therefore, waste management in modern industrial sites treats slags with a greater caution. Regardless of the potential environmental risk, these wastes are still disposed in many industrial sites, but their storage is done in accordance with strict standards of proper isolation and frequent environmental monitoring.

Chemical, textural and mineralogical characterization of slags is particularly significant for environmental risk assessment. As already mentioned, the susceptibility of slags to alterations strongly depends on their composition. Elevated concentrations of metallic elements in slags, greater porosity and the presence of phases susceptible to weathering increase the environmental risk of slag disposal. For this reason, characterization of slags is recommended as the first step of environmental investigations (Ettler et al., 2009; Piatak et al., 2015).

Numerous analytical methods can be used to study the chemical and phase composition of slags. Bulk slag chemistry analysis may be done using inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma atomic mass spectroscopy (ICP-MS) with prior material digestion. Whereas commonly used methods such as optical microscopy, scanning electron microscopy (SEM), electron microprobe analysis (EMPA), X-ray powder diffraction (XRD), X-ray fluorescence spectroscopy (XRF) and Raman spectroscopy deliver sufficient information about the phase composition of the material and the distribution of metallic elements in different phases. Combination all of these analytical methods allows a detailed slag characterization including bulk chemistry and mineralogy. These methods are considered as useful tools for laboratory simulation of the weathering as well as the further assessment of

environmental hazards through observing alteration of slag materials (Gbor et al., 2000; Kierczak et al., 2010; Jamieson, 2011; Piatak et al., 2015).

## 2.3.1  Chemical and phase composition of copper slags

The bulk chemical composition of Cu-slags varies from one smelting site to another (Table 1), depending on the type of smelted ores, fluxes and additives applied during the pyrometallurgical process (Gbor et al., 2000; Lottermoser, 2002; 2005; Harish et al., 2011; Mateus et al., 2011). Copper slags are mainly composed of $SiO_2$ with concentrations up to 70 wt.% (Sāez et al., 2003; Kierczak & Pietranik, 2011; Kierczak et al., 2013; Rozendaal & Horn, 2013; Piatak et al., 2015) and $Fe_2O_3$ up to 64 wt.% (Ettler et al., 2009). They are characterized by minor quantities of compounds such as $Al_2O_3$ and CaO. Other compounds such as MgO, $K_2O$ and S occur in much lower quantities. Additionally, they are often enriched in metallic elements such as copper, lead and zinc, reaching concentrations up to 28%, 18%, and 12%, respectively (Sāez et al., 2003; Ettler et al., 2009; Vítková et al., 2010). Other metals such as arsenic, chromium and nickel can also be present, but in much lower quantities, usually not exceeding 0.1%. Enrichment of metals in metallurgical slags reflects the inefficiency of the metallurgical process.

Variation in slag chemical composition is mainly related to the conditions of the technological process. A different silica content refers to the concentration of this compound in a primitive ore as well as the quantity of the silica flux that was added during the smelting process. Concentration of alkali compounds may also vary, reflecting its content in gangue minerals of ore (Manasse et al., 2001; Manasse & Mellini, 2002). The carbon and sulfur content may also differ. These compounds are often removed by high temperature roasting. It aims to eliminate these compounds through the conversion to $CO_2$ and $SO_2$, respectively. However, if this processing stage is inefficient, then a high sulfur (Manasse et al., 2001; Manasse & Mellini, 2002; Piatak & Seal, 2010) and carbon content may be observed in the chemical composition of the slag material. The content of metals includes a wide range of concentrations with respect to more or less efficient metallurgical processes.

Comparing the bulk metal content in slags resulting from different time periods of copper production (Table 2.1), surprisingly some ancient slags (*e.g.* São Domingos, Portugal) contain a lower content of metallic elements compared to those resulting from contemporary processing. As Roman wastes have been disposed over a long period of time, it is possible that metal concentrations were initially higher, while weathering processes leached contaminants out into the environment. Such a scenario has been proposed by Alvarez-Valero et al. (2009) who compared historical and modern slags from ore processing of the same origin.

**TABLE 2.1 Comparison of chemical and phase composition of copper rich metallurgical slags collected from several industrial areas.**

| Slag type | Location of disposal site/ Period of waste generation | Chemical composition | | Phase composition | References |
|---|---|---|---|---|---|
| | | Major compounds | Minor compounds | | |
| **Cu-slags** | USA<br>The Penn Mine California<br><br>XIXth - XXth century | **n.d.** | Cu: 0.18-6.4%<br>(1800-64 000 ppm)<br>Pb: 0.02-11%<br>(161-110 000 ppm)<br>Zn: 3.2-28%<br>(32 000-280 000 ppm) | **Glassy matrix**<br>**SILICATES:** Zn-fayalite, willemite, feldspar, quartz, pyroxene<br>**SPINEL:** gahnite, franklinite<br>**OXIDES:** magnetite, hematite<br>**SULFIDES:** pyrite, chalcopyrite, sphalerite, galena, bornite, covellite, cubanite, wurtzite<br>**SECONDARY PHASES:** barite, cerussite, chalcanthite, hydrozincite, malachite, hydrous ferric oxides | Parsons et al., (2001) |
| **Cu-slags** | ITALY<br><br>Campigilia Marittima district: Capattoli Valley<br><br>XIth -XIIIth century | **CaO-rich slags**<br>$SiO_2$: 20.06-30.06 wt.%<br>FeO : 42.53-52.17 wt.%<br>$Al_2O_3$: 2.93-5.06 wt.%<br>CaO: 8.26-15.62 wt.%<br>MgO: 0.72-0.90 wt.%<br>$K_2O$: 0.74-1.20 wt.%<br>$Na_2O$: 0.02-0.07 wt.%<br><br>**CaO-poor slags**<br>$SiO_2$ : 27.64-35.33 wt.%<br>FeO : 42.74-49.79 wt.%<br>$Al_2O_3$: 4.19-6.02 wt.%<br>CaO: 5.60-7.65 wt.%<br>MgO: 0.79-1.02 wt.%<br>$K_2O$: 0.70-1.08 wt.%<br>$Na_2O$: 0.01-0.08 wt.% | **CaO-rich slags:**<br>Cu: 0.22-0.31 wt.%<br>(2200-3100 ppm)<br>Zn: 2.22-6.07 wt.%<br>(22200-60700 ppm)<br>Pb: 0.53-1.56 wt.%<br>(5300-15600 ppm)<br><br>**CaO-poor slags:**<br>Cu: 0.25-0.31 wt.%<br>(2500-3100 ppm)<br>Zn: 1.62-3.52 wt.%<br>(16200-35200 ppm)<br>Pb: 1.70-3.40 wt.%<br>(17000-34000 ppm) | **Glassy matrix**<br>**SILICATES:** olivine: (fayalite, kirschsteinite), pyroxene: (hedenbergite), quartz<br>**SULFIDES:** galena, sphalerite | Manasse et al., (2001) |
| **Cu-Pb-Ag historical slags** | ITALY,<br><br>Massa Marittima district : Marsiliana Arialla Rochette Pannoccheschi | $SiO_2$ : 19.21-45.08 wt.%<br>FeO : 24.32-51.59 wt.%<br>$Al_2O_3$: 4.05-10.5 wt.%<br>CaO: 5.13-29.14 wt.%<br>MgO: 0.73-4.63 wt.%<br>$K_2O$: 0.85-2.05 wt.%<br>$Na_2O$: up to 0.22 wt.% | Cu: 0.07-1.23 wt.%<br>Zn: 0.31- 5.26 wt.%<br>Pb: 0.01-1.95 wt.% | <u>Marsiliana:</u><br>**Glassy matrix**<br>**SILICATES:** Pyroxenes, leucite<br>**SULFIDES:** sphalerite, galena, chalcopyrite<br>**INTERMETALLIC:** FeS, metallic lead, copper prills<br>**SPINELS**<br><u>Arialla:</u><br>**Glassy matrix**<br>**Ca-SILICATES** (mellilite, kirschsteinite), mellilite,<br>**PURE METALS:** Pb, Sb, Fe and **METAL ALLOYS:** (Cu-Sb, Fe-As) | Manasse & Mellini, (2002) |

| | | | | | |
|---|---|---|---|---|---|
| | XIIIth - XIVth century | | | Rochette Pannocchieschi: **Glassy matrix** **SILICATES:** kirchteinite **Fe-OXIDES:** (magnetite, wüstite) **SULFIDES:** chalcopyrite and pyrrhotite prills Metallic grains, Cu-Sb, Fe-As alloys | |
| **Historical Ag/Au/Cu/Pb slags** | AUSTRALIA, North Queensland XIXth - XXth century | $SiO_2$: 28.70-35.77% FeO: 31.46-43.66% $Al_2O_3$: 3.12-5.41% CaO: 9.12-15.53 wt.% MgO: 0.37-1.72 wt.% $K_2O$: <0.05-1.16 wt.% $Na_2O$: 0.04-0.26 wt.% | Cu: 0.14-0.86% (1410-8586 ppm) Zn: 1.23-5.86% (12266-58560 ppm) Pb: 0.009-5.16% (90-51620 ppm) As: 0.002-0.064% (24-635 ppm) Ag: 0.0002-0.03% (2-284 ppm) Cd: 0.001-0.002% (13-24 ppm) Ni: up to 0.003% (up to 25 ppm) | **Glassy matrix** **SILICATES:** fayalite, wollastonite, mellilite, iscorite, grossular kirschsteinite, hedenbergite, Fe-wollastonite **OXIDES:** magnetite, chromium oxides (relict phase) **SULFIDES:** pyrrhotite, bornite, galena, sphalerite, wurtzite **ALLOYS** (Ag, Cu, Sb, Pb): $Cu_3Sn$, CuSb, SbS, SbAgPb **SECONDARY PHASES:** Carbonates (cerussite, malachite, azurite, magnesite) chlorides (atacamite), Fe-(oxy)hydroxides, Sufates (gypsum, scorodite, eugsterite, syngenite) | Lottermoser, (2002) |
| **Cu-slags** | SPAIN, Huelva Province, Cabezo Jure 3000 B. C. | $SiO_2$ : 13.81-68.71 wt.% $Fe_2O_3$ : 6.72-50.6 wt.% $Al_2O_3$: 0.01-14.99 wt.% CaO: 0.2-7.85 wt.% MgO: 0.2-2.78 wt.% $K_2O$: 0.01-3.05 wt.% $Na_2O$: 0.11-1.25 wt.% | Cu: 0.14-28.06% (1400-280600) Zn: 0.006-0.14% (58-1423 ppm) Pb: 0.002-0.46% (16-4562 ppm) As: 0.006-0.86% (58-8628 ppm) Cr: 0.01-0.065% (118-653 ppm) Ni: 0.005-0.02% 53-217 ppm | **Glassy matrix** **SILICATES:** Olivine (Fe-tephorite – Mn fayalite), Pyroxene (diopside-hedenbergite), ferrobustamite, pyroxmangite, titanite **OTHERS:** quartz, Ca-rich plagioclase **OXIDES:** magnetite, maghemite, cuprite, delafossite, fluorapatite, cassiterite, ulvöspinel **SULFIDES :** chalcocite and COPPER PHASE **SECONDARY PHASES:** Fe-Mn oxides, chrosocolla, conichalcite, copper chloride | Sãez et al., (2003) |

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| **Cu historical slags** | USA<br><br>Vermont/<br>Tennessee<br><br>XIX$^{th}$ - XX$^{th}$<br>century | Si: 14.5-20.28 wt.%<br>Fe: 21-37 wt.%<br>Al: 1-4.9 wt.%<br>Ca: 0.83-4.1 wt.%<br>Mg: 0.62-2 wt.%<br>K: 0.23-1.2 wt.%<br>Na: 0.1-1.9 wt.% | Cu: 0.19-1.35%<br>(1900-13500 ppm)<br>Zn: 0.23-1.02%<br>2310-19700 ppm<br>Pb: 0.0008-0.0047%<br>(8.1-47 ppm)<br>As: up to 0.000.2%<br>(< 0.5- 2 ppm)<br>Cr: (0.004-0.028%<br>(40-276 ppm)<br>Cd: 0.00043-<br>0.00034%<br>(0.43-3.4 ppm)<br>Ni: 0.0003-0.003%<br>(2.8-27 ppm) | **Glassy matrix**<br>**SILICATES:** Fayalite-forsterite, quartz<br>Fe-Al-Ca rich glass<br>**OXIDES:** spinels, hematite<br>**SULFIDES:** pyrrhotite, Cu-Fe sulfides and pure metals<br>**SECONDARY PHASES:** amorphous Fe,Al-oxyhydroxides<br>Crystalline chalcanthite, siderotil, jarosite, brochantite, gypsum | Piatak et al.,<br>(2004) |
| **Cu/Pb historical slags** | NAMIBIA,<br><br>Tsumeb<br><br>XX$^{th}$ - XXI$^{st}$<br>century | SiO$_2$: 9.82-35.5 wt.%<br>Fe$_2$O$_3$+FeO: 8.42-64.22 wt.%<br>Al$_2$O$_3$: 2.82-18.5 wt.%<br>CaO: 2.29-17.44 wt.%<br>MgO: 0.69-5.10 wt.%<br>K$_2$O: 0.10-0.93 wt.%<br>Na$_2$O: 0.25-1.87 wt.% | Cu: 0.49-12.19 wt.%<br>(4963-121850)<br>Zn: 2.8-12.09 wt.%<br>(28188-120850)<br>Pb: 0.97-18.38 wt.%<br>(9763-183800)<br>As: 0.09-7.59 wt.%<br>(930-75865)<br>Cr: 0.02-0.16%<br>(201-1576 ppm)<br>Sb: 0.007-0.22%<br>(67-2175 ppm) | **Glassy matrix**<br>**SILICATES:** fayalite, pyroxene (monticellite), melilite, anorthite<br>**OXIDES:** spinels, wuestite, delafossite-mcconnelite<br>**SULFDES:** galena, wurtzite, sphalerite, chalcopyrite, pyrrhotite, cubanite, covellite<br>Metallic Pb and Cu<br>**OTHER PHASES:** domeykite, Cu$_5$Sb, Cu$_3$(Sn,Sb), Fe$_2$As, FeAs, Ca-Pb arsenates<br>**SECONDARY PHASES:** matrix arsenates (lammerite Cu$_3$(AsO$_4$)$_2$, bayldonite Cu$_3$Pb(AsO$_4$)$_2$(OH)$_2$ , olivenite, lavendulan) and hydrated Cu-oxides, hydrocerussite, anglesite, gypsum | Ettler et al.,<br>(2009) |

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| **Cu-historical & modern slags** | PORTUGAL<br><br>Sao Domingos District<br><br>800 B.C.-410 A.D.<br><br>XIXth century | HISTORICAL SLAG:<br>Fe: 33 wt.%<br><br><br><br><br><br><br>MODERN SLAG:<br>Fe: 41 wt.% | HISTORICAL SLAG:<br>Cu: 0.09% (926 ppm)<br>Zn: 0.03% (341 ppm)<br>Pb: 0.05% (449 ppm)<br>As: 0.0002% (2 ppm)<br>Cr: 0.006% (63 ppm)<br>Sb: 0.009% (85 ppm)<br><br>MODERN SLAG:<br>Cu: 0.27%(2739 ppm)<br>Zn: 0.89%(8940 ppm)<br>Pb: 0.51%(5051 ppm)<br>As: 0.04% (431 ppm)<br>Cr: 0.02% (164 ppm)<br>Sb: 0.01% (121 ppm) | **Glassy matrix**<br>**SILICATES:** Olivine, quartz<br>**OXIDES** grains<br>**SULFIDES:** pyrite, chalcopyrite, galena, arsenopyrite, pyrrhotite<br>Intermetallic phases: Fe-Cu-Pb<br>**SECONDARY PHASES:** jarosite | Álvarez-Valero et al., (2009) |
| **Cu-historical & modern slags** | PORTUGAL<br><br>Sao Domingos District<br><br>800 B.C –410 A.D<br><br>XX century | ROMAN SLAG:<br>$SiO_2$: 37.70 wt.%<br>$Fe_2O_3$: 52.86 wt.%<br>$Al_2O_3$: 3.93 wt.%<br>CaO: 1.14 wt.%<br>MgO: 0.40 wt.%<br>$K_2O$: 1.04 wt.%<br>$Na_2O$: 0.25 wt.%<br><br><br><br>MODERN SLAG:<br>$SiO_2$: 28.48-34.44 wt.%<br>$Fe_2O_3$: 58.15-58.52 wt.%<br>$Al_2O_3$: 1.51-1.97 wt.%<br>CaO: 4.95-6.28 wt.%<br>MgO: 0.46-0.70 wt.%<br>$K_2O$: 0.22-0.26 wt.%<br>$Na_2O$: 0.02-0.15 wt.% | ROMAN SLAG:<br>Cu: 0.03% (252 ppm)<br>Zn: 0.008% (83 ppm)<br>Pb: >0.5% (>5000 ppm)<br>As: up to 0.17% (1730 ppm)<br>Sb: 0.23% (up to 2310 ppm)<br><br><br><br>MODERN SLAG:<br>Cu: up to 0.33% (3280 ppm)<br>Zn: up to >1% (>10000 ppm)<br>Pb: up to >0.5% (> 5000 ppm)<br>As: up to 0.02% (180 ppm)<br>Sb: up to 0.05% (492 ppm) | **Glassy matrix**<br>**SILICATES:** olivine (fayalite-kirschsteinite, willemite), melilite, pyroxene (hedenbergite)<br>**OXIDES:** magnetite-franklinite, Pb-oxides, wüstite, pyrolusite, hematite-goethite<br>**SULFIDES:** pyrrhotite, pyrite, marcasite, galena, chalcopyrite<br>**SECONDARY PHASES:** Fe-oxy(hydroxides), (Cu, Fe, Pb) – sulphates | Mateus et al., (2011) |

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| **Cu/Co slags** | ZAMBIA,<br><br>Copperbelt Province<br><br>XX$^{th}$ - XXI$^{st}$ century | SiO$_2$: 15.53-60.18 wt.%<br>Fe$_2$O$_3$: 0.68-18.79%<br>FeO: 5.60-29.52%<br>Al$_2$O$_3$: 3.9-12.60 wt.%<br>CaO: 3.18-21.87 wt.%<br>MgO: 0.64-6.45 wt.%<br>K$_2$O: 1.13-4.83 wt.%<br>Na$_2$O: 0.03-0.30 wt.% | Cu <2 wt.%<br>(few samples 8.6-35 wt.%)<br>Zn: 0.004-0.23%<br>(44-2287 ppm)<br>Pb: <0.0002-0.11%<br>(<1.5-1134 ppm)<br>Co: <2% up to 2.4%<br>As: up to 0.36%<br>(603-3642 ppm)<br>Cr: 0.007-0.75%<br>(65-7510 ppm)<br>Cd: up to 0.0005%<br>(5.2 ppm)<br>Ag: up to 0.0012%<br>(12 ppm) | **Glassy matrix**<br>**SILICATES:** Olivine (fayalite-forsterite, kirschsteinite-monticellite), Pyroxene (diopside-hedenbergite), Feldspar (leucite, anorthite), quartz<br>**OXIDES:** magnetite, Cr-spinel, rutile, cuprite, delafossite<br>**SULFIDES:** bornite, digenite, chalcocite, troilite, chalcopyrite, Co-pentlandite, galena<br>**PURE METALS** (Cu, Pb, Bi) and **ALLOYS** (Fe-Co-As-Cu-Ni)<br>**INTERMETALIC COMPOUNDS** (Fe-Co)$_2$As | Vítková et al., (2010) |
| **Cu slags** | POLAND,<br><br>The Rudawy Janowickie Mountains<br><br>XIV$^{th}$ - XX$^{th}$ century | SiO$_2$: 31.88-70.72 wt.%<br>FeO: 5.58-51.13 wt.%<br>Al$_2$O$_3$: 3.84-11.91 wt.%<br>CaO: 0.59-1.68 wt.%<br>MgO: 0.53-4.19 wt.%<br>K$_2$O: 1.25-4.37 wt.%<br>Na$_2$O: 0.15-2.05 wt.% | Cu: 0.32-1.34%<br>(3030-13400 ppm)<br>Zn: 0.13-0.94%<br>(1294-9360 ppm)<br>Pb: 0.001-0.074%<br>(11-738 ppm)<br>As: 0.0003-0.03%<br>(3-315 ppm) | **Glassy matrix**<br>**SILICATES:** Olivine: fayalite, Pyroxene: ferrosillite, glass<br>**SPINEL:** hercynite, cristobalite<br>fragments of unmelted quartz<br>**SECONDARY PHASES:** Fe-silicates, Fe-oxyhydroxides, langite Cu$_4$(SO)$_4$(OH)$_6$, malachite: Cu$_2$(CO)$_3$(OH)$_2$ | Kierczak & Pietranik (2011)<br><br>Kierczak et al., (2013) |
| **Cu-slags** | South Africa<br><br>Okiep Copper District<br><br>XIX$^{th}$ - XXI$^{st}$ century | SiO$_2$: 43.76-66.52 wt.%<br>Fe$_2$O$_3$: 12.76-29.87 wt.%<br>Al$_2$O$_3$: 3.50-12.16 wt.%<br>CaO: 1.57-4.22 wt.%<br>MgO: 1.89-10.28 wt.%<br>K$_2$O: 0.32-0.82 wt.%<br>Na$_2$O: 0.19-1.54 wt.% | Cu : 0.12-0.39%<br>(1163-3871 ppm)<br>Zn : 0.015-0.53%<br>(146-5247 ppm)<br>Pb : 0.0007-0.03%<br>(6.81-339 ppm)<br>Cr : 0.04-0.22%<br>360-2238 ppm | **Glassy matrix**<br>**SILICATES:** Mg, Fe- olivine, Mg, Fe-orthopyroxene, ortho-amphibole (gedrite)<br>**SPINEL:** Cr-hercynite (picotite), hercynite, magnetite<br>**SULFIDES:** bornite, chalcocite, covelite, cobaltian, pentlandite, millerite, sphalerite, pyrrhotite, galena, castangite<br>Pb-Ni-Cu-Co-S, Re-Ni-Os-Fe-S<br>**INTERMETALLIC:** Ni-Fe, Re-Mo, Ru-Rh | Rozendaal & Horn, (2013) |

Slags are composed of various synthetic analogues of naturally occurring mineral phases (Table 2.1). However, according to the definition of a mineral (Nickel, 1995), slag constituents are not minerals because they are formed as a result of anthropogenic activities. For simplicity reasons, authors dealing with phase composition of pyrometallurgical slags use the mineral names for the synthetic equivalents (Gee et al., 1997; Manasse et al., 2001; Manasse & Mellini, 2002; Piatak & Seal, 2010; Piatak et al., 2015). Comparison of several different Cu-slags allows to distinguish the most frequently occurring phases. Generally, two types of phases are distinguished in slags: primary phases resulting from ore processing and secondary phases being the consequence of the weathering. Primary phases are volumetrically major components of slags and include silicates and silica glassy matrixes. Other primary phases such as crystalline oxides, sulfides as well as pure metals, alloys and intermetallic compounds also commonly occur in metallurgical slags, but in much lower quantities compared to silicates.

Some variations in primary phase composition are also observed due to a number of factors related to the technological process; kind of ores applied, smelting temperature, kind of additives, flux, kind of furnace material and cooling rates (Lottermoser, 2002; Mihailova & Mehandjiev, 2010; Mateus et al., 2011; Kierczak & Pietranik, 2011; Piatak et al., 2015). For each technological process these parameters may vary and consequently the phase composition in the waste materials may be diverse.

For example, studies devoted to the analysis of the slag composition revealed that the diversity of phases depends on the cooling rates. Generally, phase variety is poorer in fast cooled slags compared to those cooled at the slower rates. It is due to the fact that during slow cooling, crystallization of phases is closer to equilibrium and more phases are formed (Kierczak & Pietranik, 2011). Moreover, slow slag cooling favours partial crystallization resulting in the presence of crystalline and vitreous components, whereas rapid cooling leads to the formation of the material with amorphous structures (Gbor et al., 2000; Gorai et al., 2003; Piatak et al., 2004; Kuo et al., 2008; Álvarez-Valero et al., 2009). The smelting temperature has also great influence on the phase composition of slags. Crystallization of phases follows the general trend of formation of high temperature phases beginning from spinel, proceeding with melilite/olivine/pyroxene/plagioclase towards glass as the last formed constituent (Ettler et al., 2001; Ettler et al., 2005; Puziewicz et al., 2007; Seignez et al., 2007; Ettler et al., 2009; Piatak & Seal, 2012).

### 2.3.1.1 Primary phases

Literature focused on copper slags abounds with results of mineralogical analyses that revealed the most frequently present phases within Cu-slags. Fayalite and silicate glass are the most identified silicate phases and represent volumetrically major compounds of the materials. Pure crystals of fayalite ($Fe_2SiO_4$) correspond to the composition of FeO 70.51%

and $SiO_2$ 29.49% (Table 2.1) (Mihailova & Mehandjiev, 2010). Apart from fayalite, olivine-group phases with the composition corresponding to kirschsteinite ($CaFe^{2+}SiO_4$) and forsterite ($Mg_2SiO_4$) are also often observed (Manasse et al., 2001; Manasse & Mellini, 2002; Lottermoser, 2002; Piatak et al., 2004; Vítková et al., 2010; Mateus et al., 2011). Other phases representing pyroxene group minerals such as hedenbergite ($CaFeSi_2O_6$) and diopside ($FeCaSi_2O_6$) are commonly found in Cu-slags (Manasse et al., 2001; Lottermoser, 2002; Sāez et al., 2003; Vítková et al., 2010; Mateus et al., 2011; Piatak, 2015). Melilite ($(Ca, Na)_2(Al, Mg, Fe^{2+})(Si, Al)_2O_7$) and willemite ($Zn_2SiO_4$) represent fairly common silicates (Lottermoser, 2002; Ettler et al., 2009; Mateus et al., 2011), whereas wollastonite ($CaSiO_3$), leucite ($KAlSi_2O_6$) and iscorite ($Fe^{2+}_5Fe^{3+}_2SiO_{10}$) occur occasionally (Lottermoser, 2002; Manasse & Mellini, 2002; Vítková et al., 2010). The presence of pyroxomangite ($MnSiO_3$), titanite ($CaTiSiO_5$) and chrysocolla ($(CuAl)_2H_2Si_2O_5(OH)_4 \times n(H_2O)$) was hardly ever observed (Sāez et al., 2003).

Mineralogical examination of Cu-slags showed quite common formation of oxides such as spinels ($MgAl_2O_4$), hematite ($Fe_2O_3$), wüstite ($FeO$) and magnetite ($Fe^{2+}Fe^{3+}_2O_4$) (Parsons et al., 2001; Manasse & Mellini, 2002; Lottermoser, 2002; Sāez et al., 2003; Piatak et al., 2004; Ettler et al., 2009; Vítková et al., 2010; Mateus et al., 2011). Additionally, particular major phases (glassy matrix and silicates) demonstrate various substitutions of metallic elements (Vítková et al., 2010). Nevertheless, metallic elements (*e.g.*, Cu, Pb, Zn, As etc.) are mostly associated with copper sulfides such as bornite ($Cu_5FeS_4$), chalcopyrite ($CuFeS_2$) and chalcocite ($Cu_2S$) (Parsons et al., 2001; Manasse & Mellini, 2002; Lottermoser, 2002; Sāez et al., 2003; Ettler et al., 2009; Álvarez-Valero et al., 2009; Vítková et al., 2010; Kierczak et al., 2013) as well as other sulfide phases such as pyrrhotite ($Fe_{(1-X)}S$), sphalerite ($(Zn,Fe)S$), galena ($PbS$) and wurtzite ($(Zn,Fe)S$) (Manasse & Mellini, 2002; Lottermoser, 2002; Ettler et al., 2009; Álvarez-Valero et al., 2009; Piatak et al., 2015) due to the fact that these minerals are often associated with copper ores. Other sulfides *e.g.* cubanite ($CuFe_2S_3$), covellite ($CuS$), digenite ($Cu_9S_5$), troilite ($FeS$) and pentlandite ($(Fe,Ni)_9S_8$) are hardly observed within copper slags (Parsons et al., 2001; Ettler et al., 2009; Vítková et al., 2010).

Despite sulfides are volumetrically minor phases in slags, they are primary metal-carriers what makes them significant for environmental risk assessment. Intermetallic compounds are also considered as environmentally important metal-bearing phases because similarly to sulfides, they are very susceptible to weathering and contain high concentrations of metallic elements. As mentioned before, ores applied for the pyrometallurgical process contain sulfide minerals, hence some slag compounds reflect the kind of ores that were used for the smelting.

### 2.3.1.2   Secondary phases

A common feature of almost all Cu-slags is the presence of a number of different secondary phases resulting from weathering. They generally occur as weathering rims rising from

primary phases, poorly crystalline crusts and cemented precipitates (Lottermoser, 2010; Jamieson, 2011). Weathering related phases may be observed as effloresces occurring at/near the surface, pore fillings, fracture coatings, precipitates at seepage points and in protected overhangs (Lottermoser, 2002; Lottermoser, 2005; Lottermoser, 2010; Piatak & Seal, 2010; Piatak et al., 2015).

The secondary phases are usually represented by carbonates [*e.g.* malachite: $Cu_2CO_3(OH)_2$, azurite: $Cu_3(CO_3)_2(OH)_2$, magnesite: $MgCO_3$, cerussite: $PbCO_3$, hydrocerussite: $Pb_3(CO_3)_2(OH)_2$, hydrozincite: $Zn_5(CO_3)_2(OH)_2$], sulfates [*e.g.* anglesite: $PbSO_4$, langite: $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$, chalcanthite $CuSO_4 \cdot 5H_2O$, gypsum: $CaSO_4 \cdot 2H_2O$, eugsterite: $Na_4Ca(SO_4)_3 \cdot 2(H_2O)$, syngenite: $K_2Ca(SO_4)_2 \cdot H_2O$, chalcanthite: $CuSO_4 \cdot 5H_2O$, siderotil: $FeSO_4 \cdot 5H_2O$, jarosite: $KFe^{3+}_3(OH)_6(SO_4)_2$, brochantite: $CuSO_4 \cdot 3Cu(OH)_2$, barite: $BaSO_4$], oxides [*e.g.* Cu-oxides], (Fe,Al) (oxy)hydroxides, chlorides [*e.g.* copper chloride: $CuCl_2$, atacamite: $Cu_2Cl(OH)_3$] and arsenates [*e.g.* bayldonite: $PbCu_3(AsO_4)_2(OH)_2$, conichalcite: $CaCu(AsO_4)(OH)$, lavendulan: $NaCaCu_5(AsO_4)_4Cl \cdot 5H_2O$, scorodite: $FeAsO_4 \cdot 2H_2O$, olivenite: $CaCu(AsO_4)(OH)$] (Table 2.1). The formation of secondary phases depends on physico-chemical factors (*e.g.* pH, redox) as well as the accessibility of other compounds (cations and anions) supportive for the formation of particular phases. In some cases, secondary phases might not be observed due to short-term deposition of these materials (Ettler et al., 2009).

## 2.3.2 Environmental impact

Intensive mining and smelting activities have generated millions of tonnes of waste containing a high residual concentration of toxic or potentially toxic elements (Cu, As, Pb and Zn; Table 2.1). Metallurgical wastes disposal is nowadays unwillingly chosen and currently progressively withdrawing from waste management, because of environmental risk being a matter of rising concern. Landfill disposed slags are exposed to various bio-hydro-climatic conditions and over time undergo weathering processes leading to chemical and structural changes of the material as well as to release metallic elements. Progressive leaching of pollutants and/or fine particle dispersion in the surroundings lead to contamination of adjacent ecosystems such as soils, surface and ground waters, sediments and biota (Manz & Castro, 1997; Sobanska et al., 2000; Lottermoser, 2002; Ettler et al., 2004; Piatak et al., 2004; Vdović et al., 2006; Navarro et al., 2008; Ettler et al., 2009; Kierczak et al., 2013; Sueoka & Sakakibara, 2013). For this reason, today environmental legislation requires from the metallurgical industry safe storage of their metallurgical wastes. In the past, unfortunately, this industry did not pay so much attention to environmental protection. Hence, wastes have been often disposed off or in some cases even abandoned close to industrial areas without any environmental control. These pose a particular environmental problem if weathered (Ettlet et al., 2001; Kierczak et al., 2010; Piatak et al., 2004; Vítková et al., 2010; Tyszka et al., 2014;

Piatak et al., 2015). Therefore, the problem of the removal and disposal of pyrometallurgical wastes has become one of the key environmental issues over the last century.

Beyond slag dumps serving as metals outflow, also other wastes (*e.g.* sulfide-bearing waste rocks, tailings) and copper processing related emissions (*e.g.* atmospheric such as dust particles and volatile compounds) may be generated in industrial districts, amplifying the extent and strength of contamination. Therefore, besides local contamination, long-distance pollution might also appear in the mining and smelting sites (Tiller, 1989; Hudson-Edwards et al., 1999; Lottermoser, 2010). Most of the studies concerning environmental impact of slags and mining/smelting industries have focused on the areas restricted to the vicinities of industrial activities and revealed decreasing metal concentrations in environmental compartments away from the industrial site location (*e.g.* Çubukçu & Tüysüz, 2007). For example, enormous Cu contamination of soil even up to 500 km away from the Cu-Ni Sudbury smelting site in Canada has been demonstrated (Tiller, 1989). Thereby, potential long-distance pollution scenarios should not be neglected. Broader field monitoring is of particular relevancy, especially in historical industrial areas where slags and other wastes have been disposed for a long time and no remediation actions were introduced so far.

Soil is the first environmental component vulnerable to pollution resulting from slag alteration, because it is in direct contact with the slags (Sobanska et al., 2000; Yang et al., 2010b; Kierczak et al., 2013). Soil contamination by metallic compounds originating from mining and smelting activities has been demonstrated (*e.g.,* Sobanska et al., 2000; Ettler et al., 2004; Álvarez-Valero et al., 2009; Kierczak et al., 2013). These authors emphasized that slags constitute a real environmental problem for the areas and underline the necessity of the isolation of the wastes from the environment. Therefore, knowledge about the parameters influencing slag weathering is extremely important when slag disposal is intended. It fosters the question of which weathering parameters contribute the most to the alteration of the material.

## 2.3.3  Slags weathering

Weathering of slags can be defined as the sum of processes that affect its chemical and mineralogical composition and involve the formation of new (secondary) mineral phases. Weathering processes consist of biochemical alteration and/or physical disintegration of minerals. Physical alteration processes include cracking and/or fragmentation of slags without any chemical and mineralogical changes and is most often caused by wind, temperature changes and action of plant roots. Physical disintegration of slags increases the available surface area for further (bio)chemical weathering. The process includes several mechanisms such as hydrolysis (under humid condition), oxidation (in the presence of oxidizing agents),

reduction (in the presence of reducing agents), complexolysis (in the presence of organic or inorganic ligands) and acidolysis (under highly acidic conditions).

The extent to which weathering processes occur depends on the chemical, mineralogical and textural properties of slags, the physico-chemical conditions of the environment (pH, redox (Eh)), chemistry of solution, presence of microorganisms and the predominant (bio)chemical processes. Moreover, depending on the location in the heap profile (its external or internal part) slags undergo weathering at a different rate. Weathering processes can be more intense inside slag heaps compared to their external part (Tyszka et al., 2014). Migration of the solution (*e.g.* acid rain) inside the heap is slower than on the heap surface. Thus, longer contact time of slags with the reacting solution passing through the heap promotes greater slags weathering as shown by disintegration of the material, dissolution of primary phases and the formation of secondary phases (Tyszka et al., 2014).

Weathering of slags is thus a convoluted process, where many factors play an important role and they may vary according to local conditions and the season. For this reason, determination of the weathering behaviour of slags is a great challenge and requires understanding of the processes that they may be exposed to, when present in the environment. Although, weathering factors (physical, chemical and biological) are described separately (discussed below), they usually work together. Additionally, significant variation in the behaviour of slags may appear when weathering conditions change.

### 2.3.3.1   Primary phases: susceptibility to alteration

Slags are composed of many mineral phases (Table 2.1) present in different volumetric relations. Susceptibility of these phases to weathering is different. Hence, various slags may display different environmental behaviour when exposed to weathering. Metal-bearing sulfides are the most important from an environmental point of view. Their susceptibility to weathering is extremely high, meaning that they may be quite easily altered, especially in oxidising conditions resulting in the mobilization of metallic elements (Parsons et al., 2001; Piatak & Seal, 2010; Vítková et al., 2010). In contrast, crystalline oxides and silicates are considered as the phases with higher resistance to weathering, whereas silica glassy matrixes can be altered easily (Ettler et al., 2001; Parsons et al., 2001; Ettler et al., 2002; Lottermoser, 2002; Seignez et al., 2006; Seignez et al., 2008; Kierczak et al., 2009; Piatak & Seal, 2010; Mateus et al., 2011; Kierczak & Pietranik, 2011). Therefore, the fate of metallic elements during the weathering process depends on the resistance of the metal-bearing phases as well as the possibility of their sequestration by secondary phases.

Furthermore, an important issue related to sulfides weathering is their tendency to generate acidity when undergoing dissolution. The process corresponds to the following reaction:

$$MeS_2 + 7/2\ O_2 + H_2O \rightarrow Me^{2+} + 2\ SO_4^{2-}{}_{(aq)} + 2\ H^+ \qquad\qquad Eq\ n°4$$
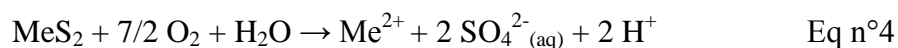
Acid generation is undesirable because it may attack other metal bearing phases (*e.g.* glass) and promote further exposure of other sulfides encapsulated within them to dissolution. The process is expected to be inhibited by carbonates. Nevertheless, carbonates do not occur abundantly in copper slags, thus silicates counteract acid generation. Although silicates such as olivine and pyroxene display an acid neutralizing capacity, their solubility is lower compared to that determined for sulfides. Therefore, the rate of their neutralization input may not be served readily enough to contribute as acid buffer (Eary & Williamson, 2006; Piatak et al., 2015). Moreover, it has to be highlighted that the strength of acid generation may be even more pronounced when waste rocks are deposited among slags in disposal sites. Waste rocks might contain sulfides in larger volumetric proportions, thereby having a greater acid generation capacity too. Such a process is known to have noxious environmental effects as has been found *e.g.* at the Rio Tinto mining site (Spain), (Lottermoser, 2010).

### 2.3.3.2 Secondary phases: formation, metal sequestration and solubility

Weathering processes lead to the formation of secondary phases such as oxides, (oxy)hydroxides, sulfates, carbonates, phosphates, arsenates, chlorides and simultaneous sequestration of metallic elements by co-precipitation or adsorption processes (Parsons et al., 2001; Lottermoser, 2002; Piatak et al., 2003; Ettler, 2003; Piatak et al., 2004; Sparks, 2005a, 2005b; Navarro et al., 2008; Piatak & Seal, 2010; Brown Jr. & Calas, 2011; Jamieson, 2011; Bolan et al., 2014). For example, compounds such as iron and manganese (oxy)hydroxides are found to be good metal scavengers (Ettler et al., 2004; Sparks, 2005b; 2005a; Ettler et al., 2005; Brown Jr. & Calas, 2011; Bolan et al., 2014). The precipitation of these phases occurs during oxidation of Fe(II) and Mn(II) ions. Furthermore, the presence of anions (*e.g.* $SO_4^{2-}$, $CO_3^{2-}$, $OH^-$ and $PO_4^{3-}$) favours precipitation of secondary phases when high concentrations of metallic elements occur nearby (Bolan et al., 2014). During the weathering of slags, the released copper is often sequestered by the precipitation of carbonates (malachite and azurite), sulfates (langite, chalcanthite and brochantite), copper oxides, chlorides (atacamite) or arsenates (conichalcite) (Parsons et al., 2001; Lottermoser, 2002; Sāez et al., 2003; Piatak et al., 2004; Kierczak et al., 2013). Lead is principally immobilized by the carbonates (*e.g.* cerussite), but also by sulfates (*e.g.* anglesite) (Gee et al., 1997; Lottermoser, 2002; Ettler et al., 2003). It was reported that cerussite plays a significant role in the regulation of metal concentrations, especially under neutral and alkaline conditions (Gee et al., 1997; Lottermoser, 2002; Ettler et al., 2003; Jamieson, 2011). Anglesite formation under acidic and neutral conditions depends on the $SO_4^{2-}$ required at a high concentration (Gee et al., 1997; Lottermoser, 2002; Ettler et al., 2003; Jamieson, 2011). Sulfates precipitation may also result from the oxidation of primary sulphides, *e.g.* pyrite or pyrrhotite (Lottermoser, 2010; Tyszka et al., 2014).

The pathway of slag weathering resulting in metal mobilization and formation of secondary phases is presented in Figure 2.2. Salt formation is intensely governed by evaporation, thus increasing the concentration of ions (anions and cations) and consequently leading to saturation and salt precipitation (Lottermoser, 2002). Sulfates may undergo further hydratation forming hydrated sulfates. In strongly oxygenated conditions, hydroxyl salts can also be formed, *e.g.* langite, malachite and azurite.

Sometimes secondary phases do not behave as stable as it would be expected (*e.g.* undergo easy erosion or dissolution). Therefore, the solubility of secondary phases is an important factor governing the fate of metals. If secondary phases do not undergo dissolution easily (*e.g.* Fe/Al-hydroxysulfates, sulfates, and carbonates), then binding of metallic elements within them is considered as the process impeding metal mobility. However, in the case that secondary phases are susceptible to erosion and dissolution in water (*e.g.* hydrous metal sulfates), then metal immobilization may be inefficient resulting in the further liberation of cations into the environment (Lottermoser, 2002; Lottermoser, 2010; Piatak et al., 2015). The solubility of secondary phases is highly variable and depends on the pH, Eh and solution chemistry. For instance, Fe/Mn oxides dissolution is faster under acidic conditions or in the presence of reductants (Sparks, 2005a).

The precipitation of secondary phases contributes to the passivation effect, limiting further accessibility to the slag surface, therefore the formation of these phases is considered as the factor reducing metal mobility (Kucha et al., 1996; Ettler et al., 2009). Secondary phases reflect the reactivity of the slag material and constitute an evidence of the weathering process (Piatak et al., 2003; Piatak et al., 2004; Piatak & Seal, 2010). Therefore, identification of these phases is an important step in risk assessment of waste materials (Ettler et al., 2001; Lottermoser, 2010).
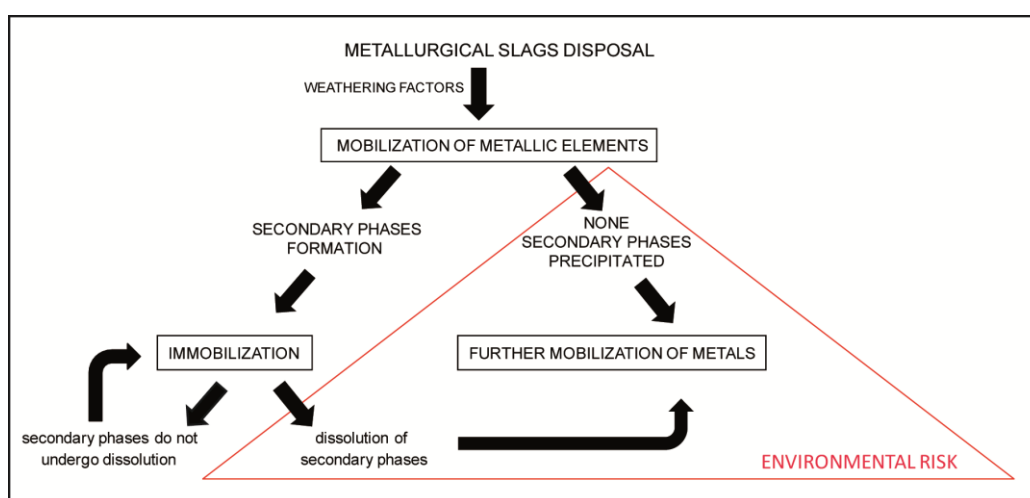


**FIGURE 2.2 Schematic picture presenting the importance of secondary phases formation.**

This scenario applies to any metallic element mobilized from metallurgical slags. The elements of particular importance depend on the slags bulk chemistry and susceptibility of the mineral phases hosting metals to weathering.

### 2.3.3.3 Weathering factors

Possible pathways of metallic elements released from slags being either disposed or abandoned in the industrial areas are presented in Figure 2.3.

### 2.3.3.3.1 Physico-chemical factors

### 2.3.3.3.1.1 Slag porosity and structure

Variation in slag structural properties and surface exposure causes that they may react at various rates under exposure to weathering. Therefore, these factors should not be neglected. The porosity of slags plays an important role in weathering processes. The pores increase the total surface area ($m^2$/g) of reaction between weathering agents and slags. Therefore, a low porosity of slags limits the surface exposure to weathering due to a decreasing accessibility to the internal part of the material. Inversely, porous material or even massive ones having holes and cracks display a larger total surface area exposed to weathering, giving easier accessibility to the internal part (*e.g.* intrusion of weathering solution) and causing that weathering processes may proceed much faster (Ettler et al., 2009; Tyszka et al., 2014). Therefore, weathering increases proportionally with the surface area. Furthermore, changes in the material structure may be observed as the result of exposure to weathering factors. Several examples showed that weathering affects the surface and shape of slags disposed into the environment. For example, Sobanska et al. (2000) observed that slags were changed to a more round-shaped morphology.

### 2.3.3.3.1.2 pH conditions

The pH is an important parameter determining the mobility of metals in the environment as well as their release from metallurgical slags. This statement is also valid for other environmental components such as soils and sediments (Sparks, 2005b; Ganne et al., 2006; Carrillo-Gonzales et al., 2006; Smith, 2007; Cappuyns and Swennen, 2008). Extreme pH values are not suitable for slags disposal, because high concentrations of $H^+$ or $OH^-$ ions attack the mineral surface, weaken the mineral binding and lead to progressive dissolution of mineral surfaces that release cations, often metallic ones. Low pH values are considered as especially inconvenient for slags disposal (Ettler et al., 2004; Kierczak et al., 2013), because these are known to have a larger impact on metal mobilization.

Higher (more alkaline) pH values play a larger role in metal immobilization through their precipitation as oxides or (oxy)hydroxides compounds or adsorption on their surface. Sorption properties of (oxy)hydroxides are efficient due to their surface charge allowing ion sorption. The negative charge of these compounds shows a high affinity to metals (Sparks, 2005b;

Sposito, 2008). At that point, pH values have also importance, because an increase in pH causes more negative charges facilitating immobilization, whereas with decreasing pH values, charges become more positive (Sparks, 2005a; Sparks 2005b; Sposito, 2008).

### 2.3.3.3.1.3   Redox potential

Another important process playing a role in slag weathering and metal fate in the environment is the reduction/oxidation (redox) potential. As oxygen is commonly present in near-surface environments, it may react with the disposed materials. Redox conditions play a role in regulation of the oxidation state of the elements, consequently their chemical speciation and mobility (Smith, 2007). Usually, oxidation enhances the release of metals, whereas metals get immobilised when oxidised metals are reduced.

Concerning secondary phases, precipitation of oxides and oxy-hydroxides is promoted at oxidizing conditions (Ettler et al., 2005; Edmunds & Shand, 2008). Due to their high sorption capacity, these secondary phases have an important contribution to the immobilization of metallic elements.

### 2.3.3.3.1.4   Organic components

Organic compounds commonly present in the soil environment may influence the stability of slags and inversely soil may be affected by slags weathering (Sobanska et al., 2000; Yang et al., 2010b; Kierczak et al., 2013). Organic acids show a high affinity to metallic elements, due to the negatively charged functional groups in their chemical structure. The strength of these organic compounds depends on the type and number of functional groups able to bind metallic cations. These compounds affect weathering by inducing the process through different mechanisms, mainly acidolysis (changing the dissolution rate of the mineral phase through delivering hydrogen ions, hence decreasing the solution pH) and complexolysis (through forming complexes with metallic cations).

It was pointed out by some studies that extremely high concentrations of organic acids, such as citric acid in the soil solution, may significantly enhance slags weathering, especially in soils rich in organic matter (Ettler et al., 2003; Ettler et al., 2004; Kierczak et al., 2013). Organic acids such as fulvic and humic acid may lead to the decomposition of the mineral phases. It happens due to acid reactions with polyvalent cations present in the minerals, consequently forming either water soluble/insoluble metal-organic complexes or chelates.

Inorganic and organic ligands involved in soil pore water may form metal complexes as follows:

$$M^{n+}_{(aq)} + xH_2O \leftrightarrow M(H_2O)^{n+}_{x(aq)} \hspace{3cm} \text{Eq. n°5}$$

$$M(H_2O)^{n+}_{x(aq)} + L^{m-} \leftrightarrow ML^{\,a-b}_{(aq)} + xH_2O \text{ ; where M: metal, L: ligand} \hspace{1cm} \text{Eq. n°6}$$
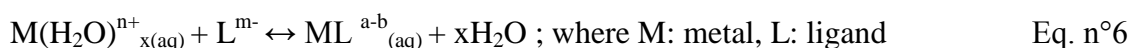
Adsorption of ligands on the mineral surface may immobilize toxic elements. However, in the case organic complexes are soluble, they increase mobility and availability of metallic elements. Stability of ligand complexes depends on metal affinity to the ligand molecule and pH value (Carrillo-Gonzales et al., 2006).
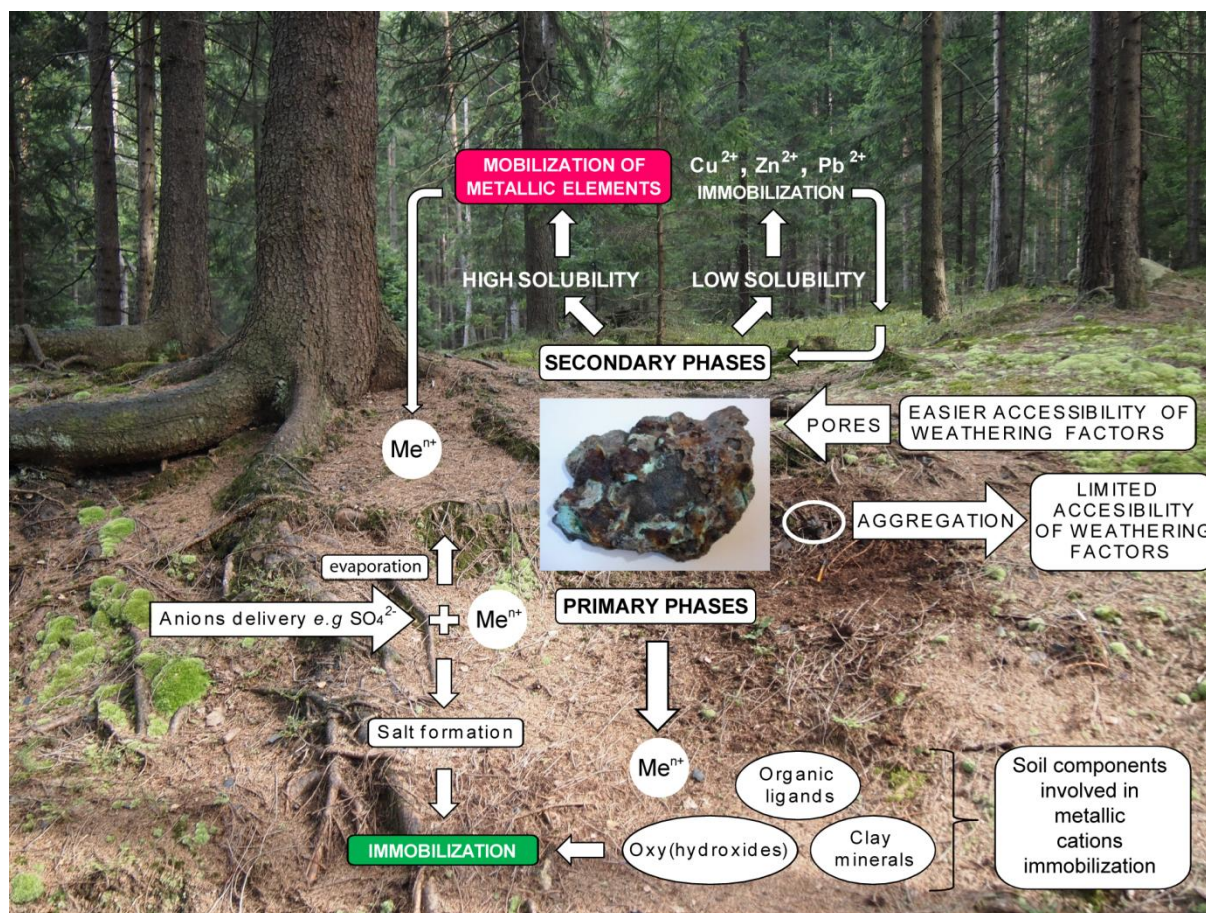


**FIGURE 2.3 Flowsheet presenting slag weathering pathways in the environment.**

### 2.3.3.3.2  Biological factors

The physico-chemical factors affecting the intensity of slags weathering are already well investigated and thus allow to predict their environmental behaviour. In contrast, little is known about the geochemical stability of these wastes in the presence of microbes.

### 2.3.3.3.2.1    Microbial actions

Microorganisms living in a soil environment undoubtedly contribute to the weathering of slags (Figure 2.4). There are many publications reporting noticeable participation of microbes in weathering of rock and minerals (Ehrlich, 1998; Brandl and Faramarzi, 2006; Uroz et al., 2009; Gadd, 2010; Lee & Pandey, 2012). Due to the fact that metallurgical slags are

composed of mineral phases similar to those formed naturally, microorganisms may significantly participate in their weathering and contribute to the mobilization/immobilization of metals (Brandl & Faramarzi, 2006). Various mechanisms such as acidolysis (by excreted inorganic and organic acids), complexolysis (by excreted metabolites such as siderophores), chemical oxidation or reduction are involved in the mobilization process (White et al., 1995; Brandl and Faramarzi, 2006; Uroz et al., 2009; Gadd, 2010). Chemical agents excreted by microbes include inorganic (*e.g.* $HNO_3$ and $H_2SO_4$) and organic (*e.g.* citric, oxalic, gluconic, formic, acetic, lactic, pyruvic, succinic and 2-ketogluconic) acids (Ehrlich, 1998). Furthermore, microorganisms can immobilize metals by biosorption to cell walls, pigments, extracellular polymeric substances (EPS), intracellular accumulation or precipitation of metal compounds in/around cells, hyphae and other structures (Gadd, 2010).

### 2.3.3.3.2.2    Biofilm formation

Microorganisms may attach to the solid surface as biofilm or microcolony and use the mineral surfaces as a source of nutrients (Gadd, 2007; Braud et al., 2009; Uroz et al., 2009; Flemming, 2011; Southam, 2012; Konhauser et al., 2011). Bioweathering is especially intensive when the surface of the mineral is covered by biofilms, due to excretion of corrosive agents (acidifying and complexing metabolites) accelerating the metal release from the underlying mineral phase (Ehrlich, 1998). However, it does not necessarily mean an increase in metal mobility in the environment because of their metal binding abilities, bacteria may also immobilize the metals.

### 2.3.3.3.2.3    Extracellular polymeric substances

There are many studies considering extracellular polymeric substances (EPS) as important players in microbial cell adhesion and biofilm formation. EPS mainly consist of polysaccharides, proteins, nucleic acids, lipids and other biological macromolecules such as humic-like substances (Wingender et al., 1999; Tsuneda et al., 2003; Comte et al., 2006; Guibaud et al., 2008; Comte et al., 2008; Vu et al., 2009; Guibaud et al., 2012). The quantity and quality of EPS in biofilms is often variable in different environmental conditions (Vu et al., 2009). EPS production is a biological response to environmental stress, allowing bacteria to protect themselves from unfavourable environmental conditions (Comte et al., 2006; Vu et al., 2009; d'Abzac et al., 2010b). These substances are also considered to assist in bacterial attachment to a solid surface (Comte et al., 2006; Vu et al., 2009; Southam, 2012; Vera et al., 2013) that may further lead to corrosion of solid materials resulting in metal mobilization.

In addition, EPS may also contribute to the immobilization of metals because of the binding properties of carboxyl, hydroxyl and amino functional groups involved in the EPS matrix (Guibaud et al., 2008; d'Abzac et al., 2010a, 2010b; Comte et al., 2006; Pal & Paul, 2008; Bourven et al., 2011; Guibaud et al., 2012; van Hullebusch et al., 2015). It has been noted that

the sorption capacity of EPS is affected by the pH (Comte et al., 2008; Guibaud et al., 2008; Guibaud et al., 2012) and metallic cation sorption is enhanced when the pH increases (Comte et al., 2008). Moreover, formation of biofilm that consists of EPS, bacteria and entrapped minerals, is considered as a diffusion barrier inhibiting mineral surface dissolution (Wingender et al., 1999).
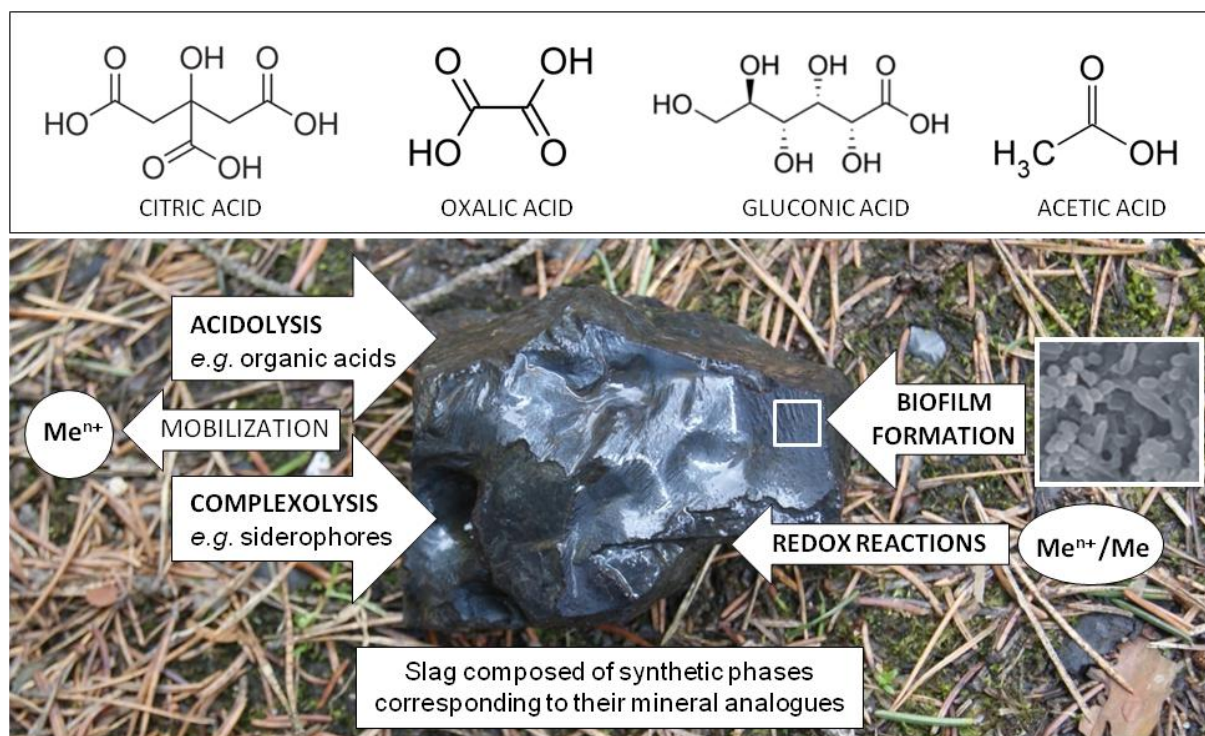


**FIGURE 2.4 Flowsheet presenting bio-weathering reactions occurring in the environment.**

Slag composed of phases being analogues of naturally occurring minerals, if disposed in the environment may be exposed to bioweathering factors. Bacterial activity may contribute to the mobilization of metallic elements through microbial interactions such as: 1) Acidolysis being secretion of acids (e.g. citrate, oxalate, gluconate, acetate, etc.) that attack surface and weaken bonds of metal consequently leading to its release and 2) Complexolysis by organic ligands. Microbial reactions also include 3) Redox reactions resulting either in mobilization or immobilization, depending on the metal form, 4) Biofilm formation on the slag surface facilitates its corrosion due to increased concentrations of excreted metabolites and extracellular polymeric substances that may sorb metals because of their binding capacity.

### 2.3.3.3.2.4    Siderophores production

Siderophores production is another aspect related to bacterial activity playing a potential role in slag weathering. Siderophores are low molecular weight organic compounds with strong binding properties, especially related to ferric ions (Gadd, 2010; Saha et al., 2013) but also to other metallic compounds (White, 1995; Hernlem et al., 1999; Braud et al., 2009; Gadd, 2010; Saha et al., 2013). Excretion of siderophores by microorganisms is an efficient way to

overcome the problem of iron-limiting conditions through Fe-acquisition from the surrounding environment (Braud et al., 2009; Konhauser et al., 2011; Saha et al., 2013). Solubility of ferric iron under circumneutral pH conditions is very low, thus the concentration of dissolved $Fe^{3+}$ can be the limiting factor for microbial and plant growth (Konhauser et al., 2011). Microbes recognize iron containing minerals (Braud et al., 2009) and siderophore production is activated. If the mineral phase has a low solubility, then the amount of siderophores produced is increased. Iron in most cases is involved in silicate minerals. However, all mineralogical phases such as oxides and (oxy)hydroxides, carbonates, sulfides, phosphates are recognized by microorganisms as a valuable source of nutrients to grow (Konhauser et al., 2011).

Metal-siderophore complexes enhance metals solubility which may facilitate the migration process. But, on the other hand, improved metal solubility (hence bioavailability) may also enhance sorption of these compounds onto microorganisms or soil particles (Hernlem et al., 1999; Saha et al., 2013).

### 2.3.3.3.2.5   Intracellular metal immobilization

Many metallic elements (*e.g.* Cu, Zn and Co) are essential for microbial life, but if their concentrations exceed the toxicity thresholds, these compounds may become deleterious (Gadd, 2010). Nevertheless, some survival mechanisms enable microorganisms to acquire metal-binding abilities by cell walls or other structural components, *e.g.* production of metal binding peptides, organic and inorganic precipitation, active transport, efflux and intracellular compartmentalization and accumulation (Gadd, 2010). The metal resistance of microorganisms is associated with the genetics of the cell. For example, bacterial plasmids code for resistance to elevated concentrations of metallic elements (Gadd, 2010). The sorption behaviour of microorganisms depends on the cell wall construction. It was noted that gram positive/negative bacteria show different sorption abilities (Kim & Gadd, 2008). The anionic charge of the carboxyl groups of peptidoglycan determines the binding abilities of Gram-positive bacteria, whereas phosphate groups are the binding sites of Gram-negative cells (White et al., 1995; Gadd, 2010; Fomina & Gadd, 2014).

One of the processes ensuring regulation of the intracellular metallic concentration is efflux transport. If metal is recognized as toxic or its concentration is too high, then transport processes are activated to decrease the intracellular metal concentration. However, if the efflux transport is not sufficient to protect the cell, then metals may be sequestrated in the cytosol (Haferburg, 2007). Another defensive property is chelation of metals outside the cell that prevents sorption onto the bacterial cell. For example, secondary metabolites such as melanin containing anionic groups (*e.g.* carboxyl or hydroxyl) that determine the cation chelating properties preventing transport of metals into the cell (Haferburg, 2007). However,

synthesis of peptides and proteins such as metallothioneins with metal binding properties may also contribute to intracellular chelation (Gadd, 2010).

Various aspects of mineral-microbial interactions may also suggest significant contributions of these organisms to the weathering of slags disposed in the environment. Participation of microorganisms in the weathering process may mobilize metallic elements, but on the other hand mechanisms of metal immobilization are also significant. Therefore, the issue of bioweathering has gained significant interests over the last several years (Yin et al., 2014; van Hullebusch et al., 2015).

Gathering all the weathering factors (physico-chemical and biological) together, it may be concluded that the most influential ones are firstly, slag exposure (*e.g.* particle size, surface area) to actions of weathering agents. Secondly, susceptibility of mineral phases hosting metals to weathering and acidity of the environment that strongly enhances the mobilization process. Additionally, the process is governed by the frequency and intensity of weathering factors and may be accelerated when one damaging factor is accompanied by another factor playing a destructive role on the slag. Therefore, differentiation of factors which contribute the most is very relative and may vary for individual slags with different geochemical characteristics.

## 2.3.4 Environmental risk assessment

The environmental impact of slags is closely related with their potential to produce hazardous leachates often containing high concentrations of metallic elements. Therefore, in order to assess a potential environmental risk caused by metallurgical slags, detailed laboratory studies are required. The traditional approach intending to assess environmental risk of slags relies on examination their activity through leaching tests (Manz & Castro, 1997; Piatak et al., 2004; Ettler et al., 2009; Piatak & Seal, 2010; Piatak & Seal, 2012; Kierczak et al., 2013; Piatak et al., 2015). Broadly defining, leaching is a process transferring metallic components from a solid material into aqueous solution using liquid solutions playing the role of leaching agents. Therefore, many leaching tests were designed to determine the reactivity of metallurgical slags under different experimental conditions. Leaching tests allow to estimate the potential leachability of inorganic components at the given experimental conditions. Concentrations of metals in the solutions give insight into the potential metal content that can be released into the environment, whereas calculated relative quantities of inorganic components passing to the solution also give information about the susceptibility of material to be weathered, allowing to assess its potential hazardousness.

It should be noted that simple leaching tests represent only possible environmental scenarios, whereas additional examination of the mineral phases (alteration) also appears to be important. Thereby, apart from chemical leaching it is also recommended to analyse mineral

phase alteration allowing to predict which conditions favour the mobilization of metals and which of them lead to their immobilization and secondary phase formation (Ettler et al., 2003). As previously discussed, mineral phases represent a different behaviour under different weathering conditions. Although metal-bearing phases can potentially release hazardous compounds, they do not have to mean a real environmental risk. Some phases may be resistant to weathering and in this case they are considered as low environmentally influential mineral phases. In contrast, other phases can be weathered easily in a given condition and should be perceived as environmentally significant. Moreover, released metals can be trapped and immobilized by precipitation of secondary phases. Therefore, leaching experiments should be coupled with mineralogical investigations to analyse interactions occurring in laboratory conditions that can subsequently be related to the weathering processes happening in the natural environment and convey important information about the reactivity of these wastes. Consequently, the combination of both of these methods is considered as an important tool for evaluation of the reactivity and environmental stability of metallurgical slags.

In the last years, growing interest has been devoted to the examination of the behaviour of slags under different leaching conditions occurring in the natural environment. Experimental set-ups applied for metallurgical slags and principal results are shown in Table 2.2. The authors presented the behaviour of slags, allowing to distinguish between metals that are mobilized easily and metals that remain immobile.

**TABLE 2.2 Leaching tests performed with metal-rich metallurgical slags.**

| Slag type/ disposal site location/ Bulk metal content | Fraction (FS)/leaching time (LT) | Leaching solution | Results | Reference |
|---|---|---|---|---|
| Ag/Pb/Zn/Cu slag<br><br>MEXICO<br>(Sta. Maria de la Paz Mining district)<br><br>Zn: 2.86%<br>As: 0.38%<br>Cu: 0.2%<br>Pb: 0.4% | FS: <2 mm and fine fraction<br>L/S: 10<br>LT: 2; 7.5; 24; 240 h<br>AS: n.i. | **Extremely aggressive conditions:** demineralized $H_2O$, pH = 1 adjusted using $HNO_3$<br>**Near neutral conditions:** Natural rain water, pH = 5.4<br>**Soil solution with high concentration of humic substances:** Water rich in humic substances, pH = 4<br>**German method for trace element extraction from soil:** 1 M $NH_4NO_3$ with pH = 4.8<br>**Calcareous soil solution:** 0.25 g $CaCO_3$/1L distilled water with pH~7 | **24 h-leaching of 2 mm fraction**<br>$HNO_3$ (Ni: 25.82% Cu: 0.16%, Zn: 9.55%, Pb: 0.34%)<br>$NH_4NO_3$ (Cu: 6.36%, Ni: 18.7%, Pb: <0.4%, Zn: <0.4%)<br>Rain water: elements below 0.07%<br>Humic substances<br>(Cu and Pb: < 0.4%)<br>$CaCO_3$: all elements below 0.05%<br><br>**24 h- leaching of fine fraction**<br>$NH_4NO_3$ (Ni: 15.5%, Cu: 8.51%, Zn: ~0.4%)<br>Humic substances (Cu < 0.4%)<br><br>**Long-term leaching:**<br>Equilibrium was achieved after 24 h, however some elements reached equilibrium after 240 h | Manz & Castro (1997) |

| | | | | |
|---|---|---|---|---|
| Cu slag<br><br>USA<br><br>Cu: up to 1.35%<br>(13500 mg/kg)<br>Zn: up to 1.02%<br>(10200 mg/kg)<br>Pb: up to 0.047%<br>(47 mg/kg)<br>As: up to<br>0.0002%<br>(2 mg/kg) | FS: <2 mm<br>L/S: 20 (50g/1L)<br>LT: 1 min<br>shaking→ settling<br>24 h | **Eastern synthetic precipitation:**<br>Leaching solution composed of mixture (ESP): $H_2SO_4$ and $HNO_3$ with deionized water adjusted to pH of 4.2<br><br>Deionized water (DW) | ESP leaching<br>Cu: up to 1800 µg/L (0.06-0.53%)<br>Pb: up to 0.3 µg/L (0.002-0.04%)<br>Zn: up to 470 µg/L (0.02-0.11%)<br>As: up to 0.3 µg/L (0.2-0.8%)<br><br>DW leaching:<br>Cu: up to 1100 µg/L (0.02-0.34%)<br>Pb up to 0.62 µg/L (0.003-0.04%)<br>Zn: up to 420 µg/L (0.02-0.11%)<br>As: up to 0.3 µg/L (0.2-1.20%)<br><br>Observations:<br>For most of the samples final pH is higher than pH of original solution. Leaching is greater in the solution with lower pH (4.2) compared to deionized water (5.0) | Piatak et al. (2004) |
| Cu/Pb slags and Cu granulated slag<br><br>NAMIBIA<br>Tsumeb area<br><br>Cu: up to 12.2%<br>(121850 mg/kg)<br>Pb: up to 18.4%<br>(183800 mg/kg)<br>Zn: up to 12.1%<br>(120850 mg/kg) | Cu/Pb slags:<br>FS:<br><4 mm (EN)<br><9.5 mm (TCLP)<br>Cu gran. slag:<br>FS <0.2mm<br><br>**EN:**<br>L/S: 10<br>LT: 24 h<br>AS: 60 rpm<br><br>**TCLP:**<br>LS ratio: 20<br>LT: 18 h<br>AS: 30 rpm | **European Norm 12457 (EN):** deionized water<br><br><br><br>**Toxicity Characteristic Leaching Procedure (TCLP):** deionized water + acetic acid + 1M NaOH<br>pH = 4.93 | **EN Historical slag - Modern slag**<br>Cu: 0.08 mg/L (0.001%) – 0.04 mg/L (0.001%)<br>Pb: <0.03 mg/L (<0.0003%)<br>Zn: 0.01 mg/L (0.0003%) – 0.005 mg/L (0.0002%)<br>As: 0.4 mg/L (0.014%) – 4 mg/L (0.17%)<br><br>**TCLP**<br>Cu: 150 mg/L (2.8%) – 20 mg/L (1.5%)<br>Pb: 50 mg/L (0.5%) – 2 mg/L (0.04%)<br>Zn: 150 mg/L (9.1%) - 6 mg/L (0.4%)<br>As: 7 mg/L (0.5%) – 5 mg/L (0.4%) | Ettler et al. (2009) |
| Cu slag<br><br>POLAND<br>The Rudawy Janowickie Mountains<br><br>Cu: up to 1.34%<br>(13400 mg/kg)<br>Pb: up to 0.07%<br>(738 mg/kg)<br>Zn: up to 0.94%<br>(9360 mg/kg)<br>As: 0.03%<br>315 mg/kg | FS: <4 mm<br>L/S: 10<br>LT: 24 h<br>AS: 200 rpm | **Neutral conditions:**<br>Deionized water<br>**Stream water**<br>**Organic rich soil conditions:** 20 mM citric acid | **Neutral conditions/Stream water conditions:** metals leaching reach the values below 0.1%<br><br>**Citric acid solution**<br>Cu: up to 2.6% (347 mg/L)<br>Zn: up to 2.2% (5 mg/L)<br>Pb: up to 1.9% (5.1 mg/L)<br>As: up to 1.1% (1.5 mg/L)<br>Fe: up to 0.8% (378 mg/L) | Kierczak et al. (2013) |

*FS: Fraction size, L/S: liquid to solid ratio, LT: leaching time, AS: agitation speed,*

*n.i.: none information provided*

Two general types of leaching tests were carried out for Cu-slags: (1) experiments under conditions corresponding to the natural environment, where slags are disposed and (2) experiments following the protocols of standardised method (Table 2.2). Experimental conditions referring to the environment cover simulation of rainfalls, peat water, calcareous soil, extremely aggressive conditions such as highly acidic (Manz & Castro, 1997) and organic matter rich (Ettler et al., 2009; Kierczak et al., 2013) soil. Standardised methods include the Eastern synthetic precipitation procedure (Piatak et al., 2004), European Norm and the Toxicity Characteristic Leaching Procedure (Ettler et al., 2009).

Generally, in most experiments that followed standardized procedures, copper showed irrelevant mobilization not exceeding 0.53% (1.8 mg/L) (Piatak et al., 2004) and reaching a maximum mobilization of 2.8% (150 mg/L) (Ettler et al., 2009). In the case of experimental designs that simulate the natural environment, the mobilization of copper was slightly higher. Although, relative values of leached metals seem to be comparable, their concentrations in the solution are variable. The quantity of leached copper was in the range of 0.16% and 2.6% for experiments representing aggressive conditions and organic matter-rich conditions, respectively (Manz & Castro, 1997; Kierczak et al., 2013). The highest extraction efficiency of 6.36-8.51% was achieved by leaching with $NH_4NO_3$ (Manz & Castro, 1997). However, it has also to be noticed that the quantity of solubilized copper was different due to the different chemical and mineral phase compositions of slags. Apart from copper, metals such as lead, zinc, nickel and arsenic were also measured. Zinc and lead revealed comparable leachability usually not exceeding 0.4%, except under aggressive conditions that reached an extraction level of 9.55% for zinc (Manz & Castro, 1997) and citric acid solution which leached up to 1.9% of lead (Kierczak et al., 2013). Arsenic showed a limited mobility achieving values not exceeding 1.2% (Piatak et al., 2004; Ettler et al., 2009; Kierczak et al., 2013).

The results obtained for particular leaching solutions showed that acidified inorganic solutions and organic acids have definitely a greater influence on the slags stability than deionised water where metals showed concentrations at least one order of magnitude lower (Piatak et al., 2004; Ettler et al., 2009; Kierczak et al., 2013). Therefore, despite the fact that the pH is an important parameter driving metal mobility, bulk solution chemistry (*e.g.* the presence of organic compounds) should also be considered as it might strongly influence the leaching process.

## 2.4  FATE OF COPPER SLAGS

The annual global production of Cu-slags is maintained on the approximate level of 24.6-64.6 million tons. Per ton of copper produced, approximately 2.2 tons of metallurgical slag is generated (Gorai et al., 2003; Harish et al., 2011; Chen et al., 2012; Muravyov et al., 2012). Disposal of these waste materials takes wide surface areas and may additionally be a source of

environmental pollution (Shen & Forssberg, 2003; Lim & Chu, 2006; Lottermoser, 2011). Therefore, alternative uses of these wastes are being explored (Reuter et al., 2004). Searching alternative management ways for slags has been the objective of studies considering the possibility of their application for civil engineering purposes (Shi & Qian, 2000; Al-Jabri et al., 2006; Moura et al., 2007; Shi et al., 2008; Al-Jabri et al., 2009; Najimi et al., 2011; Al-Jabri et al., 2011) or even land reclamation (Lim & Chu, 2006). Utilization of metallurgical slags as additives for building and construction materials appears to be a good solution to the problem of limited availability of disposal sites (Gorai et al., 2003; Mihailova & Mehandjiev, 2010; Piatak et al., 2012). Nevertheless, it has to be underlined that application of metallurgical slags as additives for civil engineering materials demands in depth examination of the material, especially considering their behaviour in the target material as well as its environmental impact. Thus, this way of utilization may be only justified in case prior analysis of the material confirms their stability at certain conditions proving their inertness (Mateus et al., 2011; Tyszka et al., 2014; Ettler & Johan, 2014). In this case, application of slags as additives may be used in practice and is fully comprehensible from environmental point of view.

Due to environmental issues related to slags disposal, these materials are perceived as unwanted wastes. On the other hand, their high metallic element content triggers research on profitable methods of metal recovery (Shen & Forssberg, 2003; Altundoğan et al., 2004; Deng & Ling, 2007; Rudnik et al., 2009; Vestola et al., 2010; Kaksonen et al., 2011; Erüst et al., 2013). The processes of (bio)leaching and (bio)recovery of valuable metals from solid materials have gained particular attention in recent years due to the fact that they have relevant practical importance for sustainable future management of slags (Lee & Pandey, 2012). That is why great efforts have been devoted to the study of the leaching behaviour of copper slags under various experimental conditions.

## 2.4.1 Metal leaching

The first stage of a (bio)recovery process relies on the leaching of metals from the solid material into a liquid solution using either chemical agents (*e.g.* strong acid) or solutions with microorganisms. Proper adaptation of leaching conditions allows to achieve high values of extracted metals.

Chemical leaching is a traditional approach in metal recovery processes and in many studies it allowed to recover significant quantities of metals of interest. Literature focused on metallurgical slags shows a variety of approaches investigating the influence of the extractant, its concentration, temperature, solid/liquid ratio, and leaching time. Different set-ups designed for leaching of Cu-slags including the overall experimental conditions and observations made are summarized in Table 2.3.

**TABLE 2.3 Leaching and recovery of metals from Cu-rich metallurgical slags.**

| Type of slag & Composition [wt. %] | Leaching conditions | Results and observations | References |
|---|---|---|---|
| **Cu-converter slag**<br><br>Fe: 38.32%<br>Cu: 4.03%<br>Co: 0.49%<br>Ni: 1.97% | Extractant: $FeCl_3$<br>FS: <100 μm – 420 μm<br>L/S: 2.5 – 10 (40 - 10% of solid)<br>T: 29 – 100°C<br>LT: 0.25 h – 3 h<br>AS: 0 – 300 rpm | • Stirring enhances metal extraction compared to extraction efficiency without stirring. (No significant difference noted when stirring speed increased from 100 rpm up to 300 rpm)<br>• Extension of leaching time improved extraction efficiency, especially in the range 0.25 – 2 h<br>• Ambient temperature (29°C) allowed to achieve good Cu extraction of 64% (25.8 g/kg), whereas higher temperature was required for Ni and Co extraction<br>• Increased temperature facilitated metal extraction, especially for Cu and Ni (29-100°C), whereas improved leaching was observed from temperature of 55°C for Co<br>• Decreasing of particle size from 350 to 105 μm enhanced metal extraction, especially in case of Cu<br>• Method was assumed to be efficient for leaching of metals from Cu-converter slags<br>• Conditions of: PS <150 μm, LT: 2.5 h, T: 85°C, amount of ferric chloride 1.25×stoichiometric were found to give optimum leaching of: Cu 92% (37.1 g/kg) #, Ni 23% (4.5 g/kg), Co 24% (1.2 g/kg) | Anand et al. (1980) |
| **Cu-flash smelter slag**<br><br>Fe: 46.46%<br>Cu: 1.76%<br>Co: 0.19%<br>Ni: 0.23% | Extractant: $FeCl_3$<br>FS: <53 – <150 μm<br>L/S: 10<br>T: 100°C<br>LT: <3h – 12 h<br>AS: 200 rpm | • Excess of ferric iron improves copper extraction from smelter slags<br>• Decreasing of particle size allowed to achieve better extraction of metals, especially when FS < 53 μm<br>• Increase of leaching time (from 3 up to 6 h) positively affects extraction of Co and Ni, whereas none significant changes were observed for Cu<br>• Method applied for smelter slags allowed to achieve maximum extraction of 54% (9.5 g/kg) #<br>• Conditions of: PS < 53 μm, LT: 6 h, T: 100°C, amount of ferric chloride 5×stoichiometric were found to give optimum leaching of: Cu 54% (9.5 g/kg) #, Ni 77% (1.8 g/kg), Co 44% (0.8 g/kg) | Anand et al. (1980) |

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| **Cu-converter slag**<br><br>Fe: 38.32%<br>Cu: 4.03%<br>Co: 0.48%<br>Ni: 1.98% | Roasting agent: charcoal, furnace oil, lignite, bituminous coal<br>Roasting T: 750°C<br>Roasting time: 0.25 – 2 h<br>Extractant: $FeCl_3$<br>FS: 150 µm (100 mesh)<br>L/S: 1.2 – 2.4 ($FeCl_3$ [g] / 10 g slag)<br>T: 100°C<br>LT: 0.5 – 3 h<br>AS: present (n.i. rpm) | • Roasting time did not have any influence on Cu leachability by ferric chloride as Cu may be leached out from unreduced slag (Anand, 1980)<br>• Roasting improved extraction of cobalt and nickel present in oxide form due to $MO + C \rightarrow M + CO$<br>• Co and Ni recovery increased at roasting (with furnace oil) temperature of 850°C having adverse effect on Cu (depletion from 95% (38.3 g/kg) # to 80% (32.2 g/kg))<br>• Reducing agents may improve Co and Ni extraction in fixed roasting temperatures | Anand et al. (1981) |
| **Cu-converter slag**<br><br>Fe: 38.32%<br>Cu: 4.03%<br>Co: 0.49%<br>Ni: 1.97% | Extractant: $H_2SO_4$ (0.2 – 0.35 N)<br>Oxygen pressure: 0.45 - 0.59 MPa<br>FS: 52 - 270 µm<br>L/S: 2.5 – 20 (40 – 5% of solid)<br>T: 130°C<br>LT: 1 – 4 h<br>AS: 840 rpm | • Maximum metals dissolution achieved at 4 h of experimental time<br>• Increasing of pulp density (especially from 10 to 40%) led to decreased metal extraction<br>• Higher acid concentration improved metals leaching<br>• Lower particle size favors metal extraction<br>• Increased oxygen pressure improved metals extraction<br>• Conditions of: SL: 10%, 0.35 N acid concentration, T: 130°C, $O_2$ pressure 0.59 MPa, LT: 4 h, stirring: 840 rpm were found to give optimum leaching of: Cu 92% (37.1 g/kg) #, Ni >95% (> 18.7 g/kg), Co >95% (> 4.7 g/kg) | Anand et al. (1983) |
| **Cu-converter slag**<br><br>Fe: 38.32%<br>Cu: 4.03%<br>Co: 0.48%<br>Ni: 1.98% | Roasting/leaching<br>Roasting agent : $(NH_4)_2SO_4$ (0.5 – 2.5 × stoichiometric)<br>Roasting T: 200 – 600°C<br>Roasting time: 0.25 – 2 h<br>Extractant: $H_2O$<br>FS: 60 – 300 µm | • Increase of roasting temperature from 200 to 400°C increased recovery of Cu, Ni, Fe, whereas Co extraction was not affected by temperature<br>• The time of 1 h was found to be suitable roasting duration<br>• Increasing amount of $(NH_4)_2SO_4$ improves metal extraction<br>• Optimal sulfation temperature is 400°C<br>• Reduction of particle size has positive effect on metals recovery, especially in the range 300-75 µm<br>• Optimal conditions: FS < 75µm, 2.5×stoichiometric requirement of $(NH_4)_2SO_4$, T: 400°C, LT: 1 h (Co 85% (4.1 g/kg), Ni 80% (15.8 g/kg), Cu 85% (34.3 g/kg) #, Fe 37% (141.8 g/kg)) | Sukla et al., (1986) |

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| **Cu-converter slag**<br><br>Fe: 38.32%<br>Cu: 4.03%<br>Co: 0.48%<br>Ni: 1.98% | Roasting/leaching<br>Roasting agent : $(NH_4)_2SO_4$ and $H_2SO_4$<br>Roasting T: 30 – 600°C<br>Roasting time: 0.25 – 2 h<br>L/S: n.i.<br>Extractant: $H_2O$ | • Temperature in the range 30-200°C appears to be suitable when $H_2SO_4$ used as sulfating agent<br>• Increase of temperature above 200° leads to $H_2SO_4$ evaporation, hence decreases metals extraction<br>• Stoichiometric quantity of $H_2SO_4$ is sufficient to reach satisfactory metal extraction Cu, Co, Ni, Fe<br>• Time of 0.5 h appears to give satisfactory extractions of: Cu 90% (36.3 g/kg), Ni 95% (18.8 g/kg), Co 100% (4.8 g/kg), Fe 50% (191.6 g/kg)<br>• Optimal conditions: stoichiometric requirement of $H_2SO_4$, T: 150°C, LT: 1 h (Co 95% (4.6 g/kg), Ni 95% (18.8 g/kg), Cu 95% (38.3 g/kg) # and Fe 70% (268.2 g/kg))<br>• Two stage roasting reduces contamination of solution by Fe to 1.5% (5.7 g/kg) | Sukla et al., (1986) |
| **Cu-converter slag**<br><br>Fe: 52%<br>Cu: 2.6%<br>Zn: 0.43%<br>Co: 0.36%<br>Ni: 0.05% | Roasting agent: $Fe_2(SO_4)_3 \times H_2O$<br>$Fe_2(SO_4)_3 \times H_2O$ /slag ratio: 1<br>Roasting T: 300 – 800°C<br>Roasting time: 0.5 – 4 h<br>Extractant: $H_2O$ and $H_2SO_4$<br>FS: < 74µm<br>L/S: 5 (20% of solid)<br>T: 25°C<br>LT: 0.5 h<br>AS: present (n.i. rpm) | • Metals recovery increases with increased roasting temperature to 500-550°C reaching Cu> 95% (24.7 g/kg) #, Zn 65% (2.8 g/kg), Co 40% (1.4 g/kg), Ni< 15% (0.08 g/kg) (0.5 h leaching)<br>• Roasting time of 2 h was found to give the best values of extracted metals during 0.5 h leaching<br>• Increase of ferric sulfate/slag ratio improves Cu extraction (Cu~75% (~19.5 g/kg) at 0.5 ratio, Cu> 95% (24.7 g/kg) # at 1-2.5 ratio | Altundoğan and Tümen (1997) |
| **Reverberatory slag**<br><br>$Fe_3O_4$: 7.58%<br>Fe: 32.2%<br>(Fe total: 37.7%)<br>Cu: 1.22%<br><br>**Flash slag**<br><br>$Fe_3O_4$: 7.35%<br>Fe: 35.8%<br>(Fe total: 41.1%)<br>Cu: 1.61% | Extractant: Chlorine solution ($Cl_2$) generated from reaction of sodium hypochlorite (NaOCl) with hydrochloric (HCl) or sulfuric ($H_2SO_4$) acids<br>Initial chlorine concentration/HCl medium: $0.65·10^{-2} – 1.5·10^{-2}$ M<br>Initial chlorine concentration/$H_2SO_4$ medium: $0.2·10^{-2} – 0.65·10^{-2}$ M<br>FS: <20 µm – <100 µm<br>L/S: 60<br>T: 7 – 45°C<br>LT: 0.083 – 0.5 h (5 – 30 min.)<br>AS: 600 rpm | • The smaller particle size allows to reach more efficient leaching (FS <20 µm: Cu 80-90% (11-12.9 g/kg) # and Fe 4-8% (15.1-32.9 g/kg); FS~90 µm: Cu ~ 50% (6.1-8.1 g/kg))<br>• Effect of temperature on Cu extraction is negligible<br>• Increased temperature favours Fe extraction: 5% (18.8 g/kg) (7 - 20°C) and 17% (64.1 g/kg) (45°C)<br>• Chlorine leaching ensures quick Cu extraction (5 min.). Extension of leaching time has negligible effect.<br>• Fe leaching increases with time: 4% (15.1 g/kg) (5 min.) and 7% (61.4 g/kg) (30 min.)<br>• Reduced leaching time and ambient temperature were found as optimal conditions for selective leaching | Herreros et al. (1998) |

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| **Cu-brass melting slag**<br><br>Cu: 6.3%<br>CuO: 14.4%<br>(Cu: 17.8%)<br>ZnO: 11.35%<br>(Zn: 9.1%)<br>PbO: 1.33%<br>(Pb: 1.23%) | Extractant: HCl, $H_2SO_4$, $H_2O_2$, $NH_4OH$<br>FS: n.i. (>8 mm f <0.9 mm)<br>L/S: n.i.<br>LT: 1 – 24 h<br>T: 10 – 90°C<br>AS: present (n.i. rpm) | Evaluated parameters: stoichiometric ratio, L/S, temperature, time, pH<br>• Increasing concentration (0-12) of HCl favours metals extraction (12 M HCl: Cu 33% (55.8 g/kg), Zn 43% (39.2 g/kg), Pb 17% (2.1 g/kg))<br>• Increasing concentration (4-16) of $H_2SO_4$ favours extraction of Cu and Zn, whereas Pb is not leached out (4 M $H_2SO_4$: Cu 55% (97.9 g/kg), Zn 65% (59.2 g/kg))<br>• $NH_4OH$ efficiently leaches Cu and Zn increasing their leachability when concentration of solution increases, whereas Pb leaching elevates not higher than 2% (0.2 g/kg) (>13 M $NH_4OH$: Cu: 81% (144.2 g/kg), Zn: 73% (66.5 g/kg))<br>• Addition of $H_2O_2$ improves metals extraction when HCl or $NH_4OH$ is used as leaching solution (6 M HCl + 25 mL $H_2O_2$/100 mL leachate: Cu 94% (167.4 g/kg), Zn 97% (88.4 g/kg), Pb 80% (9.9 g/kg)), (6.8 M $NH_4OH$ + 25 mL $H_2O_2$/100 mL leachate: Cu ~100% (~178 g/kg) #, Zn 98% (89.3 g/kg), Pb 6% (0.7 g/kg))<br>• Thermal activation was found to be a factor enhancing metals leaching using HCl, $H_2SO_4$, $NH_4OH$ as extractants | Basir & Rabah (1999) |
| **Cu slag**<br><br>Fe: 20.7%<br>Si: 15.37<br>Cu: 1.43%<br>Zn: 8.9%<br>Co: 0.72% | Extractant: $H_2SO_4$ + $H_2O_2$ (0 – 125 L/t slag)<br>FS: <100 μm<br>L/S: 10<br>T: 24 – 80°C<br>LT: 0.25 – 3 h (15 – 180 min.)<br>AS: present (n.i. rpm)<br>pH : 2.5<br>Eh : 450 – 650 mV | • Increase of the temperature to 60°C significantly improved extraction efficiency<br>• High concentration of: Cu, Co, Zn obtained during 60 min. of experiment<br>• Silica gel formation (approximately 3-8 g/L)<br>• Leaching: Cu 60% (8.6 g/kg), Co 90% (6.5 g/kg), Zn 90% (80.1 g/kg), Fe 90% (186.3 g/kg) (2 h, 80°C)<br>• Leaching: Cu 80% (11.4 g/kg), Co 90% (6.5 g/kg), Zn 90% (80.1 g/kg), Fe 5% (10.4 g/kg) (70°C, pH = 2.5, $H_2O_2$ addition)<br>• Optimal dosage of $H_2O_2$ : 62.5 L/ t slag<br>• Addition of oxidant significantly decreases Fe content in the solution<br>• Leaching at higher redox potential can improve leaching efficiency (time) *e.g.* Cu: 65% (9.3 g/kg) (450 mV, 180 min) = (650 mV, 60 min)<br>• Recovery (selective solvent metal extraction): Cu >99%, Co >96%, Zn >99%<br>• Overall recovery: Cu 80% (11.4 g/kg) #, Co 90% (6.5 g/kg), Zn 90% (80.1 g/kg) | Banza et al. (2002) |

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| **Cu-converter and flash smelter slag mixture**<br><br>Fe: 47.2%<br>Cu: 2.64%<br>Zn: 0.67%<br>Co: 0.095%<br>Pb: 0.13% | Roasting agent: $H_2SO_4$<br>$H_2SO_4$/slag ratio: 3<br>Roasting T: 150-300°C<br>Air flow rate: 2.5 L/min<br>Extractant: $H_2O$, $H_2SO_4$<br>FS: <100 μm (<0.1 mm)<br>L/S: 5 g slag + water 500 mL or 5 g slag + 100 mL solution (20 g/L $H_2SO_4$)<br>T: 70°C<br>LT: 0.5 – 4 h<br>AS: 400 – 450 rpm | Evaluated parameters: effects of roasting time, acid/slag ratio, roasting temperature<br>• Acid roasting following hot water leaching (2 h, 150°C, A/S ratio: 3) gives the highest metals extraction of: Cu: 88% (23.2 g/kg), Co: 87% (0.8 g/kg), Zn: 93% (6.3 g/kg), Fe: 83% (391.8 g/kg)<br>• Roasting time: metals extraction increases with time until 2 h, but further extension of time up to 4 h allows to extract even 95% (25.1 g/kg)# of Cu<br>• Increase of roasting temperature to 250°C allows to extract even 100% of Cu (26.4 g/kg)<br>• Thermal decomposition decreases metal extraction (Cu 79% (20.9 g/kg), Co 66% (0.6 g/kg), Zn 41% (2.7 g/kg)), but allows to maintain Fe extraction on a very low level<br>• In order to ensure higher efficiency of recovery, leaching solution may be re-submitted to leaching until expected metal content is reached<br>• $H_2S$ precipitation proposed as the recovery method | Arslan & Arslan (2002) |
| **Converter slag**<br><br>Fe: 45.20%<br>Cu: 2.97%<br>Zn: 1.54% | Extractant: $H_2O$ saturated with $Cl_2$ gas (flow rate: 180-220)<br>FS: 150 μm (100 mesh)<br>L/S: 6.02-10 (S/L: 0.166 – 0.1)<br>T: 30°C<br>LT: 1.5 – 3.5 h (90 – 210 min.)<br>AS: 350-750 rpm | • Stirring is a parameter affecting Cu dissolution, whereas temperature showed lower importance<br>• Reaction time is a parameter affecting Fe and Zn dissolution<br>• Optimum parameters for designed setup are as follow: 220 mL/min flow rate, LS = 0.1, 550 rpm, time of 90 min.<br>• At optimum working conditions ($Cl_2$ flow: 220 ml/min., LS: 10, stirring: 550 rpm, LT: 1.5 h) 98.35% (29.2 g/kg) # (Cu) and 25.17% (3.9 g/kg) (Zn) were dissolved | Beşe et al. (2003) |
| **Converter slag**<br><br>Fe: 52.18%<br>Cu: 4.36%<br>Zn: 0.64%<br>Co: 0.45% | Extractant: $H_2SO_4$ (0.1 – 1.0 M) + $K_2Cr_2O_7$ (0 – 0.3 M)<br>FS: <74 μm<br>L/S: 100<br>T: 25°C<br>LT: 2 h (120 min.)<br>AS: 400 rpm | Evaluated parameters: effect of $H_2SO_4$ and $K_2Cr_2O_7$ concentration on metal extraction<br>• Higher concentration of $H_2SO_4$ increases metal extraction (*e.g.* 1 M $H_2SO_4$: Cu: 20.5% (8.9 g/kg), Co: 66.6% (3 g/kg), Fe: 62.1% (324 g/kg), Zn: 65.7% (4.2 g/kg))<br>• Cu leaching is more efficient when $K_2Cr_2O_7$ is added, whereas decreasing efficiency was observed for other metals *e.g.* 1 M $H_2SO_4$: Cu: 81.2 % (35.4 g/kg) #, Co: 12 % (0.5 g/kg), Fe: 3.15% (16.4 g/kg), Zn: 10.27% (0.7 g/kg)<br>• $K_2Cr_2O_7$ is suggested as the chemical agent enhancing copper leaching having adverse effect on extraction of other metals (Fe, Co, Zn) | Altundoğan et al. (2004) |

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| **Cu-converter slag**<br><br>Fe: 44.17%<br>Cu: 3.25%<br>Zn: 1.56%<br>Co: 0.05% | Extractant: $H_2SO_4$ (0.05 – 0.20 M) - $Fe_2(SO_4)_3$ (0 – 0.15 M)<br>FS: <125 μm<br>L/S: 25<br>T: 25 – 65°C<br>LT: 0.67- 3 h (40 – 180 min)<br>AS: 650 rpm<br>Ultrasound | Evaluated parameters: temperature, $H_2SO_4$ concentration, $Fe_2(SO_4)_3 \times H_2O$ concentration, time, effect of ultrasound (presence/absence)<br>• Application of ultrasound generally improves the levels of metals extraction<br>• $Fe_2(SO_4)_3$ improves Cu extraction, having adverse effect on other metals (Zn, Co, Fe)<br>• Optimal conditions: 65°C, 0.2 M $H_2SO_4$, 0.15 M $Fe_2(SO_4)_3$, LT: 3 h (without application ultrasound: Cu 80.41% (26.1 g/kg), Zn 48.28% (7.5 g/kg), Co 64.52% (0.3 g/kg), Fe 12.16% (53.7 g/kg); with application ultrasound: Cu 89.28% (29 g/kg) #, Zn 51.32% (8 g/kg), Co 69.87% (0.3 g/kg), Fe 13.73% (59.1 g/kg)) | Beşe (2007) |
| **Cu-converter slag**<br><br>Fe: 51.04%<br>Cu: 2.33%<br>Zn: <0.1%<br>Co: 0.44% | Aging agent: $H_2SO_4$<br>$H_2O$/slag ratio: 0-5<br>Aging temperature: 20-250°C<br>Aging time: 1.5 – 12 h<br>Extractant: $H_2O$<br>FS: < 0.074μm; 0.147 > f > 0.104; 0.246 > f > 0.147<br>L/S: 1 – 25<br>T: 25 – 80°C<br>LT: 2 h (120 min)<br>AS: 200 rpm | • Rapid addition $H_2SO_4$ causes heat generation leading to volatilization of water excess<br>• Increased quantity of acid favors metals yield<br>• Decreased particle size is found to give better leachability of metals<br>• Increased ageing temperature allows to achieve greater metal extraction (for Co until 100°C, whereas for Cu and Fe continuously improved extraction up to 250°C)<br>• Higher temperature allows easier separation of liquid and solid hence avoid metal absorption within silica gel<br>• Ageing time does not have a significant effect on Co extraction, but influences Cu and Fe extraction<br>• Optimum quantity of water ensures proper mixing of slag with acid and avoids formation of gelatinous products<br>• Increased leaching temperature favours metal extraction<br>• Enhanced decomposition of magnetite and sulfide oxidation through extension of ageing time suggested as the way to improve extraction process<br>• Following conditions for the process were found to be optimal: slag/water ratio during ageing: 1:1, LT: 15 days, slag/leachate ratio of 5, 80°C, 60-80 min.<br>• Extraction efficiency: ~98% (4.3 g/kg) Co, ~93% (21.7 g/kg) # Cu | Deng & Ling (2007) |

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| **Ni/Co/Cu slags**<br><br>**Converter slag**<br><br>Fe: 42.3-51.1%<br>Cu: 0.17-1.40%<br>Zn: 0.01-0.02%<br>Co: 0.77-1.59%<br>Ni: 2.87-4.80<br><br>**Electric furnace slag**<br><br>Fe: 34.3-37.4%<br>Cu: 0.21-0.28%<br>Zn: 0.06-0.1%<br>Co: 0.09-0.13%<br>Ni: 0.22-0.32% | Oxidative pressure leaching test (oxygen pressure 520 kPa, total pressure: 2100-4500 kPa)<br><br>Extractant: $H_2SO_4$ (5 g/L) and $H_2O$<br>FS: 50 μm<br>A/S ratio: 0.3 – 0.5<br>L/S: 4.55 – 2.63 (S/L: 0.22- 0.38)<br>T: 250°C<br>LT: up to 1 h<br>AS: 700 rpm | • Oxidative pressure leaching facilitate leaching of metals (low concentration of metals observed in the setup without oxygen overpressure)<br>• Extraction of Cu, Co and Ni from converter slag reached high approximate levels of 80% (Cu: 1.5-12.6 g/kg #, Co: 5.5-15.7 g/kg, Ni: 22.4-47.5 g/kg) within 60 minutes of experiment duration, whereas results obtained for experiment with absence of oxygen were much lower (Co: 37% (0.3 g/kg), Ni: 20% (0.6 g/kg), Cu: 0%)<br>• In absence of oxygen only oxides associated metals are leached (metals associated with sulfides do not undergo dissolution)<br>• Greater acidity results in faster dissolution and higher extraction of Ni and Co<br><br>• Higher degrees of extraction obtained for slow cooled (crystalline) slags than for rapidly cooled ones<br>• Values of leached metals from electric furnace slag with oxygen overpressure within 1 h: rapidly cooled slag (Cu 40% (1.2 g/kg), Co 30-50% (0.4-0.7 g/kg), Zn 25% (0.3 g/kg), Ni 25% (0.6 g/kg)), slow cooled slag (Cu 75% (1.6 g/kg)#, Co 80% (0.7 g/kg), Zn 60% (0.4 g/kg), Ni >80% (> 2.6 g/kg)) | Baghalha et al. (2007) |
| **Cu slag**<br><br>Fe: 40 %<br>Cu: 9.13 %<br>Zn: 1.36 | Extractant: $Fe_2(SO_4)_3$ (11 g/L)<br>FS: 22 μm > f > 840 μm<br>L/S: 10 – 50 (10 – 2% pulp density)<br>T: 25 – 80°C<br>LT: 2h<br>AS: 240 rpm | Evaluated parameters: ferric iron concentration, pulp density, fraction size, temperature, time<br>• Cu extraction decrease as pulp density increase (because of $Fe^{3+}$ depletion)<br>• Ferric leaching is activated by the temperature (especially in the range of the temperature 25-50°C)<br>• Optimal conditions can be achieved with low pulp density or high ferric iron concentrations<br>• Smaller fraction size allows reach better results of leaching<br>• Increasing temperature improves Cu extraction<br>• Extension of leaching time slightly improves extraction efficiency<br>• Fe(III) = 11.5 g/L; T = 60°C, PD = 2%: Cu recovery : >93% (84.9 g/kg) # | Carranza et al. (2009) |

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| **Cu slag**<br><br>Fe: 28.43 %<br>Si: 15.38%<br>Cu: 1.35 %<br>Zn: 1.70 %<br>Co: 4.09 %<br>Pb: 1.16% | Extractant: $H_2SO_4$ / $NaClO_3$/NaOH or $Ca(OH)_2$<br>FS: 180 μm (80 mesh)<br>$H_2SO_4$/slag ratio: 15.2 – 17.6 g acid/20 g slag<br>T: 50 – 100°C<br>LT: 0.25 – 5.5 h<br>AS: present (n.i. rpm) | Evaluated parameters: acid concentration, amount of oxidant, reaction time, temperature<br>• Metal extraction is more efficient with increasing concentration of $H_2SO_4$<br>• Excess of acid is favourable for extraction, but requires higher quantity of neutralizing agent<br>• High $NaClO_3$ consumption improves Cu, Co, Zn recovery<br>• Final pH 2 allowed to achieve maximum leaching of Cu, Co, Zn and minimum of Si, Fe<br>• Preferred neutralizing agent for process is $Ca(OH)_2$<br>• Optimal conditions for metal extraction: 17.6 g sulfuric acid/20 g sample; 2.5 g sodium chlorate oxidant, 3 h, 95°C<br>• Metal recovery: Co 98% (40.1 g/kg), Zn 97% (16.5 g/kg), Cu 89% (12 g/kg) #, Si 3.2% (4.9 g/kg), Fe 0.02% (0.1 g/kg) | Yang et al. (2010a) |
| **Cu-water jacket furnace slag**<br><br>FeO: 27%<br>(Fe: 21%)<br>Cu: 0.2%<br>Co: 1.7%<br>Zn: 5%<br>PbO: 0.9%<br>(Pb: 0.8%) | Extractant: $HNO_3$ and ammonia<br>FS: <212 μm<br>L/S: 10<br>LT: 2 – 20 h<br>T: 25 – 80°C<br>AS: 500 rpm | • Extraction of original sample (25°C, pH=0, LT: 20 h, Cu 46% (0.9 g/kg), Co 95% (16.2 g/kg), Zn 86% (43 g/kg), Pb 92% (7.7 g/kg), Fe 79% (165.8 g/kg))<br>• Cold-water-quenching slag (25°C, pH =12, LT: 20 h, Cu 90% (1.8 g/kg) #, Co (0.2 g/kg), Zn (0.5 g/kg), Pb (0.1 g/kg), Fe (2.1 g/kg) < 1%) shows good selectivity in leaching at high alkaline conditions<br>• Air-cooled slag (25°C, pH=12, LT: 20 h Cu, Co, Zn, Pb 22-36%, Fe 5%)<br>• Slow-cooled slag (T: 25 – 80°C, pH=12, LT: 20 h, extraction <2%) was found to prevent metal extraction<br>• Increase of temperature is favorable for metal extraction<br>• Water-granulated slag is found as useful material if recovery intended | Tshiongo et al. (2010) |
| **Brass slag**<br><br>FeO: 1.3%<br>(Fe: 1%)<br>CuO: 13%<br>(Cu: 10.4%)<br>ZnO: 69%<br>(Zn: 55.4%) | Extractant: $H_2SO_4$ (25 g, 30%)<br>FS: <100 μm<br>L/S: 3 – 8<br>T: 10 – 70°C<br>LT: 0.083 – 1.33 h (5-80 min)<br>AS: 60 – 400 rpm | Evaluated parameters: acid concentration, particle size, reaction time, temperature<br>• Rotation speed does not affect leaching of copper (9%) (9.2 g/kg), whereas faster rotation increases Zn leaching from 60% (332.4 g/kg) (50 rpm) to 93% (515.3 g/kg) (150 rpm)<br>• Time necessary to reach Zn and Cu maximum leaching were 10 min. and 30 min., respectively. Afterwards leaching may decrease<br>• Optimum $H_2SO_4$ concentration for Zn extraction: 25-35%, $H_2SO_4$ and for Cu extraction 30-45% $H_2SO_4$. Higher $H_2SO_4$ concentrations increase the viscosity of the solution and inhibit the leaching process<br>• Under conditions of 30% $H_2SO_4$, T 35°C, ~90% (93.5 g/kg) # of Cu is leached<br>• Increase of LS ratio gives greater metal extraction. L/S of 5 is suggested as optimum (Cu 9% (9.2 g/kg), Zn 93% (515.3 g/kg))<br>• Increasing temperature favours Cu and Zn leaching: up to 70°C enhanced Cu leaching, whereas for Zn only up to 35°C | Ahmed et al. (2012) |

| Cu-slag<br><br>Fe: 36.41%<br>Cu: 2.20%<br>Zn: 5.92% | Thermal treatment agent: $NH_4Cl$<br>Extractant: $H_2O$<br>FS: 75 µm (200 mesh)<br>L/S: 2<br>T: 280 – 320°C<br>LT: 0.33 – 2.33 h (20-140 min) up to 5 h (Fe)<br>AS: n.i. | Evaluated parameters: temperature, heat treatment time,<br>• Increasing reaction time and temperature are favourable to obtain water-soluble components<br>• Cu, Zn recovery reaches 89.7% (19.7 g/kg) # and 91.5% (54.2 g/kg) during 120 min. at 320°C, whereas Fe recovery reached approximately 35% (127.4 g/kg)<br>• Increasing time of thermal treatment allows to improve Fe recovery (300 min., 320°C)<br>• Two stage treatment is more favourable for selective recovery (heating 120 min. + treatment with $NH_4Cl$. 1st step: (approximately 90% of Cu and Zn and 35% Fe recovery), 2nd step: (improved Fe recovery up to 88.3%)<br>• Selective precipitation: pH adjusted to 4, 5.5, 7, 10 aimed to precipitate compounds in the form of: $Fe(OH)_3$, $Cu(OH)_2$, $Zn(OH)_2$ and $Ca(OH)_2$/ $Mg(OH)_2$<br>• Reagents recovery: $NH_4Cl$ recovered by evaporation of solution after selective precipitation stage and reused in the process, ammonia water used for pH adjustment | Nadirov et al. (2013) |

*FS: fraction size, L/S: liquid to solid ratio S/L: solid to liquid ratio, T: temperature, LT: leaching time, AS: agitation speed, n.i.: none information provided,*
*# presented in Figure 2.5*

## 2.4.1.1  Influence of extractant

Extraction of metals from different types of copper slags includes a variety of experimental designs with application of various extractants playing a role of leaching or roasting agents such as ferric chloride (Anand et al., 1980; Anand, 1981), ferric sulphate (Altundoğan and Tümen, 1997; Beşe, 2007, Carranza et al., 2009), ammonium sulphate (Sukla et al., 1986), ammonium chloride (Nadirov et al., 2013), chlorine solution (Herreos et al., 1998; Beşe et al., 2003), sulfuric acid (Anand et al., 1983; Sukla et al., 1986; Altundoğan and Tümen, 1997; Basir & Rabah, 1999; Banza et al., 2002; Arslan & Arslan, 2002; Altundoğan et al., 2004; Beşe, 2007; Baghalha et al., 2007; Deng & Ling, 2007; Yang et al., 2010; Ahmed et al., 2012), hydrochloric acid, ammonium hydroxide (Basir & Rabah, 1999) and nitric acid (Tshiongo et al., 2010). A number of these experiments have also combined additional treatment such as slag roasting following leaching (Anand, 1981; Sukla et al., 1986; Altundoğan and Tümen, 1997; Arslan & Arslan, 2002), aging of slag (Deng & Ling, 2007), oxidant addition (Basir & Rabah, 1999; Banza et al., 2002; Altundoğan et al., 2004; Yang et al., 2010a), high temperature leaching (Anand et al., 1980; Basir & Rabah, 1999; Banza et al., 2002; Deng & Ling, 2007; Beşe, 2007; Carranza et al., 2009; Ahmed et al., 2012; Nadirov et al., 2013) or oxidative pressure (Anand, 1983; Baghalha et al., 2007) intended to further improve the extraction efficiency.

Sulfuric acid ($H_2SO_4$) is considered as an efficient agent for the leaching of metals. Several experiments performed with copper slags using sulfuric acid as the leachate revealed that metal extraction may reach high values. Nevertheless, acid concentrations applied for the leaching is an important issue having an influence on the process. These assumptions are in accordance with the work of Anand et al. (1983), Basir & Rabah (1999); Ahmed et al. (2012), Altundoğan et al. (2004), Yang et al. (2010a), Deng & Ling (2007) and Baghalha et al. (2007). These authors noted a positive correlation between the extraction efficiency and acid concentration, meaning that stronger acidity enhances metal extraction. On the other hand, experimental studies of metal extraction with strong acids also showed an important limitation of this process. Although high leaching efficiencies with sulfuric acid are obtained, the formation of silica gel (Eq. n°7) during the process causes that metal extraction and pulp filtration is much more difficult (Anand et al., 1983; Banza et al., 2002; Deng & Ling, 2007; Yang et al., 2010a).

$2\ MO{\times}SiO_2 + H_2SO_4 \rightarrow 2\ MSO_4 + H_4SiO_4$ (M: Fe, Co, Zn, Cu)            Eq. n°7
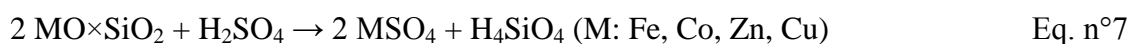
Yang et al. (2010a) demonstrated that the addition of oxidants such as sodium chlorate ($NaClO_3$) and calcium hydroxide ($Ca(OH)_2$) as neutralizing agent during extraction could be a way to avoid the problem of silica gel formation, consequently facilitating filtration of the

solution. Sodium chlorate ($NaClO_3$) plays the role of reaction inhibitor of silica gel formation due to the oxidation of $Fe^{2+}$ to $Fe^{3+}$:

$6\ FeSO_4 + NaClO_3 + 3\ H_2SO_4 \rightarrow 3\ Fe_2(SO_4)_3 + NaCl + 3\ H_2O$ \hspace{1cm} Eq. n°8
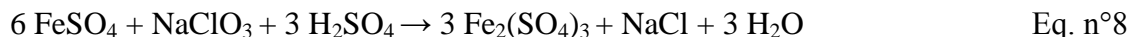
The addition of calcium hydroxide aims to neutralize the solution (Eq. n°9) and precipitate silica (Eq. n°10) and $Fe^{3+}$ (Eq. n°11) (Yang et al., 2010a) according to the following reactions:

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \times H_2O$ \hspace{2cm} Eq. n°9

$H_4SiO_4 \rightarrow 2\ H_2O + SiO_2$ \hspace{3cm} Eq. n°10

$3\ Fe_2(SO_4)_2 + 12\ H_2O \rightarrow 2\ NaFe_3(SO_4)_2(OH)_6$ \hspace{1cm} Eq. n°11
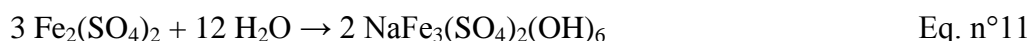
Although increasing concentrations of sulfuric acid favour the leaching process, more calcium hydroxide is also required to neutralize (Eq. n°9). Therefore, the optimal amount of sulfuric acid should be calculated in order to achieve efficient leaching as well as to avoid using too much neutralizing agent. In addition, too high concentrations of ferrous iron inhibit the recovery process due to possible co-precipitation of metals with hydroxides during neutralization by $Ca(OH)_2$. That is why oxidation of $Fe^{2+}$ to $Fe^{3+}$ is so important for leaching conditions (Anand et al., 1983; Banza et al., 2002; Yang et al., 2010a).

Another approach taking into consideration the problem of silica gel formation was presented in the study of Banza et al. (2002), where sulfuric acid leaching was performed in the presence of hydrogen peroxide ($H_2O_2$) that oxidized ferrous into ferric iron according to the following reaction:

$2\ FeSO_4 + H_2O_2 + 2\ H_2O \rightarrow 2\ FeOOH + 2\ H_2SO_4$ \hspace{1cm} Eq. n°12
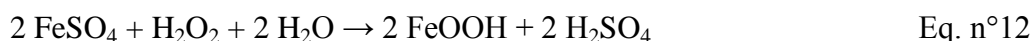
Therefore, oxidant addition can be an efficient solution to overcome the problem of silica gel formation with simultaneous iron removal from the solution through its oxidation. For the experiments done by Banza et al. (2002) and Yang et al. (2010a) as much as 80% (11.4 g/kg) Cu, 90% (6.5 g/kg) Co, 90% (80.1 g/kg) Zn, 5% (10.4 g/kg) Fe and 89% (12.7 g/kg) Cu, 98% (7.1 g/kg) Co, 97% (86.3 g/kg) Zn, 0.02% (0.04 g/kg) Fe could be extracted when oxidant ($H_2O_2$ and $HClO_3$) was added to the leaching solution. Moreover, other studies revealed that oxygenated conditions appear to be a factor promoting metal extraction (Basir & Rabah, 1999; Baghalha et al., 2007; Yang et al., 2010a) with simultaneous accomplishment of a low iron extraction efficiency (Anand et al., 1983; Banza et al., 2002). Results of oxidative pressure sulfuric acid leaching performed by Baghalha et al. (2007) have evidently proven this statement showing extraction of Cu (1.5-12.6 mg/kg), Co (5.5-15.7 mg/kg) and Ni (22.4-47.5 mg/kg) on the approximate level of 80%, whereas extraction of Co (37%) (0.3 g/kg), Ni (20%) (0.6 g/kg) and Cu (0%) has been achieved in the experiment in the absence of oxygen. Anand et al. (1983) also observed improved metal extraction efficiencies with increased

oxygen pressure indicating oxygen delivery as an important factor for $Fe^{2+}$ oxidation, hence allowing to minimize iron extraction in relation to other metals. In the experiment with higher oxygen pressure extraction efficiencies of Cu (90%) (36.3 g/kg), Ni (19.3 g/kg) and Co (4.8 g/kg) (>98%), Fe (0.81%) (3.1 g/kg), whereas only 1.2% (4.6 g/kg) of Fe was noted at lower pressure confirming inefficient oxidation of $Fe^{2+}$. However, according to Altundoğan et al. (2004) who conducted sulfuric acid leaching with chromate ($K_2Cr_2O_7$), it was observed that oxidant addition improves copper leaching, whereas it has adverse effects on the extraction of other metals. For instance, using 1 M $H_2SO_4$ allowed to extract only 20.5% (8.9 g/kg) of copper, whereas the amount of extracted copper raised up to 81.15% (35.4 g/kg) when oxidant was added.

Additionally, other experimental approaches of sulfuric acid leaching coupled with high temperature treatment have been applied (Arslan & Arslan, 2002; Deng & Ling, 2007; Ahmed et al., 2012). Arslan & Arslan (2002) proposed acid roasting following hot water leaching, whereas thermal acid aging following water leaching as extraction method has been performed by Deng & Ling (2007). Acid treatment coupled with high temperatures and water leaching was reported as an efficient method allowing to achieve copper extraction efficiencies as high as 93% (21.7 g/kg) (Deng & Ling, 2007) or even 100% (26.4 g/kg) of Cu (Arslan & Arslan, 2002).

Generally, experimental designs with sulfuric acid as leaching agent allowed to extract even up to 93-100% of copper depending on different leaching parameters such as leaching temperature, particle size, acid concentration, L/S ratio, processing time (Deng & Ling, 2007; Ahmed et al., 2012) and oxygen delivery (Baghalha et al., 2007). The common observation from most experiments is that increased acid concentrations are the main factor improving the metal extraction (Anand et al., 1983; Altundoğan et al., 2004; Deng & Ling, 2007; Yang et al., 2010; Ahmed et al., 2012).

Nevertheless, the use of other extractants for Cu-slag leaching also allowed to achieve satisfactory levels of extracted metals. Anand et al. (1980; 1981) investigated ferric chloride leaching without or with prior reduction and reported this extractant as efficient for leaching of metal residues from Cu-slag, especially when reduction roasting was applied prior to extraction. Ferric sulfate chosen as leaching agent was found to give satisfactory leaching when combined with high temperatures (Carranza et al., 2009) or sulfuric acid/ferric sulphate and ultrasound (Beşe, 2007). This agent ($Fe_2(SO_4)_3$) improves Cu extraction, but may also have adverse effects on the extraction of other metals (Beşe, 2007).

Experiments done by Beşe at al. (2003) relied on converter slag leaching using $Cl_2$-saturated water. Beşe at al. (2003) attempted to determine the optimum conditions for copper dissolution, maintaining the level of iron dissolution inversely proportional, as was also intended in the experiment of Arslan & Arslan (2002) and Herreros et al. (1998). Application of optimal conditions led to 98.35% (29.2 g/kg) recovery of copper (Beşe at al., 2003). Ferric chloride leaching revealed that 92% (37.1 g/kg) of Cu, 23% (4.5 g/kg) of Ni and 24% (1.2

g/kg) of Co may be extracted, whereas application of reduction roasting improved the Ni and Co extraction efficiency to 95% (18.8 g/kg) and 80% (3.8 g/kg), respectively and a slightly lower efficiency for copper (82%) (33 g/kg) (Anand et al., 1980; 1981). Application of a ferric sulfate solution allowed to achieve a Cu extraction efficiency as high as 88-94% (88-94 g/kg) (Carranza et al., 2009). Herreros et al. (1998) performed chlorine solution treatment of slags that led to the extraction of high quantities of Cu (80-90%) (11-12.9 g/kg), maintaining iron dissolution on a low (4-8%) (15.1-32.9 g/kg) level. Nadirov et al. (2013) achieved extraction efficiencies of ~85% (18.7 g/kg) for Cu, ~90% (53.3 g/kg) for Zn and 40-90% (145.6-327.7 g/kg) for Fe through thermal slag treatment following ammonia leaching.

### 2.4.1.2   Influence of agitation

Generally, the agitation speed used for metal extraction is in the range of 60-840 rpm. An influence of agitation on the extraction process is restricted by its presence rather than the agitation speed itself. Anand et al. (1980) showed that stirring enhanced the metal extraction compared to metal concentrations obtained for experiments devoid of stirring, while no significant difference between the values of extracted metals was noted when the stirring speed increased from 100 to 300 rpm. Nevertheless, results of experiments performed by Ahmed et al. (2012) showed that even though it is not important for leaching of copper, more elevated zinc concentrations were obtained with faster flask rotation (Ahmed et al., 2012). This conclusion is not consistent with the results obtained by Beşe et al. (2003), who reported that copper dissolution was affected by stirring, however it may be due to differences in experimental design.

### 2.4.1.3   Influence of temperature

The temperature is an important factor in the kinetics of solid degradation affecting the metal leaching rate. In order to improve the extraction efficiency, higher temperature values are desirable and for this reason wide ranges of temperatures have been studied in different experimental designs. Thermal treatment of slags includes approaches such as high temperature leaching using various leaching agents at temperatures ranging 24 – 100°C (Anand et al., 1980; Basir & Rabah, 1999; Banza et al., 2002; Carranza et al., 2009; Yang et al., 2010; Ahmed et al., 2012), thermal aging of slag moisture combined with leaching at 20 – 250°C (Deng & Ling, 2007) as well as slag roasting (30 - 800°C) following leaching (Anand et al., 1981; Sukla et al., 1986; Altundoğan and Tümen, 1997; Arslan & Arslan, 2002; Nadirov et al., 2013).

The most common conclusion from experiments applying thermal treatment is that temperature enhances both the metal leachability for slag pre-treatment as well as their leaching efficiency. However, in some cases thermal activation was noted to be a catalysing

factor only to a certain level of temperature elevation due to evaporation of the leaching agents at higher temperatures (Sukla et al., 1986; Tshiongo et al., 2010; Nadirov et al., 2013). Anand et al. (1980) observed that copper may be efficiently leached by ferric chloride even at ambient temperature reaching values of 64% (25.8 g/kg), but increased temperature facilitated its leaching, promoting Ni and Co leaching as well. Basir and Rabah (1999) reported thermal activation had a favourable effect on leaching when hydrochloric acid, sulfuric acid and ammonium hydroxide were used as extractants. Banza et al. (2002) studied the effect of temperature in the range of 24-80°C and observed a significant increase of the metal extraction efficiency with increased temperature, especially when temperature rises up to 60°C. Banza et al. (2002) achieved high levels of metals recovery up to 60% (8.6 g/kg) Cu, 90% (6.5 g/kg) Co, 90% (80.1 g/kg) Zn and 90% (186.3 g/kg) Fe within 2 hours at 80°C. Carranza et al. (2009) indicated a similar temperature range (25-50°C) where copper extraction by ferric sulphate was noticeably improved (30% more Cu). Enhanced Cu extraction was obtained by increasing the temperature to 70°C using sulfuric acid as leaching agent, whereas the optimum temperature for Zn was already achieved at 35°C (Ahmed et al., 2012).

Thermal aging of an acid moisture following water leaching proposed by Deng & Ling (2007) was found to give satisfactory extractions of metals. In this case, the increased aging temperature was concluded to be the favourable factor for Co (100°C) as well as Cu and Fe (250°C) extraction.

Slag roasting as thermal pre-treatment of slag following leaching gives a possibility to extract high quantities of metals. Anand et al. (1981) performed reduction roasting following ferric chloride leaching. This approach has a higher importance for Co and Ni present in slags in the oxide form, whereas it may slightly decrease Cu leachability. Roasting/leaching done by Sukla et al. (1986) has shown a greater extraction efficiency along with increasing roasting temperature. However, the authors pointed out that increasing the temperature is favourable only to the certain level, because temperatures above 200°C may decrease the metal extraction efficiency due to the evaporation of $H_2SO_4$. Altundoğan and Tümen (1997) who proposed ferric sulphate as roasting agent noticed a positive effect of elevated temperatures on the metal extraction efficiency even until 500-550°C. This roasting temperature may give as much as 95% (24.7 g/kg) for Cu during 0.5 h leaching (Altundoğan and Tümen, 1997). Arslan & Arslan (2002) reported slightly lower Cu extraction efficiencies (88%) (23.2 g/kg) at 150°C using sulfuric acid as roasting agent. However, elevated roasting temperatures (250°C) allow to extract even 100% (26.4 g/kg) of Cu. Furthermore, results of the thermal treatment using ammonium chloride following water leaching also confirmed higher temperatures as the factor promoting metal extraction. A temperature of 320°C allows to extract 89.7% (19.7 g/kg) of Cu during 2 h leaching, while maintaining the Fe extraction efficiency on a low level (35%) (127.4 g/kg) (Nadirov et al., 2013).

**2.4.1.4   Influence of liquid to solid ratio and particle size**

The liquid to solid ratio used for metal extraction includes a wide range of 1-100. Its optimum value depends on other parameters as well. Usually higher recovery efficiencies can be achieved when the pulp density is lower due to the greater contact of the leachate with the surface of slag particles. This was confirmed by the results obtained by Anand et al. (1983) and Carranza et al. (2009), who observed decreasing metal extraction efficiencies along with increasing pulp density. In the case of ferric sulphate leaching, the extraction efficiency decreased due to ferric iron depletion in the solution (Carranza et al., 2009), whereas the lower efficiency when leaching with sulfuric acid was probably due to acid depletion in relation to the slag volume (Anand et al., 1983). Observations are also congruent with Ahmed et al. (2012) who observed that an increase of the liquid to solid ratio (lower pulp density) results in a greater metal extraction efficiency.

Apart from the liquid to solid ratio, the parameter particle size has an impact on the leaching efficiency. Sulfides are the most interesting components for metal leaching. First of all, they contain elevated concentrations of metals, higher compared to silicate phases. Secondly, their susceptibility to be leached is better. As sulfides have a small size and are often embedded in a glassy matrix or between crystal phases, its exposure is limited. For this reason reduction of the size fraction is important to provide more contact of the leaching agent with the metal-bearing minerals. For example, Carranza et al. (2009) studying the effect of Cu-bearing phases exposed to a leaching solution showed that the smallest size fraction reached the highest level of extraction, whereas the larger fraction size did not reach this level, even if the duration of the experiment was 3 times longer than for the fine fraction which may be due to the fact that Cu-bearing particles were included in the silica matrix. The positive effect of metal leachability along with decreasing particle size was also noted by Anand et al. (1980, 1983), Sukla et al. (1986), Herreros et al. (1998) and Deng & Ling (2007).

**2.4.1.5   Influence of leaching time**

The time necessary to reach equilibrium level is different for each particular experiment and depends on other factors affecting the leaching process. However, in the case of application of optimal conditions, slightly longer leaching times are suggested in order to accomplish higher levels of metal recovery.

**2.4.1.6   Slag structure**

Slags display different structures (amorphous or crystalline) resulting from the cooling regime (rapid or slow cooling rate). For this reason, their leaching behaviour may vary. The amorphous glassy phase of slags does not provide sufficient encapsulation of metallic

elements and exhibits greater susceptibility to be leached (Maweja et al., 2010; Tshiongo et al., 2010; Mostafa et al., 2001). In contrast, the crystalline structure of slags is considered as ensuring greater prevention of metals to be leached (Maweja et al., 2010; Tshiongo et al., 2010). Nevertheless, in some cases slags having a crystalline structure were found to show higher susceptibility to leaching (Baghalha et al., 2007; Kuo et al., 2008), whereas amorphous ones revealed greater metal encapsulation (Kuo et al., 2008; Moustakas et al., 2012). However, it has to be noticed that the glass composition itself has also a great importance for the leaching behaviour. Kuo et al. (2008) pointed out that the silica content, an important glass forming element in slag, seems to also determine the slag behaviour. It was noted that the silica content has a great importance because its more dense and uniform distribution ensures better immobilization of metallic compounds (Kuo et al., 2008).

### 2.4.1.7   Optimal parameters

The experiments mentioned above considerably contribute to the evaluation of the optimal conditions of recovery as well as constitute significant background for further studies. These experiments combine a variety of conditions, applied for copper slag samples displaying various chemical compositions. Comparison of the results allowed to summarize that some parameters such as acid concentration, oxidant addition, temperature, leaching time and liquid to solid ratio are particularly significant for efficient recovery of metals. In most experimental setups mentioned above, higher acid concentration, increased temperature, lower pulp density and smaller size fraction give greater metal extraction efficiencies. However, specific conditions for metal recovery should be established separately for individual samples of interest. A comparison of the bulk Cu content in slags studied and substantial results are presented in Figure 2.5.
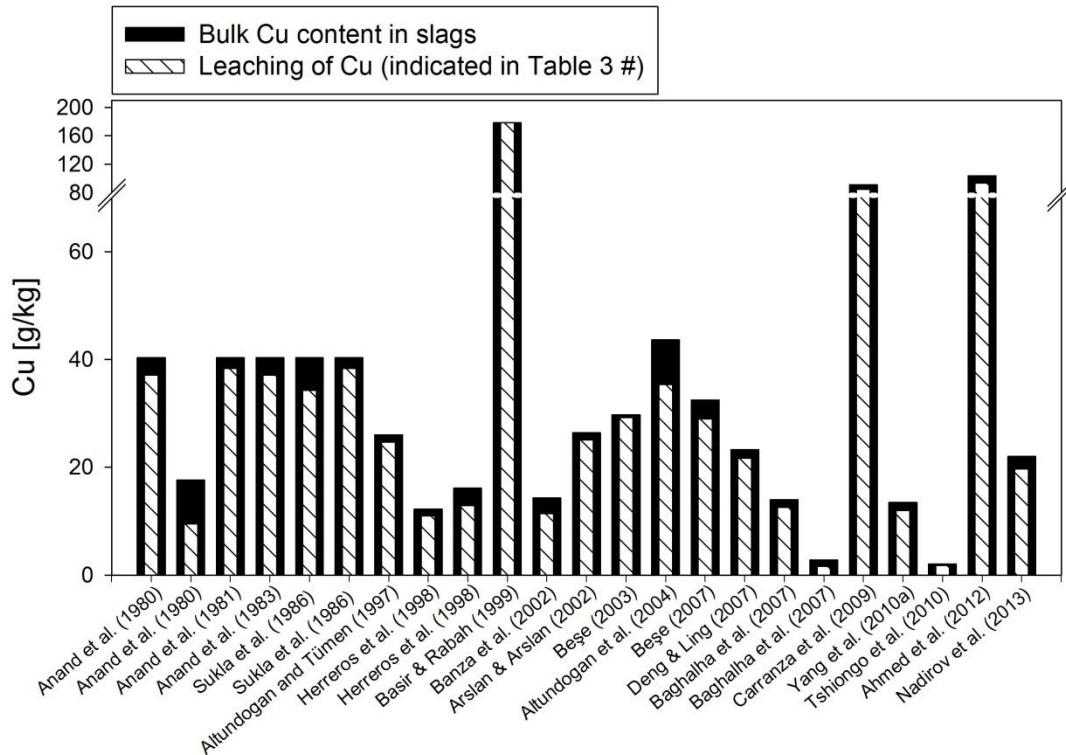
**FIGURE 2.5 Bulk Cu content in slags studied and examples of leaching efficiencies.**

Based on the experimental results presenting the levels of recovered metals it can be concluded that the research devoted to this process has been successful and has a substantial contribution to the field of Cu-slags leaching. The findings have direct relevance for the future of metallurgical slags. However, more investigations are still necessary before establishing the best parameter combination for metal recovery from Cu-slags. Results demonstrated the superior performance of strong acid over less concentrated solutions. Obviously, considering application of chemical leaching at industrial scale, efficiency will be a matter of primary importance. Undoubtedly, feasibility of recovery in a large scale will only be possible in the case of economical profitability of the process. Therefore, optimization of the leaching parameters has a great importance for the future fate of copper slags.

## 2.4.2 Copper recovery

Many experimental setups of chemical leaching have shown the possibility to dissolve important quantities of metals remaining in metallurgical slags. As a result of chemical leaching, solutions with high concentrations of metals have been produced. However, in order to complete the recovery process, further treatment leading to separation of the dissolved forms of metals from the solution is required. This final stage of the process can be completed by solvent extraction (Kordosky, 1992; 2002), galvanic reaction (Davenport, 2002) or metal precipitation (Kaksonen et al., 2011). Although recovery methods for metals from solution are

already well established, optimizing the parameters for their recovery from slags leachates is still a great industrial challenge.

In the case of selective solvent extraction, depending on the target metal, a suitable extractant (*e.g.* di-2-ethylhexylphosphoric acid) is added to the solution. The target metal is bound to a ligand according to the following equation (Teng et al., 2012):

$$M^{n+}_{(aq)} + x\ RH_{(org)} \leftrightarrow R_xM_{(org)} + x\ H^+_{(aq)} \hspace{2cm} \text{Eq. n°13}$$
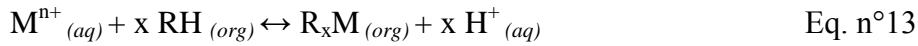
where:

M- metal ion

$RH_{(org)}$ – organic extractant

n – oxidation number

x- stoichiometric coefficient

*org*- organic phase

Transfer of extracted metal-ligand complexes to the aqueous solution allows to reverse the reaction by acid addition and the metal ions can come back into solution, whereas the organic phase (ligand) may be stripped. Therefore, this stage of the recovery process is named stripping and proceeds according to the following equation (Spence & Soderstorm, 1999):

$$R_xM_{(org)} + x\ H^+_{(aq)} -> M^{n+}_{(aq)} + x\ RH_{(org)} \hspace{2cm} \text{Eq. n°14}$$

where:

$R_nM$ – metal/extractant complex

$RH_{(org)}$ – stripped metal complex

Metals can also be extracted by electro-winning. Electric current passing through the solution allows to collect metallic ions on a negative electrode (Kordosky, 2002; Davenport et al., 2002). For instance, Rudnik et al. (2012) intended to recover copper and cobalt from Cu-slags through hydrometallurgical methods comprising of several treatment stages, viz. roasting, electrolytic alloy dissolution and electrowinning. This gave very high recovery efficiencies of 99.9% of Cu and 92% of Co.

## 2.4.3 Metal bioleaching and biorecovery

Biorecovery processes have developed into a good alternative for traditional chemical leaching (Banza et al., 2002; Vestola et al., 2010; Erüst et al., 2013). Therefore, several laboratory studies have attempted to apply bioleaching methods for metal extraction from Cu-slags (Sukla et al., 1992, 1995; Mehta et al., 1999; Vestola et al., 2010; Kaksonen et al., 2011; Muravyov and Fomchenko, 2013). In the bioleaching process, biotic solutions are applied for

metal solubilization instead of chemicals (Brandl & Faramarzi, 2006). Biotic solutions contain microbial organisms (*e.g.* bacteria and fungi) that accelerate the leaching. There are many species of bacteria and fungi that have the ability to leach metals (Brandl & Faramarzi, 2006; Lee & Pandey, 2012).

There are many publications in the literature describing interactions between microbes and mineral solids (Banfield et al., 1999; Suzuki, 2001; Watling, 2006; Brandl & Faramarzi, 2006; Haferburg & Kothe, 2007; Vera et al., 2013). These papers deliver deep insight into the microbial behaviour in the presence of a mineral surface. The bacterial ability to improve metal extraction was extensively studied with sulfide minerals. It was pointed out that metal extraction from metal-bearing sulfides can be achieved by bacterial leaching (Suzuki, 2001; Watling, 2006; Vera et al., 2013). As sulfides are important metal-carriers in metallurgical slags, this microbial ability can have a substantial contribution for the bioleaching process.

Regarding the bacterial contribution to metal extraction, two general types of interactions can be distinguished: direct (contact) bacterial leaching and indirect (non-contact) leaching by ferric iron regenerated from ferrous iron by bacterial oxidation (Bosecker, 1997; Suzuki, 2001; Watling, 2006). The direct interaction of microbes relies on the oxidation of sulfide minerals and solubilisation of metals as follow:

$$MS + H_2SO_4 + 0.5\ O_2 \rightarrow MSO_4 + S + H_2O \qquad\qquad \text{Eq. n°15}$$

$$S + 0.5\ O_2 + H_2O \rightarrow H_2SO_4 \qquad\qquad \text{Eq. n°16}$$
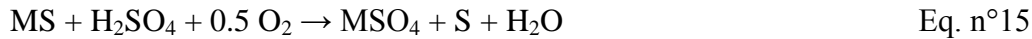
Oxidation of sulfur or sulfide to sulfuric acid increases the acid concentration, hence the metal leaching efficiency raises. In the indirect reaction, microbes regenerate ferric iron by oxidising ferrous iron. The process is expressed by the following chemical reactions:

$$MS + 2\ Fe^{3+} \rightarrow M^{2+} + 2\ Fe^{2+} + S \qquad\qquad \text{Eq. n°17}$$

$$2\ Fe^{2+} + 0.5\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O \qquad\qquad \text{Eq. n°18}$$

Both reactions contribute to metal bioleaching. However, in the case when acid insoluble minerals are submitted to bioleaching, the indirect impact of microorganisms is considered as the major role in the leaching process (Suzuki, 2001; Watling, 2006). The redox potential determined by the oxidation of $Fe^{2+}$ to $Fe^{3+}$ is a factor affecting leaching. The leaching rate increases with increasing redox potential and achieves a maximum efficiency at optimum redox potential. Regeneration of the oxidant ($Fe^{3+}$) increases the value of the redox potential in the bioleaching solution. Precipitation of $Fe^{3+}$ with sulfate may also happen when alkali cations are present:

$$3\ Fe^{3+} + 2\ SO_4^{2-} + 6\ H_2O + A^+ \rightarrow AFe_3(SO_4)_2(OH)_6 + 6\ H^+ \qquad\qquad \text{Eq. n°19}$$
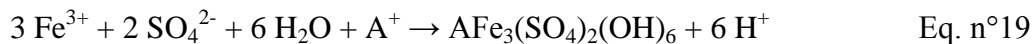
where: A is cation such as $K^+$, $Na^+$ or $NH_4^+$ (Watling, 2006).

Therefore, controlling the pH during bioleaching and maintaining the value of 1-2 is important for the regeneration of ferric iron and acid by microbial organisms (Watling, 2006). Commonly used bacteria for bioleaching are *Acidithiobacillus ferroxidans* and *Acidithiobacillus thiooxidans* (Suzuki, 2001; Lee and Pandey, 2012). They are commonly known as acidophilic bacteria that belong to the lithoautotrophic group. Both oxidize the reduced forms of sulfur, while *Acidithiobacillus ferrooxidans* also oxidizes $Fe^{2+}$. As the result of the process, solubilization of metals and acid generation are perceived (Ehrlich, 1998; Suzuki, 2001; Watling, 2006; Gadd, 2010). Additionally, acidophilic bacteria are extremely tolerant to highly acidic conditions (Erüst et al., 2013). They are able to survive in the environment reaching even a pH of 0.7 (Watling, 2006), which makes them especially interesting for bioleaching. Because of the growth in strong acidity, high temperature and at high $Fe^{3+}/Fe^{2+}$ ratio, it is possible to use these microbes as accelerators of bioleaching (Suzuki, 2001).

The efficiency of the leaching process can be improved by modification of the experimental conditions. For example, mixing of different microbial consortIa including both autotrophic and heterotrophic bacteria is suggested to accelerate the process of sulfide minerals leaching. Another example is the application of indigenous bacteria. Due to the fact that these bacteria are more adapted to high concentrations of metals, their leaching ability is higher (Watling, 2006). Additionally, bacterial attachment to the mineral surface is improved by the production of extracellular polymeric substances where the thiol group and $Fe^{3+}$ cause the corrosion of the surface. It was concluded that bacterial cell contact with the solid surface as energy source is an additional factor facilitating bioleaching (Watling, 2006).

Furthermore, bacteria that belong to thermophile and hyperthermophile groups improve the bioleaching efficiency because of their resistance to higher temperature (Bosecker, 1997; Lee & Pandey, 2012; Erüst et al., 2013). Then, increasing the temperature in the bioleaching process allows achieving faster dissolution rates.

Biochemical interactions between bacteria and different kind of solid materials were broadly studied. However, very few publications considering bacterially assisted leaching of copper slags have been reported in the literature (Table 2.4). Experiments revealed that the application of microorganisms for metal extraction leads to satisfactory results reaching even up to 95% of copper. Additionally, other metals such as cobalt, nickel and zinc may be simultaneously extracted.

**TABLE 2.4 Bioleaching and biorecovery experiments tested for copper slags**

| Type of slag & composition [wt.%] | Bio/leaching conditions | Results and observations | References |
|---|---|---|---|
| **Cu-converter slag**<br><br>Fe: 38.82%<br>Cu: 4.03%<br>Co: 0.48%<br>Ni: 1.98% | Bioleaching culture: *Aspergillus niger*<br>Medium: pH 6.5, T: 35 +/-1°C, time: 4-5 days<br><br>FS: <150 µm<br>L/S: 20 – 100 (5 – 1 %)<br>T: 30 – 60°C<br>LT: 24 – 120 h<br>AS: 120 rpm<br><br>Abiotic experiments: succinic acid, citric acid and their mixture | • Metals bioextraction reaches maximum after 48 of experiment duration (30°C, 5% pulp density): Cu ~ 12% (4.8 g/kg) «, Ni ~ 3-3.7% (0.6-0.7 g/kg), Co <1% (<0.05 g/kg), Fe < 0.2% (0.8 g/kg), extension of bioleaching time does not enhance metals leachability<br>• Increased pulp density shows negative effect on metal extraction<br>• Factor of temperature does not enhance bioleaching<br>• Addition of HCl to bioleaching culture and its quantity have positive effect on metals leaching (Cu~ 40-45% (16.1-18.1 g/kg) #, Ni 10-30% (2-5.9 g/kg), Co 7-40% (0.3-1.9 g/kg), Fe 7-25% (27.2-97.1 g/kg))<br>• Abiotic leaching using organic acid present in biotic experiment: succinic acid (Cu 17% (6.9 g/kg), Ni 4.87% (1 g/kg), Co 4% (0.2 g/kg), Fe 1.2% (4.7 g/kg)), citric acid (Cu 23% (9.3 g/kg), Ni 4% (0.8 g/kg), Co 5.7% (0.3 g/kg), Fe 1.5% (5.8 g/kg)), mixture (Cu 46.52% (18.7 g/kg) , Ni 7.9% (1.6 g/kg), Co 9.6% (0.5 g/kg), Fe 23% (89.3 g/kg)) | Sukla et al. (1992) |
| **Cu-converter slag**<br><br>Fe: 38.82%<br>Cu: 4.03%<br>Co: 0.48%<br>Ni: 1.98% | Bioleaching culture: *Aspergillus niger*<br>Medium: potato dextrose, pH 6.8<br><br>FS: <150 µm<br>L/S: 10 – 50<br>T: 37°C<br>LT: 72 h<br>AS: 120 rpm<br><br>Abiotic experiments: acetic, succinic, oxalic acids (1 M)<br>Control: distilled water | • Considerable decrease in metal extraction observed along with increased pulp density (L/S 50: Cu 47.14% (19 g/kg) «, Co 49.87% (2.4 g/kg), Ni 23% (4.6 g/kg), Fe 4.2% (16.3 g/kg), L/S 10: Cu 7.3% (2.9 g/kg), Co 5.4% (0.3 g/kg), Ni 2.5% (0.5 g/kg), Fe 1.2% (4.7 g/kg))<br>• Increasing dextrose concentration was favourable for microbial activity and increased metal extraction (Cu 78.5% (31.6 g/kg) #, Co 90% (4.3 g/kg), Ni 45.5% (9 g/kg), Fe 40.15% (155.9 g/kg))<br>• Indigenous microorganisms are recommended for leaching process due to their well-developed metal tolerance<br>• Tolerance of microbes for metal for leaching purpose may be developed through enrichment of medium that they grow in<br>• Abiotic experiment revealed stronger effect of succinic acid than oxalic one (succinic acid Cu ~50% (~20.2 g/kg), Co ~100% (~4.8 g/kg), Ni ~40%, Fe~60% (~232.9 g/kg); oxalic acid: Cu ~6% (2.4 g/kg) and Co ~6% (0.3 g/kg), Ni 0%, Fe 20% (77.6 g/kg)). Acetic acid shows comparable, but slightly lower effect than succinic acid | Sukla et al. (1995) |

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| **Cu-converter slag**<br><br>Fe: 48%<br>Cu: 1.8%<br>Ni: 0.95%<br>Co: 0.6% | Bioleaching culture: *Thiobacillus ferroxidans, Thiobacillus thiooxidans*<br>Medium: ferrous sulphate, elemental sulfur<br>FS: <200 μm and -425 + 200 μm to f < 75 μm<br>L/S: 20 (25 g slag +450 mL of water + 50 mL of bacteria) or<br>L/S: 10 – 30 (when nutrient addition: ammonium sulphate/sodium chloride effect studied)<br>T: 32°C (305 K)<br>LT: up to 80 days (1920 h)<br>pH = 1 – 3.5 adjusted using 10 N $H_2SO_4$<br>AS: absent | • Time required to achieve almost complete biorecovery of Cu was 1920 h, whereas abiotic leaching allowed to recover 80% (14.2 g/kg) of copper. Within 1680 h 22% (2.1 g/kg) and 18% (1.7 g/kg) Ni recovery for bioleaching and abiotic-leaching respectively. 1200 h 30% (1.8 g/kg) and 16% (1 g/kg) of Co for biotic and abiotic leaching, respectively.<br>• $Fe^{2+}/Fe^{3+}$ ratio and $Fe^{2+}$ concentration lower under abiotic conditions<br>• Jarosite formation on slag surface caused decreased value of $Fe^{2+}$<br>• Acid consumption is higher in abiotic conditions<br>• Ammonium sulphate did not have significant influence for leaching result, whereas 1% sodium chloride addition allowed to recover ~99% (~17.8 g/kg) # Cu, extraction of Ni and Co was also improved | Mehta et al. (1999) |
| **Cu-slag**<br><br>Fe: 40.7%<br>Cu: 0.35%<br>Zn: 1.7%<br>Pb: 0.08% | Bioleaching culture: *Acidithiobacillus spp., Leptospirillum spp.*<br>Medium: mineral salt medium supplemented with 1% $S^0$, and 4.5 g/L $Fe^{2+}$ / NaCl (5 g/L)<br><br>FS: n.i.<br>L/S: 10 and 100 (10 or 1% of solid)<br>T: 25°C<br>LT: 22 – 79 days<br>pH: 0.5, 1.0, 1.5 adjusted with $H_2SO_4$<br>AS: 150 rpm | • The most efficient conditions for bioleaching were as follow:<br>pH = 1.0-0.5, culture supplemented with elemental S<br>Leaching (1% pulp density) that allowed to recover:<br>Cu up to 100% (3.5 g/kg) «, Ni up to 100% (1.9 g/kg), Zn up to 64% (10.9 g/kg))<br>• Microbial oxidation of elemental sulfur led to sulfuric acid formation that enhanced metal solubilization from the material<br>• Metal extraction was not influenced by $Fe^{2+}$ or NaCl addition<br>• Inhibition test considering impact of leachates on bacterial activity revealed that slag material does not have any inhibitory effect on sulfur oxidation by microbial organisms | Vestola et al. (2010) |

| | | | |
|---|---|---|---|
| **Cu slag**<br><br>Fe: 40.7%<br>Zn: 1.7%<br>Cu: 0.35%<br>Ni: 0.19%<br>Co: 0.05%<br>Cd: 0.001% | Bioleaching:<br>Continuously Stirred Tank Reactor (CSTR)<br>Bioleaching culture: *Acidithiobacillus ferroxidans,*<br>*A. thiooxidans, A. caldus, Leptospirillum ferroxidans,*<br>*Sulfobacillus thermotolerans*<br>Medium: mineral salt medium supplemented with 1% $S^0$, and 4.5 g/L$^{-1}$ $Fe^{2+}$, pH: 1.8<br><br>FS: < 47 µm<br>L/S: 20 (5% of solid)<br>T: 22°C ± 2°C<br>LT: 39 days<br>AS: 1380 rpm<br>pH = 1 adjusted with $H_2SO_4$<br><br>Recovery:<br>Metal precipitation using biogenic sulfide<br>Sulfidogenic fluidized-bed reactors (25°C) 0.55 L with 0.32 L biomass carrier (silicate mineral) and mixed culture of *Desulfovibrio, Desulfotomaculum, Desulfobulus, Desulfurispora, Desulfohrabdus, Desulfobacca* | Bioleaching:<br>• 29 days: Fe 41% (166.9 g/kg), Cu 35% (1.2 g/kg) «, Zn 35% (6 g/kg), Ni 44% (0.8 g/kg)<br>• 39 days: Cu 68% (2.4 g/kg) #, Fe 58% (236.1 g/kg), Mn 53%, Zn: 65% (11.1 g/kg), Co 63% (0.3 g/kg), Cd 92% (0.01 g/kg)<br>• At the beginning of leaching $Fe^{2+}$ concentration increased due to solubilization from slag and further decrease as the result of biological oxidation<br>Recovery:<br>• Titration of bioleaching solution by biologically produced sulfide containing alkaline effluent<br>• Optimal pH for metal precipitation: 3.9-4.7 (Cu), 4.7-6.5 (Zn), 6.5 (Ni) | Kaksonen et al. (2011) |
| **Cu-converter slag**<br><br>Fe: 42.7%<br>Cu: 2.74%<br>Zn: 2.49% | Bioleaching culture: *Acidithiobacillus ferrooxidans, Sulfobacillus thermotolerans, Leptospirillum ferrooxidans*<br>T: 40°C, aeration: 4 min$^{-1}$, pH: 1.5 adjusted with $H_2SO_4$<br>$Fe^{3+}$ concentration: 33.6 g/L<br><br>Chemical leaching of slag using biologically produced $Fe^{3+}$<br>$Fe^{3+}$ concentration: 10.1, 15.1, 20.6 g/L<br>L/S: 3.33, 5, 10, 20 (30, 20, 10, 5% of solid)<br>T: 28 – 70°C<br>AS: 760 rpm | • Extraction efficiency depends on temperature with extension of leaching time<br>• 5 min. of experiment duration allows to reach copper extraction of 40-50% (11-13.7 g/kg) « independently of the temperature, whereas extension of leaching time up to 2.5 h improves Cu extraction to ~95% (26 g/kg) # when temperature of 70°C is used<br>• Zn extraction neither depends on temperature within 5 min. of extraction (10-15%) (2.5-3.7 g/kg), whereas 46% (11.5 g/kg) may be extracted within 2.5 h at 70°C<br>• Increasing concentration of $Fe^{3+}$ improves Cu recovery, having adverse effect on Zn (2.5 h)<br>• Cu extraction shows better performance when pulp density is lower, whereas no significant effect is observed for Zn<br>• Optimum condition of 10% pulp density allows to obtain Cu 89.4% (24.5 g/kg) and Zn 39.3% (9.8 g/kg) | Muravyov & Fomchenko (2013) |

*FS: fraction size; L/S liquid to solid ratio, T: temperature, LT: leaching time, AS: agitation speed, # presented in Figure 2.6*

Sukla et al. (1992, 1995) proposed bioleaching of Cu-converter slag using an *Aspergillus niger* culture that was found to efficiently leach metal residues. The authors pointed out that increased pulp density in bioleaching experiments has a negative effect on the process efficiency (Sukla et al., 1992, 1995). This observation is congruent with results of other studies (Muravyov and Fomchenko, 2013). Furthermore, in order to improve process feasibility, modification of conditions through hydrochloric acid addition or providing higher concentrations of substrate necessary for energy production (*e.g.* dextrose) may be a solution. As the result of two experimental designs proposed by Sukla et al. (1992, 1995), it was concluded that application of indigenous microorganisms seems to be more suitable due to their higher tolerance for high metal concentrations. Nevertheless, considering the adaptation of microbes to bioleaching conditions, this tolerance may be developed prior to bioleaching through the gradual enrichment of growth medium in toxic compounds (Sukla et al., 1995; Brandl et al., 2001; Vestola et al., 2010).

Mixed cultures of microorganisms were used by Vestola et al. (2010), Kaksonen et al. (2011) as well as by Muravyov and Fomchenko (2013). In the experiment as practised by Vestola et al. (2010), the most suitable condition for leaching with a bacterial culture of *Acidithiobacillus spp.* and *Leptospirillum spp.* is a pH in the range of 1-2. Moreover, lower pulp density is considered as more favourable for metal leaching at particular conditions. Besides leaching behaviour, the authors have also taken into consideration whether the leachate can affect the bacterial activity. Therefore, in order to check if bacterial activity may be inhibited by the leachate chemistry, additional tests were performed. It relied on the observation of iron and sulfur oxidation in the leachate with bacteria. Obtained results revealed no changes in bacterial activity (Vestola et al., 2010). The addition of sulfur to a leaching solution allowed to obtain greater leaching efficiencies. It was due to bacterial oxidation of sulfur leading to sulfuric acid formation that improved the metal dissolution from solid material (Vestola et al., 2010).

Another biorecovery experiment performed by Kaksonen et al. (2011) included two experimental stages: bioleaching in a continuously stirred tank reactor and biogenic metal sulfide precipitation. Leaching conditions allowed to leach relatively high amounts of metals including 68% (2.4 g/kg) of Cu, whereas the final copper recovery reached 98%. Muravyov & Fomchenko (2013) combined slag leaching using a solution containing biologically produced $Fe^{3+}$ at higher temperatures (28-70°C). It was found to be a good method to recover even 90% (24.5 g/kg) of Cu and 40% (9.8 g/kg) of Zn.

Bioleaching performed by Mehta et al. (1999) follows different experimental procedures compared to others. The main difference of this experiment was the lack of agitation. 1920 h (80 days) was required to reach copper dissolution at the level of 80% (14.2 g/kg), whereas in the flask devoid of bacteria, leaching achieved the level of 22% (4 g/kg). For nickel, the difference between biologically assisted leaching and abiotic conditions was not as important and showed values of 22-18% (2.1-1.7 g/kg) within 1680 hours (70 days). In the case of

cobalt, biotic leaching allowed to recover two times more metal compared to abiotic conditions, that was 30 (1.8 g/kg) and 16% (1 g/kg) during 1200 h (50 days), respectively. The $Fe^{2+}/Fe^{3+}$ ratio as well as the $Fe^{2+}$ content varied under biotic and abiotic conditions, resulting in greater recovery values in biotic conditions. It confirms the indirect action of bacteria in the leaching process. It is not common with the results of Vestola et al. (2010), who determined that the $Fe^{2+}/Fe^{3+}$ ratio did not contribute to the leaching process, but $Fe^{2+}$ acted only as electron donor for bacterial reactions.

The low extraction efficiencies of other metals in comparison to copper can be explained by distribution of these metals in the slag samples. Cobalt and nickel mainly distributed in fayalite and magnetite gave a lower efficiency of the process. Regarding the pH condition suitable for the process, a value of 2 was found to be the most convenient. Moreover, comparison of acid consumption demonstrated that it was higher for abiotic conditions. Due to the presence of bacteria, more acid was produced. Furthermore, the authors studied the effect of nutrient addition on the process efficiency. In the case of ammonium sulfate, the recovery of cobalt and nickel were higher, whereas the influence on the copper recovery was negligible. The addition of sodium chloride resulted in a better leaching efficiency for copper. When nutrients were added to the solutions, a higher $Fe^{2+}/Fe^{3+}$ ratio was observed due to the adaptation phase of bacteria. The lower ratio was noted after 960 h (40 days). It was found that the liquid to solid ratio ensuring the best results was 1:20. A comparison of copper levels of each slag investigated and the amount of metal extracted is presented in Figure 2.6.
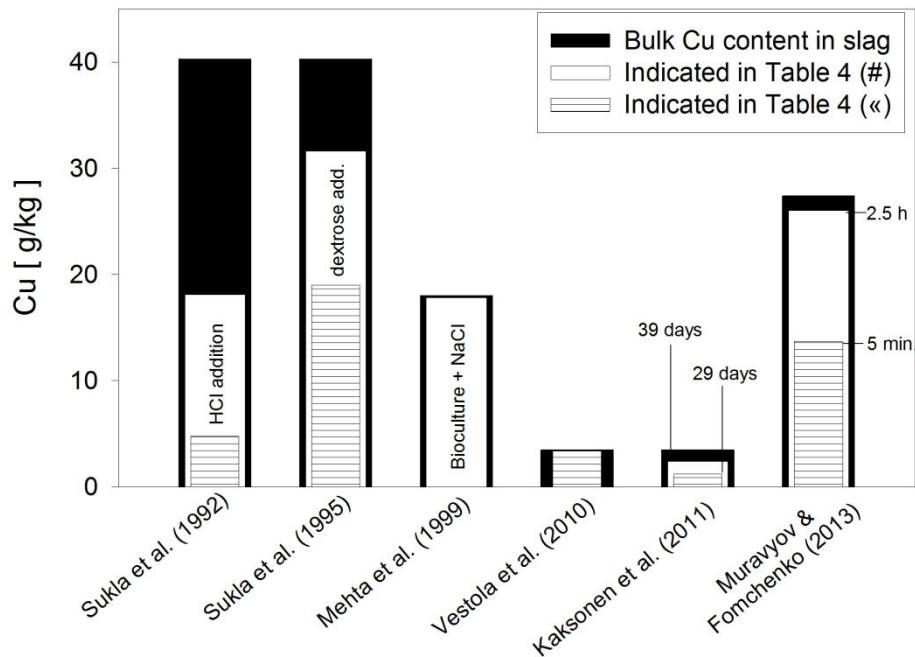


**FIGURE 2.6 Bulk Cu content in slags studied and biological leaching yield.**

## 2.5 CONCLUDING REMARKS

Although pyrometallurgy is an industrial sector that meets demands for metals production, it can also bring adverse consequences to the environment. An important issue inherited from slag disposal is a risk of waste weathering often resulting in metal mobilization. Several publications documented evidence of the significant negative impact of slags on the environment. For this reason metallurgical slags are undesirable for any dumping strategy. Indeed, the state of current knowledge about environmental stability of slags allows to predict potential risk caused by their disposal. Therefore, in the case no other management strategy can be applied, proper isolation of the disposal site as well as frequent environmental monitoring are strongly recommended.

Undoubtedly, the recovery process seems to be a promising alternative to overcome environmental problems as well as to limit surface areas needed for slags disposal. The application of these materials as secondary resources may be beneficial for the industrial sector and have direct environmental relevance. Apart from advantages arising from the reduction of disposal areas, this solution may bring significant profits for the metallurgical industry. In order to solve the problem of slags disposal through application of metal recovery, many researchers proposed various approaches to this process. For most of them, experimental setups gave great achievements due to recovery of significant quantities of metals. Examined experimental conditions allowed to state which factors are important for the recovery process, however it does not enable to determine general optimal conditions for any kind of copper slag. These experiments exhibited distinct advances of (bio)recovery over the traditional disposal of these wastes. Nevertheless, further studies devoted to the optimization of process parameters for a particular slag type as well as a larger scale application need attention and are crucial points for establishing well developed conditions. Even though examination of metal biorecovery from copper slags has given a lot promising results, more research devoted to biologically enhanced leaching is necessary to improve the efficiency of the bioprocess.

### ACKNOWLEDGEMENTS

# REFERENCES

1. **Ahmed L.M., Nayl A.A., Daoud J.A. (2012):** *„Leaching and recovery of zinc and copper from brass slag by sulfuric acid".* Journal of Saudi Chemical Society. http://dx.doi.org/10.1016/j.jscs.2012.11.003

2. **Al-Jabri K.S., Al-Saidy A.H., Taha R. (2011):** *„Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete".* Construction and Building Materials 25 (2), 933–938.

3. **Al-Jabri K.S., Hisada M., Al-Oraimi S.K., Al-Saidy A.H. (2009):** *„Copper slag as sand replacement for high performance concrete".* Cement & Concrete Composites 31 (7), 483–488.

4. **Al-Jabri K.S., Taha R.A., Al-Hashmi A., Al-Harthy A.S. (2006):** *„Effect of copper slag and cement by-pass dust addition on mechanical properties of concrete".* Construction and Building Materials 20 (5), 322–331.

5. **Alp I., Deveci H., Süngün H. (2008):** *„Utilization of flotation wastes of copper slag as raw material in cement production".* Journal of Hazardous Materials 159 (2), 390–395.

6. **Altundoğan H.S. & Tümen F. (1997):** *„Metal recovery from copper converter slag by roasting with ferric sulphate".* Hydrometallurgy 44 (1), 261-267.

7. **Altundoğan H.S., Boyrazli M., Tümen F. (2004):** *„A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate".* Minerals Engineering 17 (3), 465-467.

8. **Álvarez-Valero A.M., Pérez-López R., Nieto J.M., (2009):** *„Prediction of the environmental impact of modern slags: A petrological and chemical comparative study with Roman age slags".* American Mineralogist 94, 1417-1427

9. **Anand S., Das R.P., Jena P.K. (1981):** *„Reduction-roasting and ferric chloride leaching of copper converter slag for extracting copper, nickel and cobalt values".* Hydrometallurgy 7 (3), 243-252.

10. **Anand S., Rao K.S., Jena P.K. (1983):** *„Pressure leaching of copper converter slag using dilute sulphuric acid for the extraction of cobalt, nickel and copper values".* Hydrometallurgy 10 (3), 305-312.

11. **Anand S., Rao P.K., Jena P.K. (1980):** *„Recovery of metal values from copper converter and smelter slags by ferric chloride leaching".* Hydrometallurgy 5 (4), 355-365.

12. **Arslan C. and Arslan F. (2002):** *„Recovery of copper, cobalt, and zinc from copper smelter and converter slags".* Hydrometallurgy 67 (1), 1-7.

13. **Ash Ch., Borůvka L., Tejnecký V., Šebek O., Nikodem A., Drábek O. (2013):** *„Temporal dissolution of potentially toxic element from silver smelting slag by synthetic environmental solutions"* Journal of environmental management 129, 157-163.

14. **Baghalha M., Papangelakis V.G., Curlook W. (2007):** *„Factors affecting the leachability of Ni/Co/Cu slags at high temperature".* Hydrometallurgy 85 (1), 42-52.

15. **Banfield J.F., Barker W.W., Welch S.A., Taunton A. (1999):** *„Biological impact on mineral dissolution: Application of the lichen model to understanding mineral weathering in the rhizosphere".* Proc. Natl. Acad. Sci. USA, 96 (7), 3404-3411.

16. **Banza A.N., Gock E., Kongolo K. (2002):** *„Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction".* Hydrometallurgy 67 (1), 63-69.

17. **Basir S.M.A. & Rabah M.A. (1999):** *„Hydrometallurgical recovery of metal values from brass melting slag".* Hydrometallurgy 53 (1), 31-44.

18. **Beşe A.V. (2007):** *„Effect of ultrasound on the dissolution of copper from copper converter slag by acid leaching".* Ultrasonics Sonochemistry 14 (6), 790-796.

19. **Beşe A.V., Ata O.N., Çelik C., Çolak S. (2003):** *„Determination of the optimum conditions of dissolution of copper in converter slag with chlorine gas in aqueous media".* Chemical Engineering and Processing: Process Intensification 42 (4), 291-298.

20. **Bolan N., Kunhikrishnan A., Thangarajan R., Kumpiene J., Park J., Makino T., Kirkham M.B., Scheckel K. (2014):** *„Remediation of heavy metal(oid)s contaminated soils – To mobilize or to immobilize?".* Journal of Hazardous Materials 266, 141-166.

21. **Bosecker K. (1997):** *„Bioleaching: metal solubilization by microorganisms".* FEMS Microbiology reviews 20 (3), 591-604.

22. **Bourven I., Joussein E., Guibaud G. (2011):** *„Characterisation of the mineral fraction in extracellular polymeric substances (EPS) from activated sludges extracted by eight different methods".* Bioresource Technology 102 (14), 7124–7130

23. **Brandl H. & Faramarzi M.A. (2006):** *„Microbe-metal interactions for the biotechnological treatment of metal containing solid waste".* China Particuology 4 (2), 93-97.

24. **Brandl H., Bosshard R., Wegmann M. (2001):** *„Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi".* Hydrometallurgy 59 (2), 319–326.

25. **Braud A., Hoegy F., Jezequel K., Lebeau T., Schalk I.J. (2009):** *„New insights into the metal specificity of the Pseudomonas aeruginosa pyoverdine–iron uptake Pathway".* Environmental Microbiology 11 (5), 1079–1091

26. **Brown Jr. G.E & Calas G. (2011):** *„Environmental mineralogy – Understanding element behavior in ecosystems"* Comptes Rendus Geoscience 343 (2), 90-112.

27. **Cappuyns V. & Swennen R. (2008):** *„The application of $pH_{stat}$ leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials".* Journal of Hazardous Materials 158 (1), 185-195.

28. **Carranza F., Romero R., Mazuelos A., Iglesias N, Forcat. O. (2009):** *„Biorecovery of copper from converter slags: Slags characterization and exploratory ferric leaching tests".* Hydrometallurgy 97 (1), 39-45.

29. **Carrillo-Gonzalez R., Simunek J., Sauve S., Adriano, D. (2006):** *„Mechanisms and pathways of trace element mobility in soils".* In: Sparks D. L. (Ed.), Advances in agronomy, vol. 91 (pp. 111–178). San Diego: Academic.

30. **Chen M.S., Han Z.R., Wang L.Z. (2012):** *„Recovery of valuable metals from copper slags by hydrometallurgy".* Advanced Material Research 402, 35-40.

31. **Comte S., Guibaud G., Baudu M. (2006):** *„Biosorption properties of extracellular polymeric substances (EPS) resulting from activated sludge according to their type: Soluble or bound".* Process Biochemistry 41 (4), 815-823.

32. **Comte S., Guibaud G., Baudu M. (2008):** *„Biosorption of extracellular polymeric substances (EPS) towards Cd, Cu and Pb for different pH values".* Journal of Hazardous Materials 151 (1), 185-193.

33. **Çubukçu A. & Tüysüz N. (2007):** *„Trace element concentrations of soils, plants and waters caused by a copper smelting plant and other industries, Northeast Turkey".* Environmental Geology 52 (1), 93-108.

34. **D'Abzac P., Bordas F., van Hullebusch E.D., Lens P.N.L., Guibaud G. (2010a):** *„Effects of extraction procedures on metal binding properties of extracellular polymeric substances (EPS) from anaerobic granular sludges".* Colloids and Surfaces B: Biointerfaces 80 (2), 161-168

35. **D'Abzac P., Bordas F., van Hullebusch E.D., Lens P.N.L., Guibaud G. (2010b):** *„Extraction of extracellular polymeric substances (EPS) from anaerobic granular sludges: comparison of chemical and physical extraction protocols".* Applied Microbiology Biotechnology 85 (5), 1589–1599.

36. **Davenport W.G., King M., Schlesinger M., Biswas A.K. (2002):** *„Extractive metallurgy of copper".* Fourth edition/Pergamon 1-417.

37. **Deng T. & Ling Y. (2007):** *„Processing of copper converter slag for metal reclamation. Part I: extraction and recovery of copper and cobalt".* Waste Management and Research 25, 440-448.

38. **Eary L.E. & Williamson M.A. (2006):** *„Simulations of the neutralizing capacity of silicate rocks in acid mine drainage environments".* 7th International Conference on Acid Rock Drainage. American Society of Mining and Reclamation.

39. **Edmunds M. & Shand P. (2008):** *„Natural groundwater quality".* Chapter 1: *Baseline Inorganic chemistry of European Groundwaters"* Blackwell Publishing.

40. **Ehrlich H. L. (1998):** *„Geomicrobiology: its significance for geology".* Earth-Science Reviews 45 (1-2), 45-60.

41. **Erüst C., Akcil A., Gahan C.S, Tuncuk A., Deveci H. (2013):** *„Biohydrometallurgy of secondary metal resources: a potential alternative approach for metal recovery".* Journal of Chemical Technology and Biotechnology 88, 2115-2132.

42. **Ettler V. & Johan Z. (2014):** *„12 years of leaching of contaminants from Pb smelter slags: geochemical/mineralogical controls and slag recycling potential".* Applied Geochemistry 40, 97-103.

43. **Ettler V., Jehlička J., Mašek V., Hruška J. (2005):** *„The leaching behaviour of lead metallurgical slag in high-molecular-weight (HMW) organic solutions".* Mineralogical Magazine 69 (5), 737-747.

44. **Ettler V., Johan Z., Křibek B., Šebek O., Michaljevič M. (2009):** *„Mineralogy and environmental stability of slags from Tsumeb smelter, Namibia".* Applied Geochemistry 24 (1), 1-15.

45. **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 (7), 567- 577.

46. **Ettler V., Legendre O., Bodénan F., Touray J.C. (2001):** *„Primary phases and natural weathering of old lead-zinc pyrometallurgical slag from Pribram, Czech Republic".* Canadian Mineralogist 39, 873-888.

47. **Ettler V., Mihaljevič M., Touray J.C., Piantone P. (2002):** *„Leaching of polished sections: an integrated approach for studying the liberation of heavy metals from lead-zinc metallurgical slags".* Bull. Soc. Geol. Fr. 2, 161-169.

48. **Ettler V., Piantone P., Touray J.C. (2003):** *„Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long- term assessment".* Mineralogical Magazine 67 (6), 1269-1283.

49. **Flemming H.C. (2011):** *„The perfect slime".* Colloids and Surfaces B: Biointerfaces 86 (2), 251-259.

50. **Fomina M. & Gadd G.M. (2014):** *„Biosorption: current perspectives on concept, definition and application".* Bioresource Technology 160, 3-14.

51. **Gadd G.M. (2007):** *„Geomycology: biogeochemical transformations of rocks, minerals, metals and radionuclides by fungi, bioweathering and bioremediation".* Mycological Research 111 (1), 3-49.

52. **Gadd G.M. (2010):** *„Metals, minerals and microbes: geomicrobiology and bioremediation".* Microbiology 156, 609-643.

53. **Ganne P., Cappuyns V., Vervoort A., Buvé L., Swennen R. (2006):** *„Leachability of heavy metals and arsenic from slags of metal extraction industry at Angleur (eastern Belgium)".* Science of The Total Environment 356 (1), 69-85.

54. **Gbor P.K., Mokri V., Jia Ch.Q. (2000):** *„Characterization of smelter slag".* Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering 35 (2), 147-167.

55. **Gee C., Ramsey M.H., Maskall J., Thornton I. (1997):** *„Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead".* Journal of Geochemical Exploration 58 (2), 249-257.

56. **Gorai B., Jana R.K., Premchand (2003):** *„Characteristics and utilization of copper slags-a review".* Resources, Conservation and Recycling 39 (4), 299-313.

57. **Guibaud G., Bhatia D., d'Abzac P., Bourven I., Bordas F., van Hullebusch E. D., Lens P. N. L. (2012):** *„Cd(II) and Pb(II) sorption by extracellular polymeric substances (EPS) extracted from anaerobic granular biofilms: Evidence of a pH sorption-edge".* Journal of the Taiwan Institute of Chemical Engineers 43 (3), 444–449.

58. **Guibaud G., Bordas F., Saaid A., D'abzac P., van Hullebusch E. (2008):** *„Effect of pH on cadmium and lead binding by extracellular polymeric substances (EPS) extracted from environmental bacterial strains".* Colloids and Surfaces B: Biointerfaces 63 (1), 48–54.

59. **Haferburg G. & Kothe E. (2007):** *„Microbes and metals: interactions in the environment".* Journal of Basic Microbiology 47, 453-467.

60. **Harish V., Sreepada R. A., Suryavanshi U., Shanmuganthan P., Sumathy A. (2011):** *„Assessing the effect of leachate of copper slag from the ISASMELT process on cell growth and proximate components in microalgae Chlorella vulgaris (Beijerinck)".* Toxicological and Environmental Chemistry 93 (7), 1399-1412.

61. **Hernlem B.J., Vane L.M, Sayles G.D. (1999):** *„The application of siderophores for metal recovery and waste remediation: examination of correlations for prediction of metal affinities".* Water Research 33 (4), 95-960.

62. **Herreros O., Quiroz R., Manzano E., Bou C., Viñals J. (1998):** *„Copper extraction from reverberatory and flash furnace slags by chlorine leaching".* Hydrometallurgy 49 (1), 87-101.

63. **Hong S., Candelone J.P., Soutif M., Boutron C.F. (1996):** *„A reconstruction of changes in copper production and copper emissions to the atmosphere during the past 7000 years".* The Science of the Total Environment 188 (2), 183-193

64. **Hudson-Edwards K.A., Schell Ch., Macklin M.G. (1999):** *„Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain".* Applied Geochemistry 14 (8), 1015-1030.

65. **Jamieson H.E. (2011):** *„Geochemistry and mineralogy of solid mine wastes: Essential knowledge for predicting environmental impact".* Elements magazine 7 (6), 381-386

66. **Kaksonen A.H., Lavonen L., Kuusenaho M., Kolli A., Närhi H., Vestola E., Puhakka J.A., Tuovinen O.H. (2011):** *„Bioleaching and recovery of metals from final slag waste of the copper smelting industry".* Minerals Engineering 24 (11), 1113-1121.

67. **Kierczak J. & Pietranik A. (2011):** *„Mineralogy and composition of historical Cu slags from the Rudawy Janowickie Mountains, Southwestern Poland".* Canadian Mineralogist 49 (5), 1281-1296.

68. **Kierczak J. Néel C., Puziewicz J., Bril H. (2009):** *„The mineralogy and weathering of slag produced by the smelting of Ni-ores, Szklary, southwestern Poland".* The Canadian Mineralogist 47 (3), 557-572.

69. **Kierczak J., Bril H., Néel C., Puziewicz J. (2010):** *„Pyrometallurgical slags in upper and lower silesia (Poland): From Environmental Risk to use of slag-based products- A review".* Archives of environmental protection 36 (3), 111-126.

70. **Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Néel C., Ettler V., Mihaljevič M. (2013) :** *„Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland).* Journal of Geochemical Exploration 124, 183-194.

71. **Kim B.H. & Gadd G.M. (2008):** *„Bacterial physiology and metabolism".* Cambridge University Press.

72. **Konhauser K.O., Kappler A., Roden E.E. (2011):** *„Iron in microbial metabolism".* Elements magazine 7 (2), 89-93.

73. **Kordosky G.A. (1992):** *„Copper solvent extraction: the state of the art".* The Journal of The Minerals, Metals & Materials Society 44 (5), 40-45.

74. **Kordosky G.A. (2002):** *„Copper recovery using leach/solvent extraction/electrowinning technology: Forty years of innovation, 2.2 million tonnes of copper annually".* The Journal of The South African Institute of Mining and Metallurgy SA ISSN 0038–223X/3.00 +0.00.

75. **Kucha, H., Martens, A., Ottenburgs, R., De Vos W., Viaene W. (1996):** *„Primary minerals of Zn–Pb mining and metallurgical dumps and their environmental behavior at Plombieres, Belgium".* Environmental Geology 27, 1-15.

76. **Kuo Y., Wang J., Wang Ch., Tsai Ch. (2008):** *„Effect of water quenching and $SiO_2$ addition during vitrification of fly ash Part 1: On the crystalline characteristics of slags".* Journal of Hazardous Materials 152 (3), 994–1001.

77. **Lee J-ch. & Pandey B.D. (2012):** *„Bio-processing of solid wastes and secondary resources for metal extraction-A review",* Waste Management 32 (1), 3-18.

78. **Lim T.T. & Chu J. (2006):** *„Assessment of the use of spent copper slag for land reclamation".* Waste Management & Research 24 (1), 67–73.

79. **Lottermoser B.G. (2002)**: *„Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia".* Mineralogical Magazine 66 (4), 475-490.

80. **Lottermoser B.G. (2010)**: „Mine Wastes: Characterization, Treatment and Environmental Impact: [2.1]: Early Historical Observations on Sulfide Oxidation and Acid Mine Drainage, [2.7]: Acid generation prediction". Springer 3rd edition.

81. **Lottermoser B.G. (2011) :** *„Recycling, reuse and rehabilitation of mine wastes"* Elements magazine 7 (6), 405-410

82. **Lottermoser, B.G. (2005):** *„Evaporative mineral precipitates from the historical smelting slag dump, Rio Tinto, Spain".* Journal of Mineralogy and Geochemistry 181 (2), 183–190.

83. **Manase A. & Mellini M. (2002):** *„Chemical and textural characterization of medieval slags from the Massa Marittima smelting sites (Tuscany, Italy)".* Journal of Cultural Heritage 3, 187-198.

84. **Manasse A., Mellini M., Viti C. (2001):** *„The copper slags of the Capattoli Valley, Campiglia Marittima, Italy".* European Journal of Mineralogy 13, 949-960.

85. **Manz M. & Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District, Mexico".* Environmental Pollution 98 (1), 7-13.

86. **Mateus A., Pinto A, Alves L.C., Matos J.X., Figueiras J., Neng N.R. (2011):** *„Roman and modern slag at S. Domingos mine (IPB, Portugal): Compositional features and implications for their long-term stability and potential reuse".* Int. Journal of Environment and Waste Management 8, 133-159.

87. **Maweja K., Mukongo T., Mbaya R.K., Mochubele E.A. (2010):** *„Effect of annealing treatment on the crystallisation and leaching of dumped base metal smelter slags".* Journal of Hazardous Materials 183 (1), 294–300

88. **Mehta K.D., Pandey B.D., Premchand (1999):** *„Bio-assisted Leaching of copper, nickel and cobalt from copper converter slag".* Materials Transactions JIM 40 (3), 214-221.

89. **Mihailova I. & Mehandjiev D. (2010):** *„Characterization of fayalite from copper slags".* Journal of University of Chemical Technology and Metallurgy 45 (3), 317-326.

90. **Mostafa N.Y., El-Hemaly S.A.S., Al-Wakeel E.I., El-Korashy S.A., Brown P.W. (2001):** *„Characterization and evaluation of the hydraulic activity of water-cooled slag and air-cooled slag".* Cement and Concrete Research 31 (6), 899-904.

91. **Moura W.A., Gonçalves J.P., Lima M.B.L. (2007):** *„Copper slag waste as a supplementary cementing material to concrete".* Journal of Materials Science 42 (7), 2226-2230.

92. **Moustakas K., Mavropoulos A., Katsou E., Haralambous K. J., Loizidou M. (2012):** *„Leaching properties of slag generated by a gasification/vitrification unit: The role of pH, particle size, contact time and cooling method used".* Journal of Hazardous Materials 207, 44-50.

93. **Muravyov M.I. & Fomchenko N.V. (2013):** *„Leaching of Nonferrous Metals from Copper Converter Slag with Application of Acidophilic Microorganisms".* Applied Biochemistry and Microbiology 49 (6), 561-569.

94. **Muravyov M.I., Fomchenko N.V., Usoltsev A.V., Vasilyev E.A., Kondrat'eva T.F., (2012):** *„Leaching of copper and zinc from copper converter slag flotation tailings using $H_2SO_4$ and biologically generated $Fe_2(SO_4)_3$".* Hydrometallurgy 119, 40-46.

95. **Nadirov R.K, Syzdykova L.I., Zhussupova A.K., Usserbaev M.T. (2013):** *„Recovery of value metals from copper smelter slag by ammonium chloride treatment".* International Journal of Mineral Processing 124, 145–149

96. **Najimi M., Sobhani J., Pourkhorshidi A.R. (2011):** *„Durability of copper slag contained concrete exposed to sulfate attack".* Construction and Building Materials 25 (4), 1895–1905.

97. **Navarro A., Cardellach E., Mendoza J.L., Corbella M., Domènech L.M. (2008):** *„Metal mobilization from base-metal smelting slag dumps in Sierra Almagrera (Almerıa, Spain)".* Applied Geochemistry 23 (4), 895–913.

98. **Nickel E. (1995):** *„The definition of a mineral".* Canadian Mineralogist 33, 689-690.

99. **Pal A. & Paul A.K. (2008):** *„Microbial extracellular polymeric substances: central elements in heavy metal bioremediation (Review)".* Indian Journal of Microbiology 48 (1), 49-64.

100. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California".* Applied Geochemistry 16 (14), 1567–1593.

101. **Piatak N.M. & Seal R.R. (2010):** *„Mineralogy and the release of elements from slag from the Hegeler Zinc smelter, Illinois (USA)".* Applied Geochemistry 25, 302-320.

102. **Piatak N.M. & Seal R.R. (2012):** *„Mineralogy and environmental geochemistry of historical iron slag, Hopewell Furnace National Historic site, Pennsylvania, USA".* Applied Geochemistry 27, 623-643.

103. **Piatak N.M., Parsons M.B., Seal R.R. (2015):** *„Characteristics and Environmental Aspects of Slags: A review".* Applied Geochemistry. 57, 236-266..

104. **Piatak N.M., Seal 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".* Applied Geochemistry 19, 1039-1064.

105. **Piatak N.M., Seal R.R., Hammarstrom J.M., Meier A.L., Briggs P.H. (2003):** *„Geochemical Characterization of Slags, Other Mine Waste, and Their Leachate from the Elizabeth and Ely Mines (Vermont), the Ducktown Mining District (Tennessee), and the Clayton Smelter Site (Idaho)".* U.S. Department of the Interior, U.S. Geological Survey

106. **Puziewicz J., Zainoun K., Brill H. (2007):** *„Primary phases in pyrometallurgical slags from a zinc-smelting waste dump, Swietochlowice, Upper Silesia, Poland".* The Canadian Mineralogist 45, 1189-1200.

107. **Radetzki M. (2009):** *„Seven thousand years in the service of humanity-the history of copper, the red metal".* Resources Policy 34 (4), 176-184.

108. **Reuter M., Xiao Y., Boin U. (2004):** *„Recycling and environmental issues of metallurgical slags and salt fluxes".* VII International Conference on Molten Slag Fluxes and Salts, The South-African Institute of Mining and Metallurgy.

109. **Rozendaal A. & Horn R. (2013):** *„Textural, mineralogical and chemical characteristics of copper reverb furnace smelter slag of the Okiep Copper District, South Africa".* Minerals Engineering 52, 184–190.

110. **Rudnik E., Burzyńska L., Gumowska W. (2009):** *„Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag".* Minerals Engineering 22 (1), 88-95**.**

111. **Sãez R., Nocete F., Nieto J.M., Capitãn M.A., Rovira S. (2003):** *„The extractive metallurgy of copper from Cabezo Jurē, Huelva, Spain: Chemical and mineralogical study of slags dated to the third millennium b.c.".* The Canadian Mineralogist 41, 627-638.

112. **Saha R., Saha N., Donofrio R.S., Bestervelt L.L. (2013):** *„Microbial siderophores: a mini review".* Journal of Basic Microbiology 53 (4), 303-317.

113. **Seignez N., Bulteel D., Damidot D., Gauthier A., Potdevin J.L. (2006):** *„Weathering of metallurgical slag heaps: multi-experimental approach of the chemical behaviours of lead and zinc".* Waste Management and the Environment III, WIT Transactions on Ecology and the Environment 92, 31-40.

114. **Seignez N., Gauthier A., Bulteel D., Bautier M., Recourt P., Damidot D., Potdevin J.L. (2007):** *„Effect of Pb-rich entities during alteration of a partially vitrified metallurgical waste".* Journal of Hazardous Materials 149, 418-431.

115. **Seignez N., Gauthier A., Bulteel D., Damidot D., Potdevina J.L. (2008):** *„Leaching of lead metallurgical slags and pollutant mobility far from equilibrium conditions".* Applied Geochemistry 23 (12), 3699–3711

116. **Shanmuganathan P., Lakshmipathiraj P., Srikanth S., Nachiappan A.L., Sumathy A. (2008):** *„Toxicity characterization and long-term stability studies on copper slag from the ISASMELT process".* Resources, Conservation and Recycling 52 (4) 601–611.

117. **Shen H. & Forssberg E. (2003):** *„An overview of recovery of metals from slags".* Waste Management 23 (10), 933–949.

118. **Shi C & Qian J. (2000):** *„High performance cementing materials from industrial slags — a review".* Resources, Conservation and Recycling 29 (3), 195–207.

119. **Shi C., Meyer Ch., Behnoodc A. (2008):** *„Utilization of copper slag in cement and concrete".* Resources, Conservation and Recycling 52 (10), 1115–1120.

120. **Smith K.S. (2007):** *„Strategies to predict metal mobility in surficial mining environments".* In: DeGraff J. V. *„Understanding and Responding to Hazardous Substances at Mine Sites in the Western United States".* The Geological Society of America. Reviews in Engineering Geology XVII, 25-45.

121. **Sobanska S., Ledésert B., Deneele D., Laboudigue A. (2000):** *„Alteration in soils of slag particles resulting from lead smelting".* Earth and Planetary Sciences 331 (4), 271-278.

122. **Southam G. (2012):** *„Minerals as substrates for life: The Prokaryotic view".* Elements magazine 8 (2), 101-106.

123. **Sparks D.L. (2005a):** *„Environmental Catalysis"* Chapter 1: *Metal and oxyanion sorption on naturally occurring oxide and clay mineral surfaces*, 3-36. Chapter 3: *Precipitation and Dissolution of Iron and Manganese Oxides*, 61-83. Taylor and Francis Group, 2005.

124. **Sparks D.L. (2005b):** *„Toxic metals in the environment: the role of surfaces".* Elements magazine 1 (4), 193-196.

125. **Spence J.R. and Soderstorm M.D. (1999):** *„Practical Aspects of Copper Solvent Extraction from Acidic Leach Liquors"* in Jergensen G. V.: *Copper leaching, solvent extraction and electrowinning Technology*, Chapter 4: *Theory and practice of solvent extraction*. Society for Mining, Metallurgy and Exploration

126. **Sposito G. (2008):** *„The Chemistry of Soils",* NY: Oxford University Press, 2nd edition.

127. **Sueoka Y. & Sakakibara M. (2013):** *„Primary Phases and Natural Weathering of Smelting Slag at an Abandoned Mine Site in Southwest Japan".* Minerals 3 (4), 412-426.

128. **Sukla L.B., Kar R.N., Panchanadikar V. (1992):** *„Leaching of copper converter slag with Aspergillus niger culture filtrate".* BioMetals 5, 169-172.

129. **Sukla L.B., Kar R.N., Panchanadikar V. (1995):** *„Bioleaching of copper converter slags using Aspergillus niger isolated from lateritic nickel ore".* International Journal of Environmental Studies 47 (2), 81-86.

130. **Sukla L.B., Panda S.C., Jena P.K. (1986):** *„Recovery of cobalt, nickel and copper from converter slag through roasting with ammonium sumphate and sulphuric acid".* Hydrometallurgy 16 (2), 153-165.

131. **Suzuki I. (2001):** *„Microbial leaching of metals from sulfide minerals".* Biotechnology Advances 19, 119-132.

132. **Svedberg P. & Tilton J. E. (2006):** *„The Real, Real Price of Nonrenewable Resources: Copper 1870–2000".* World Development 34, 501-519.

133. **Taylor K. & Konhauser K.O. (2011):** *„Iron in Earth surface systems: A major player in chemical and biological processes".* Elements Magazine 7 (2), 83-88.

134. **Teng T.T., Yusup Y., Low L.W. (2012):** *„Heavy Metal Ion Extraction Using Organic Solvents: An Application of the Equilibrium Slope Method. Stoichiometry and Research - The Importance of Quantity in Biomedicine".* Dr Alessio Innocenti (Ed.), ISBN: 978-953-51-0198-7, InTech, Available from: http://www.intechopen.com/books/stoichiometry-and-research-the-importance-of-quantity-inbiomedicine/stoichiometry-of-metal-complexes-extracted-using-organic-solvents

135. **The International Copper Study Group (ICSG):** *„The world copper factbook 2013".* 1-57.

136. **Themelis M.J. (1994):** *„Pyrometallurgy near the end of 20th century".* Industrial Insight 46 (8), 51-57.

137. **Tiller, K.G. (1989):** *„Heavy metals in soils and their environmental significance".* Advances in Soil Science, 9, 113 142.

138. **Tshiongo N., Mbaya R.K.K., Maweja K. (2011):** *„Leaching kinetics of Cu, Co, Zn, Pb and Fe from copper smelting slags cooled in different ways after tapping".* The Southern African Institute of Mining and Metallurgy 6th Southern African Base Metals Conference 2011.

139. **Tshiongo N., Mbaya R.K.K., Maweja K.L.C. Tshabalala (2010):** *„Effect of Cooling Rate on base Metals Recovery From Copper Matte Smelting Slags".* World Academy of Science, Engineering and Technology 4, 236-240.

140. **Tsuneda S., Aikawa H., Hayashi H., Yuasa A., Hirata A. (2003):** *„Extracellular polymeric substances responsible for bacterial adhesion onto solid surface".* FEMS Microbiology Letters 223, 287–292

141. **Tyszka R., Kierczak J., Pietranik A., Ettler V., Mihaljevič M. (2014):** *„Extensive weathering of zinc smelting slag in the heap in Upper Silesia (Poland): potential environmental risks posed by mechanical disturbance of slag deposits".* Applied Geochemistry 40, 70-81.

142. **U.S. Congress, Office of Technology Assessment (1988):** *„Copper: Technology and Competitiveness",* OTA-E-367 (Washington, DC: U.S. Government Printing Office). Chapter 6.

143. **Uroz S., Calvaruso Ch., Turpault M-P., Frey-Klett P. (2009):** *„Mineral weathering by bacteria: ecology, actors and mechanisms".* Trends in Microbiology 17 (8), 378-387.

144. **van Hullebusch E.D., Yin N-H., Seignez N., Labanowski J., Gauthier A., Lens P.N.L., Avril C., Sivry Y. (2015):** *„Bio-alteration of metallurgical wastes by Pseudomonas aeruginosa in a semi flow-through reactor".* Journal of Environmental Management 147, 297-305.

145. **Vaughan D.J. & Lloyd J.R (2011):** *„Mineral-organic-microbe interactions: Environmental impacts from molecular to macroscopic scales".* Comptes Rendus Geoscience 343 (2), 140-159.

146. **Vdović N., Billon G., Gabelle C., Potdevin J.L. (2006):** *„Remobilization of metals from slag and polluted sediments (Case Study: The canal of the Deûle River, northern France)".* Environmental Pollution 141 (2), 359-369.

147. **Vera M., Schippers A, Sand W. (2013):** *„Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation—part A".* Applied Microbiology Biotechnology 97 (17), 7529–7541.

148. **Vestola E. A., Kuusenaho M.K, Narhi H.M., Tuovinen O.H., Puhakka J.A., Plumb J.J., Kaksonen A.H. (2010):** *„Acid bioleaching of solid waste materials from copper, steel and recycling industries".* Hydrometallurgy 103 (1-4), 74-79.

149. **Vítková M., Ettler V., Johan Z., Kříbek B., Šebek O., Michaljevič M. (2010):** *„Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province, Zambia".* Mineralogical Magazine 74 (4), 581-600.

150. **Vu B., Chen M., Crawford R.J., Ivanowa E.P. (2009):** *„Bacterial extracellular polysaccharides in biofilm formation (Review)".* Molecules 14 (7) 2535-2554.

151. **Watling H.R. (2006):** *„The bioleaching of sulphide minerals with emphasis on copper sulphides".* Hydrometallurgy 84 (1), 81-108.

152. **White Ch., Wilkinson S.C., Gadd G.M. (1995):** *„The role of Microorganisms in Biosorption of Toxic Metals and Radionuclides".* International Biodeterioration and Biodegradation 35 (1-3), 17-40.

153. **Willscher S. & Bosecker K. (2003)**: *„Studies on the leaching behaviour of heterotrophic microorganisms isolated from an alkaline slag dump".* Hydrometallurgy 71 (1-2), 257–264

154. **Wingender J., Neu T.R., Flemming H.C. (1999):** *„Microbial extracellular polymeric substances. Characterization, Structure and Function".* Chapter 1: *„What are bacterial extracellular polymeric substances?",* Chapter 5: *„EPS and Macro-Environment".* Springerlink

155. **Yang Y., Li S., Bi X., Wu P., Liu T., Li F., Liu C. (2010b):** *„Lead, Zn and Cd in slags, stream sediments and soils in an abandoned Zn smelting region, southwest of China, and Pb and S isotopes as source traces"* Journal of soils and sediments 10 (8), 1527-1539.

**156. Yang Z., Rui-lin M., Wang-dong N. Hui W., (2010a):** *„Selective leaching of base metals from copper smelter slag".* Hydrometallurgy 103 (1-4), 25-29.

**157. Yin N.-H., Sivry Y., Avril C., Borensztajn S., Labanowski J., Malavergne V., Lens P.N.L., Rossano S., van Hullebusch E.D. (2014):** *„Bioweathering of lead blast furnace (LBF) metallurgical slags by Pseudomonas aeruginosa",* International Biodeterioration & Biodegradation 86, 372-381.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1  MATERIALS AND METHODS

### 3.1.1  Materials

#### 3.1.1.1   Historical slags

Historical slags used in this PhD work were collected in the study area representing historical centre of copper mining and smelting. This site is located in the vicinity of Miedzianka and Ciechanowice towns in Lower Silesia, (South-western Poland) (Figure 3.1). The beginning of mining in this historical district is dated on middle ages. The industrial activity developed there due to occurrence of Cu-rich ores (mainly chalcopyrite with minor bornite and pyrite) that were exploited at the time. Pollymetalic (Cu, Ag and As-rich) veinlets were formed as the result of intrusion of granitoid magma (western part of Rudawy Janowickie Mountains) into the surrounding metamorphic rocks (eastern part of Rudawy Janowickie Mountains) 300-350 million years ago (Variscan Orogeny) (Figure 3.1).
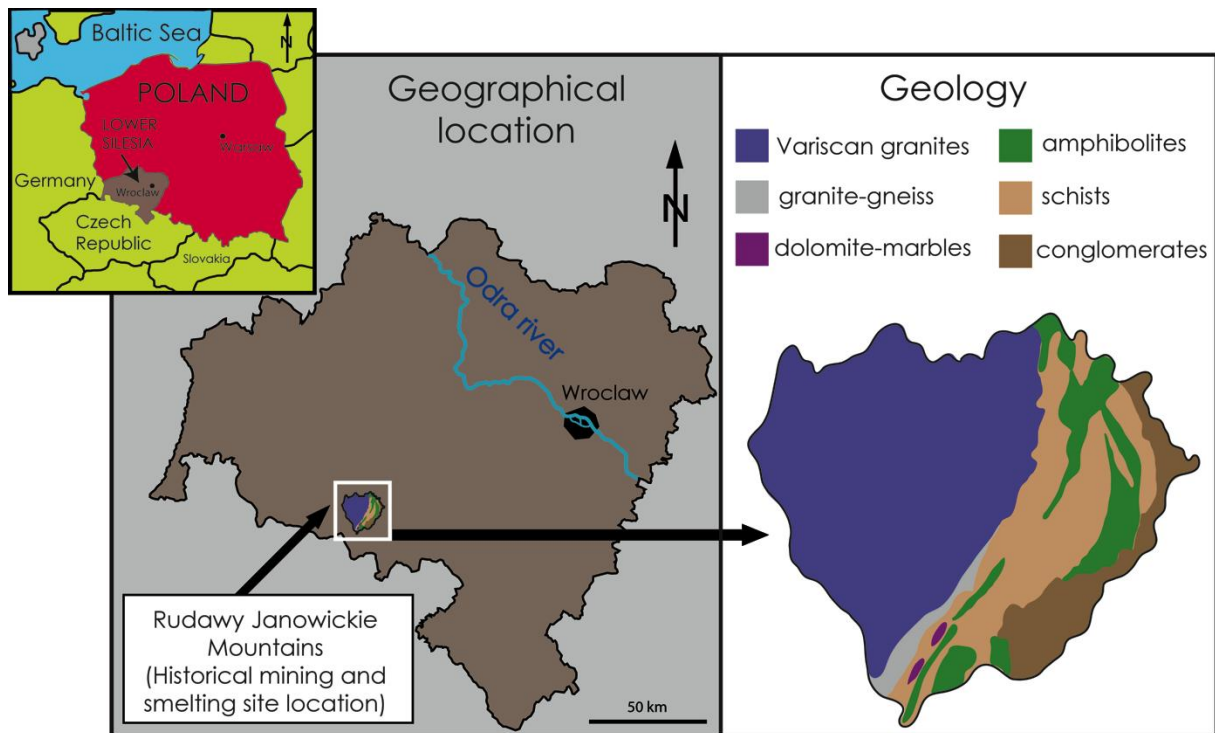


**FIGURE 3.1 Geographical location and geology of the study area.**

The smelting activity begun in XIV century, however the literature lacks precise information concerning technologies applied at that time. Presumably, the ores were hand-sorted. The process of metal production was based on roasting and smelting. The roasting aimed at elimination of sulfur and other volatile compounds, whereas smelting the ore resulted in

obtaining alloys of sulfides, mainly Cu and Fe. Next the product was subjected to roasting and ore was smelted again to bind iron in the slag (Figure 3.2). In order to receive copper with a higher grade of purity, the sulfur and other remaining unwanted metals were removed. The activity of smelters in Miedzianka and Ciechanowice has been terminated at the end of XIX century (Dziekoński, 1972). The environmental relevance of mining and smelting activity of this area is related to large-volume of mining pits and dumps that were left unattended since activity ceased (Figure 3.3). Slags are currently present on the surface ground, in stream beds and soil profiles. The total copper production estimated for this area is approximately 2000 tones based on volumetric capacity of dumps (Kierczak & Pietranik, 2011).



STAGE I: ROASTING

T = 500 - 900°C (solid compounds)
Oxidative conditions
$CuFeS_2 + 2O_2 = CuO + FeO + 2SO_2$

STAGE II: SMELTING

T = 1200°C (liquid compounds)
Reductive conditions
$2 CuO + Cu_2S = 4Cu + SO_2$
$2FeO + SiO_2 = Fe_2SiO_4$
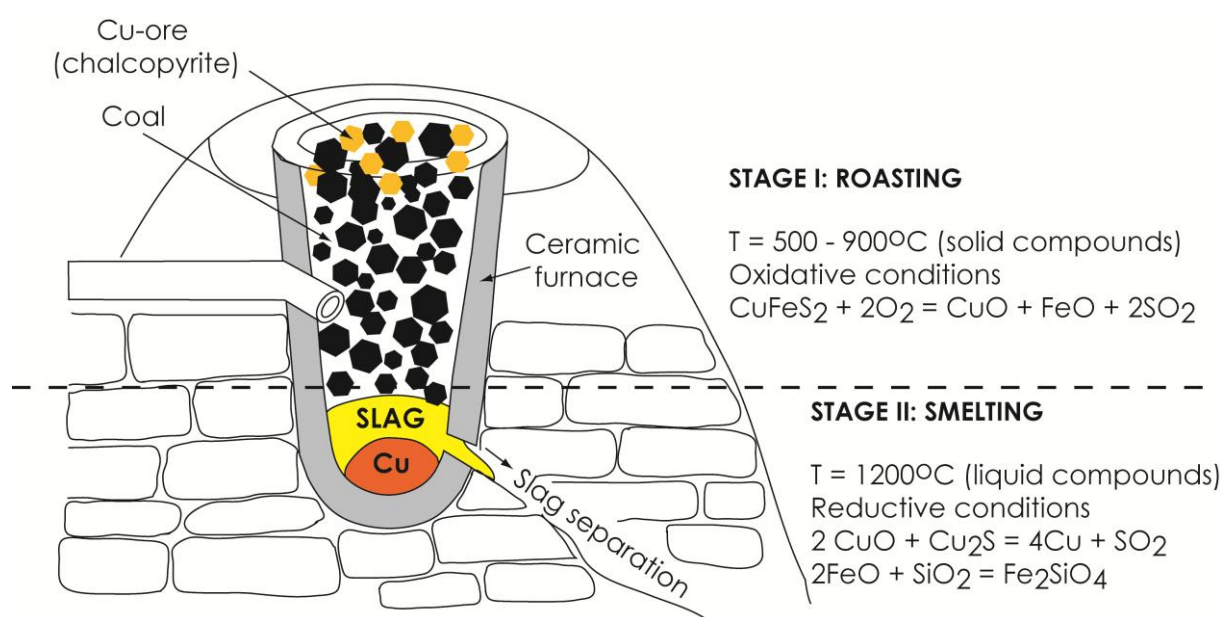
**FIGURE 3.2 Schematic picture presenting historical Cu production.**



**FIGURE 3.3 Historical dumping site (A: mining waste-rock dump in Miedzianka,**

**B: historical slags found in study area).**

### 3.1.1.2 Modern slags

Modern slags were collected from currently operating company perceived as a large Cu producer in Europe. Due to the signature of non-disclosure agreement the name of sample provider could not be given. Modern slags group includes three different samples representing separate on-going smelting processes. 15 kilograms of each sample has been collected in in order to ensure individual slags are representative for respective smelting processes. The company processes Cu-minerals mainly chalcocite, bornite, chalcopyrite and covellite incorporated in rocks such as sandstone, blackshale and dolomite.

The first stage of Cu production is preparing the concentrate. As the average Cu content in ores is approximately 1.3-2.6% company subjects the ore to the concentration and gets concentrate of approximately 23% Cu content. The ore enrichment strategy is based on froth flotation process where Cu-rich minerals are being separated improving total Cu content in the initial product. Such prepared smelting input is then subjected to various smelting processes resulting in formation different slag wastes such as: *shaft furnace slag and granulated slag.* The flow sheet of generation of these slags is presented in Figures 3.4 and 3.5 for SFS and GS, respectively.
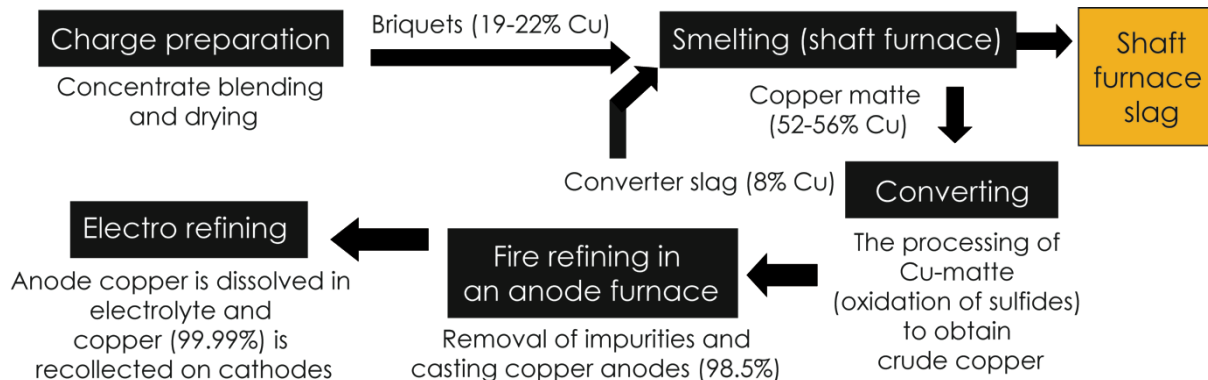


**FIGURE 3.4 Flowchart presenting the process at which shaft furnace slag is generated.**
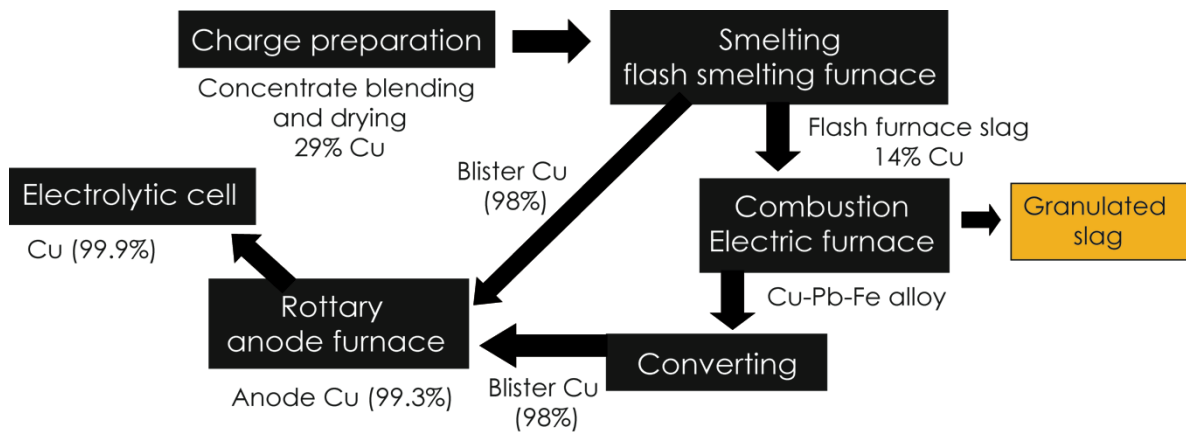
**FIGURE 3.5 Flowchart presenting the process at which granulated slag is generated.**

Since copper concentrate applied to production contains over 2.5% of lead, the metal is concentrated in various by-products generated during the smelting process. Lead-rich by-products are the base materials for the process aiming at lead recovery. Process relies on reductive smelting in reverberatory-rotary Dörschel furnace. Finally, lead is separated from slags and further subjected to refining, where raw lead is obtained (Figure 3.6).
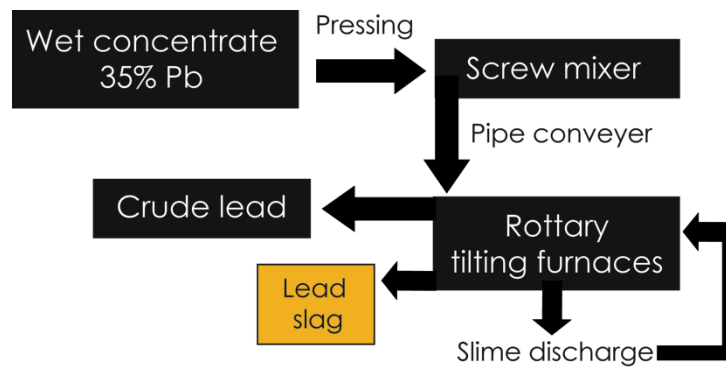


**FIGURE 3.6 Flowchart presenting the process at which lead slag is generated.**

**FIGURE 3.7 Modern slags (A1 and A2: shaft furnace slag, B: granulated slag, C: lead slag).**

## 3.1.2  Methods

### 3.1.2.1   Sample preparation

*i) For determining bulk chemical composition*

Slag samples were crushed such that fraction was reduced to particles smaller than 0.3 mm. Samples were sent to ACME Analytical Laboratory (Vancouver, Canada) to determine bulk chemical composition of each slag. For determining the content of major elements, the slags were prepared by fusion of the samples by $LiBO_2/Li_2B_4O_7$ and dissolving the residue with nitric acid ($HNO_3$).

The complete acid digestion procedure was applied for analysis of minor compounds (such as As, Cu, Pb and Zn). Digestion was done in two steps of treatment. The first step followed the total digestion of 0.1 g slag sample using 10 mL 40% HF (hydrofluoric acid) and 0.5 mL concentrated $HClO_4$ (perchloric acid) at 150°C for 2.5 h. Then samples were re-subjected to digestion using 5 mL HF and 0.5 $HClO_4$ for 2 hours. At the end of the digestion procedure, 2% (v/v) $HNO_3$ was added and samples were diluted to 50 mL using distilled water (Tyszka et al., 2012).

## ii) For mineralogical analysis

Several grams of slags were homogenized in an agate mortar for powder X-ray diffraction analyses. Polished thin sections and polished sections were prepared for phase observations and mineralogical characterization with an employment of analytical techniques such as scanning electron microscope (SEM) and electron microprobe analyzer (EMPA).

## iii) For leaching/weathering experiments

Each slag type was crushed using a steel crusher in order to reduce the fraction size. Fractions were then prepared using a steel sieve to separate the fraction smaller than 0.3 mm, fraction 0.3-1 mm and fraction 1-2 mm. Particles with a size below 0.3 mm and 1-2 mm were used for different leaching experiments.

## iv) For granulometry

The granulometry (4 mm < f < 0.06 mm) was determined only for granulated slags. The material was sieved to separate different grain sizes and fractions were weighed to determine the relative distribution of particular fractions per kilogram of granulated slag.

### 3.1.2.2   Leaching solutions preparation

## i) Solutions for organic acid leaching

Leaching experiments were performed using humic (HA) and fulvic acids (FA) as well as artificial root exudates (ARE). The HA and FA solutions were prepared by dissolving 20 mg of commercial (Suwannee River, International Humic Substances Society) humic (HA) or fulvic acid (FA) in 1 L of MilliQ water (20 mg/L) and were pre-set at initial pH of 4.4. The ARE solution corresponded to the rhizosphere composition described by Baudoin et al. (2003) and contained: glucose (3.31 g/L), fructose (3.31 g/L), sucrose (3.15 g/L), citric acid (1.77 g/L), lactic acid (1.66 g/L), succinic acid (1.63 g/L), alanine (0.74 g/L), serine (0.97 g/L) and glutamic acid (0.81 g/L). The initial pH of ARE solution was 2.9 and 4.4 for two different treatments. The pH value of the solutions was adjusted using $HNO_3$ or NaOH. The ARE solution is composed of simple, low molecular weight organic acids, whereas HA/FA are characterized by a more complex structure and higher molecular weight (Schulten & Schnitzer, 1993).

## ii) Solutions for bioweathering experiments

Growth medium was prepared by dissolution in ultrapure water (per liter): 4 g of succinic acid ($C_4H_6O_4$), 1 g of ammonium sulfate (($NH_4$)$_2SO_4$), 0.2 g of disodium hydrogen phosphate

($Na_2HPO_4$) and 6 g of Tris buffer ($C_4H_{11}NO_3$). The initial pH of the growth medium was adjusted to the value of $7.8 \pm 0.1$ using 5 M NaOH. The solution was sterilized for 20 min. at 121°C prior to use in the experiments.

*iii) Solutions for bioleaching experiments*

The bioleaching experiments with *A. thiooxidans* were performed in a mineral salt medium composed of 0.1 g di-potassium hydrogen phosphate ($K_2HPO_4$), 0.25 g magnesium sulfate ($MgSO_4·7H_2O$), 2.0 g ammonium sulfate ($NH_4)_2SO_4$, 0.1 g potassium chloride (KCl) and 2% (*w/v*) of elemental sulfur per 1 L of ultrapure water. The initial pH value of growth medium was set at 2.5.

Growth medium used in the experiment with *Pseudomonas fluorescence* consisted of succinic acid (4 g), ammonium sulfate (1 g), disodium hydrogen phosphate (0.2 g) and Tris buffer (6 g) per 1 L of ultrapure water (Yin et al., 2014).

The solutions were autoclaved for 20 min. at 121°C prior to use in the experiments.

### 3.1.2.3   Bacteria preparation

*i) Bacteria used in bioweathering experiments*

A gram-negative bacterial strain of bacilli *Pseudomonas aeruginosa* (n° CIP 105094) used in the bioweathering experiments was available from the Institute Pasteur (Paris, France). Before the employment in the biotic experiments, bacteria were grown in Luria Bertani medium for 24 h. Afterwards, cells were harvested and cleaned 3 times with sterile 5% NaCl and re-suspended in ultrapure water. Thereafter, cells were introduced to the experimental bottles. No adaptation of bacteria to high metallic element concentrations was done. All biotic experiments began with initial optical density at a wavelength of 600 nm ($OD_{600}$) of 0.008 in order to ensure equal bacterial cell number for all replicates.

*ii) Bacteria used in bioleaching experiments*

A gram-negative bacterial strain of *A. thiooxidans* (DSM 9463) was grown in salt medium composed of 2 g ammonium sulfate ($NH_4)_2SO_4$, 0.25 g of magnesium sulfate ($MgSO_4·7H_2O$), 0.1 g di-potassium hydrogen phosphate ($K_2HPO_4$), 0.1 g potassium chloride (KCl) and 1% (*w/v*) of elemental sulfur (S) per 1 L of ultrapure water. pH of the growth medium was adjusted to 2.5 and bacteria was grown two times over one week in order to adjust to pH conditions lower than its optimal (pH=3.5). Two percent (*v/v*) of pre-grown inoculum was introduced to each biotic batch flask.

A gram-negative bacterial strain of *P. fluorescens* (DSM 50091) used as the bioleaching agent was purchased from DSMZ. This bacterium was initially grown in nutrient broth medium (pH=6.9) for 24 h. Afterwards, the cells were harvested and washed 3 times using sterile 5% NaCl. This bacterium was then re-suspended in ultrapure water and 2% (*v/v*) of inoculum was supplemented into respective batch incubations.

### 3.1.2.4   Analytical methods

#### i) Bulk chemical composition-element measurement

Major elements were measured by inductively coupled plasma emission spectrometry (ICP-ES). Total sulfur and carbon contents were determined by LECO combustion analysis (ACME Analytical Laboratory). The analytical reproducibility ($2\sigma$), as estimated from replicate analyses of sample LS, ranges from 0.5% ($Al_2O_3$) to 4% ($Na_2O$) at 95% confidence limits. The analytical accuracy ($2\sigma$), as estimated from four measurements of standard SO-18, amounted between 0.1 (MgO) to 2.5% ($K_2O$) at 95% confidence limits. Obtained results are expressed in respective oxides for individual elements (Table 4.1, Chapter 4). Loss on ignition (LOI) was determined by sintering a sample at 1000°C.

The concentrations of the minor elements were determined using quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, X Series 2, Thermo Scientific) according to the operating conditions of Mihaljevič et al. (2011). The data concerning quality control of these analyses are presented in Tyszka et al. (2012).

#### ii) Mineralogical characterization

Identification of phases present in the slags and determination of their chemical composition were done using optical microscopy, X-ray powder diffraction (XRD), scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS) and electron microprobe analyser (EMPA) at the University Pierre and Marie Curie (Paris, France).

Preliminary observations of polished thin sections were performed with the optical microscope Leica DM2500P in transmitted and reflected light mode. The phase composition was established using powder X-ray diffraction (XRD) analyses. XRD patterns for selected samples were obtained using a Bruker D8 Advance diffractometer (at 40 kV and 40 mA, with CuKα radiation, $2\theta$ range from 2° to 80°, step 0.12° $2\theta$ min$^{-1}$). Results were compared with standard reference patterns. The phase composition was also examined using scanning electron microscope (ZEISS Supra 55) equipped with an X-ray energy dispersive system (SEM-EDS) at 15 kV working conditions. The chemical composition of the identified phases was determined on a CAMECA SX100 microprobe with two individual analyze programs for

silicates and sulfides, respectively. For electron microprobe analysis of silicates and oxides phases, the following conditions were used: accelerating voltage 15 keV, beam current 10 nA, and 5 seconds of counting time and beam diameter of 5 µm, whereas conditions applied for the analysis of sulfides and intermetallic phases were: 15 keV of accelerating voltage, 40 nA of beam current and 3 seconds of counting time.

### iii) Quantification of metals accommodated in mineral phases

Modal phase composition was estimated by point counting using JMicro Vision 1.2.7 software. Furthermore, the distribution of metals between mineral phases was estimated from modal phase composition and average concentration of metals in individual phases based on microprobe data. Due to proportional variability of mineral phases and the extent to which individual compounds vary in proportions, values present only approximate percentage of metals accommodated in the mineral phases relative to the bulk composition of the materials.

### iv) Elements measurement in the leachates

The leachates from organic acids leaching experiments were analyzed for their Cu, Zn and Pb content using ICP-MS (Agilent 7700x) with $^{45}$Sc and $^{115}$In as internal standards. Quality control included systematic analysis of certified reference materials (SLRS-5 standard). The detection limits were typically 0.04, 0.4 and 0.05 µg/L for Cu, Zn and Pb, respectively. Additionally, some samples were measured using an atomic absorption spectrometer (AAS). The detection limits for AAS measurements were 0.01 mg/L (10 µg/L), 0.02 mg/L (20 µg/L) and 0.1 mg/L (100 µg/L) for Cu, Zn and Pb respectively.

The concentrations of major (Si, Fe) and minor (Cu, Zn, Pb) elements in the solutions from bioweathering experiments were analyzed using ICP-MS (inductively coupled plasma mass spectrometry, Agilent 7700x) with $^{45}$Sc and $^{115}$In as internal standards. Detection limits were typically 0.01-0.04 µg/L and 1.69 µg/L for minor and major elements, respectively. Quality control included systematic analysis of certified reference materials (SLRS-5 standard).

Concentrations of metals (Cu, Zn and Fe) in the leachates from bioleaching experiments were measured using Atomic Absorption Spectrometer (AAS 200 Perkin Elmer). The detection limits were between 0.01 and 0.02 mg/L for all elements analyzed. The calibration was done using standards of known metal concentrations. Quality control included systematic analysis of calibration standards. The procedure was repeated at least once for every 10 samples analyzed. Additionally, repeated analysis of randomly chosen samples was done in order to confirm the values obtained from the previous measurement. The quantities of metals in the solutions were converted to express the values in mg of element released per kilogram of the slag by multiplying the metal concentration in the solution by the liquid to solid ratio.

### v) Alteration of slags (Scanning electron microscopy)

Slag samples resulting from treatments with the organic solutions were observed by SEM with respect to presence of weathering features. At the end of the experiments, grains were dried and coated with Au. Microscopic observations of slags were conducted using SEM (JEOL JSM-601OA) coupled with an Energy Dispersive Spectrometer at high vacuum and 15-20 kV working mode.

At the end of bio/weathering experiments, slags grain were observed with respect to surface changes using Scanning Electron Microscope (QEMSCAN 650F) at 10-20 kV and high vacuum working mode.

Slags from abiotic and biotic leaching experiments were examined with respect to alteration features resulting. Dried slag grains were coated with Au and mineralogical analysis was performed under SEM equipped with Energy Dispersive Spectrometer (EDS) (JEOL JSM-601OA) at high vacuum and 15-20 kV working mode.

### vi) Anions measurement

Sulfate, phosphate and nitrate concentrations in the solutions from bioweathering experiments were measured colorimetrically using Permachem reagents (HACH). The carbonates content was determined by titration with HCl.

### vii) Microbial metabolite measurement

Microbially-derived metabolites were analyzed after termination of bioweathering experiments. The fluorescence properties of released microbial metabolites were analyzed using three dimensional excitation-emission spectrofluorophotometry (Shimadzu RF-5301 PC) equipped with a 150-W Xenon lamp. The fluorescence matrixes (3D-EEM) were done over an excitation (Ex) and emission (Em) range of 220-450 nm and 250-550 nm, respectively (Bourven et al., 2012). Measurement settings were fixed at 10 nm, scan wavelength intervals of 1 nm and a speed of 24 nm/s. Measurements were performed in 1 cm quartz optical cells. Prior to measurements, filtered (<0.22 µm) samples were diluted (15 µL/1000 µL) in 50 mM phosphate buffer adjusted to pH of 7.0 (±0.1) in order to diminish fluorescence signal saturation as well as to maintain the fluorescence at the same protonation degree. The data was processed using Panorama fluorescence 3.1 software (LabCognition, Japan).

### viii) Bacterial growth

Bacterial growth rate in bioweathering experiments was monitored by frequent measurements of optical density ($OD_{600}$) using UV spectrophotometer (CADAS 50S, Dr Lange) at a wavelength of 600 nm. The pH measurements were done using a (GLP 22) pH meter.

*ix) Visual MinteQ modeling*

The geochemical simulation for bio/weathering experiments was performed using Visual MinteQ modeling software (version 3.1 http://vminteq.lwr.kth.se/) in order to determine the degree of saturation of the leaching solutions with respect to possible secondary precipitates. The modeling was performed using the chemical composition of the leaching solution for every incubation time.

## 3.1.3 Experimental designs

Five major experiments were carried out in frame of this PhD project. Those included: *i) mineralogical characterization of slags, ii) pH-dependent leaching, iii) leaching with soil organic acids, iv) bioweathering experiments and v) bioleaching experiments.* Experimental approaches designed for respective experiments are presented in Figures 3.8-3.11 and comparison of experimental conditions and analytical techniques is summarized in Table 3.1.

**TABLE 3.1 Comparison of experimental conditions and analytical techniques employed in the experiments.**

| **Characterization** | Bulk chemical composition | Loss of ignition | Mineral phase composition | Modal phase composition |
|---|---|---|---|---|
| | *Major elements:* ICP-ES *Minor elements:* ICP-MS | Sintering the sample at 1000°C | Optical microscope Scanning electron microscope Electron microprobe analyzer | JMicroVision Software |
| **Experiment Conditions** | **pH dependent leaching** | **Soil organic acids leaching** | **Bioweathering** | **Bioleaching** |
| Leaching solution (composition) | 2 M HNO₃ 1 M KOH | Humic acid Fulvic acid Artificial root exudates | Abiotic growth medium Growth medium inoculated with bacteria *Pseudomonas aeruginosa* | Abiotic growth medium Growth medium inoculated with bacteria *Pseudomonas fluorescens* or *Acidithiobacillus thiooxidans* |
| Slag used | Historical slag Shaft furnace slag Granulated slag Lead slag | Historical slag Shaft furnace slag Granulated slag Lead slag | Historical slag (crystalline slag) Granulated slag (amorphous slag) | Historical slag (crystalline slag) Granulated slag (amorphous slag) |
| Fraction size | < 0.3 mm | < 0.3 mm | 1-2 mm | < 0.3 mm and 1-2 mm |
| Liquid/solid ratio (pulp density [%]) | 10 (10%) | 10 (10%) | 25 (4%) | 100 (1%) and 33.33 (3%) |
| Agitation speed [rpm] | 150 | 150 | 120 | 100 |
| Temperature [°C] | room-temp. | 21±1 | 21±1 | 30 |
| Experiment duration (sampling intervals) | 1 day (24 h) | 1 - 40 days (24, 48, 72, 168 and 960 hours) | 112 days (every 14 days) | 1 - 40 days *Pseudomonas fluorescens* and corresponding abiotic controls: 3, 7, 14, 21, 30 and 40 days *Acidithiobacillus thiooxidans* and corresponding abiotic controls: 1, 2, 3, 6, 9, 14, 21 and 40 days. |
| Filtration [μm] | 0.45 | 0.45 | 0.22 | 0.45 |
| Elements analyzed | Cu, Zn, Pb | Cu, Zn, Pb | Si, Fe, Cu, Zn, Pb | Cu, Zn, Fe |
| Metal measurements | ICP-OES | ICP-MS | ICP-MS | AAS |

### 3.1.3.1 pH-dependent leaching experiments

Leaching tests were performed according to the standard protocol (US EPA 1313) in the pH range of 2-13. For each slag type, a different quantity of water-diluted acid (2 M $HNO_3$) and base (1 M KOH) were prepared depending on the amount required to reach particular pH values. Additionally, extraction with ultrapure water (Milli-Q) was performed to show the slags behaviour at their natural pH. The experiments were carried out with a liquid to solid ratio of 10 using 5 g of slag and 50 mL of solution at a rotation speed of 150 rpm during 24 hours. Afterwards, leachates were filtered using 0.45 μm nitrocellulose syringe filters (GVS filter technology) and acidified using (1% vol.) of concentrated (65%) $HNO_3$. Analyses of leachates were conducted using ICP-OES (Perkin-Elmer Optima 8300). Leaching experiments were done in triplicates. Statistical analysis of triplicates slag samples in individual pH treatments was carried out using t-test in order to assure quality of the results. An assumption made for the t-test was that $α=0.05$ to judge whether the statistical difference of the replicates was significant at the 95% confidence level.



**FIGURE 3.8 Experimental approach for pH-dependent leaching carried out for each slag.**

### 3.1.3.2 Soil organic acids leaching

The leaching experiments included five approaches at which each slag was submitted to leaching tests with: i) humic acid at pH (4.4), ii) fulvic acid at pH (4.4), iii) artificial root exudates solution at pH (4.4), iv) artificial root exudates solution at pH (2.9) and v) ultrapure water. A mass of 3 g of each slag, crushed to size fraction below 0.3 mm, was placed into batches and 30 mL of leaching solutions were added to maintain liquid to solid ratio of 10. Independent batches in triplicates were accompanied by procedural blanks. The batches were wrapped up in aluminium paper in order to avoid photo-oxidation of organic compounds, kept at ambient temperature (21±1°C) on a table shaker continuously agitated at 150 rpm. Leaching solutions with slags were left at free pH drift. The leachates were sampled after 24, 48, 72, 168 and 960 hours. At each sampling time, the pH of the leaching solution was

measured, solutions were filtered using 0.45 μm nitrocellulose filters (Whatman), immediately acidified using suprapure $HNO_3$ (2% v/v) to prevent precipitate formation and stored at 4°C until analysis.



**FIGURE 3.9 Schematic picture presenting organic acids leaching experiment carried out for each slag.**

### 3.1.3.3   Bioweathering experiments

All incubations were performed according to the same protocol. Crushed and sieved slags (1-2 mm) were placed in perforated polypropylene tubes and then introduced to glassy bottles containing the weathering solution. The holes in polypropylene tubes (0.5±0.1 mm) ensured contact between the weathering solution and the slag. Three different solutions were used in this study: i) growth medium inoculated with the bacteria *Pseudomonas aeruginosa* (biotic incubation - GMB), ii) abiotic growth medium (GM) and iii) abiotic ultrapure water (UPW). Growth medium was prepared by dissolution in ultrapure water (per liter): 4 g of succinic acid ($C_4H_6O_4$), 1 g of ammonium sulfate (($NH_4)_2SO_4$), 0.2 g of disodium hydrogen phosphate ($Na_2HPO_4$) and 6 g of Tris buffer ($C_4H_{11}NO_3$). The initial pH of the growth medium was adjusted to the value of 7.8 ± 0.1 using 5 M NaOH. The growth medium was deliberately devoid of iron and trace elements as these compounds were expected to be sustained by the slags (Aouad et al., 2006; Yin et al., 2014). Furthermore, inoculated slag-free GM solution was used for a comparison purpose of bacterial growth.

75 mL of solution and 3 g of slag were used in order to maintain a liquid to solid ratio at 25 (v/w). The experiments were extended up to 112 days with the regular sampling interval of 14 days when slags were replaced by fresh solutions. Experiments were carried out at room temperature (21±1°C) and bottles were continuously agitated on the table shaker at 120 rpm. All experiments were performed in acid (10% $HNO_3$) washed glassy bottles of 250 mL. Prior to experiments, all solutions, slag samples, and glass/polypropylene materials were autoclaved for 20 minutes at 120°C. Slag grains were sterilized separately from the medium. Every handling was performed under sterile conditions. Experiments were carried out in triplicates except slag-free treatment which was not replicated.

Sampling protocol: The pH of the weathering solution was measured during sampling immediately after slag removal; the solutions were then divided onto three aliquots. The first aliquot was filtered through 0.22 µm cellulose acetate filters (Minisart) and acidified with 65% $HNO_3$ (2% v/v., Suprapur, Merck) in case of abiotic experiments, while filtered biotic aliquots were subjected to 70% perchloric acid ($HClO_4$) digestion at 80°C for the determination of the dissolved fraction. One biotic aliquot was not filtered but submitted to perchloric acid ($HClO_4$) digestion at 80°C for the determination of total elements released from slag upon incubation experiments. It was assumed that the difference between the total and dissolved fraction represents microbial uptake of elements and/or mineral precipitate formation. The last aliquot was filtered through 0.22 µm acetate cellulose filers (Spartan 13/0.2 RC Whatman) for metabolites determination. In order to confirm sterile conditions were maintained, weathering solutions were plated onto agar plates every sampling and observed with respect to bacterial growth.



**FIGURE 3.10 Schematic picture presenting experimental approach for bioweathering experiment.**

### 3.1.3.4 Bioleaching experiments

Bioleaching experiments were designed to study the effect of particle sizes (1-2 mm and <0.3 mm) and pulp density (1% and 3% (*wt./v*)) on Cu, Zn and Fe extraction efficiencies. The experiments were carried out in acid (10% $HNO_3$) washed Erlenmeyer flasks. All materials were sterilized at 121°C for 20 minutes prior to use. Every experimental step was done under sterile conditions. The reactors were kept closed using cotton plug on an orbital shaker, at 100 rpm, at a controlled temperature of 30°C. Solutions sampled from the batches were filtered using 0.45 µm nitrocellulose filters (Whatman) for determination of element concentrations in the leachates. The pH of the solutions was measured immediately after opening the flasks.

Experiments were performed in duplicates. After experiment termination, solid samples were gently rinsed with ultrapure water and kept for drying at room temperature and further scanning electron microscopic observations.

### 3.1.3.4.1 Bioleaching with *A. thiooxidans*

The bioleaching experiments with *A. thiooxidans* were performed in a mineral salt medium composed of 0.1 g di-potassium hydrogen phosphate ($K_2HPO_4$), 0.25 g magnesium sulfate ($MgSO_4 \cdot 7H_2O$), 2.0 g ammonium sulfate ($NH_4)_2SO_4$, 0.1 g potassium chloride (KCl) and 2% (*wt./v*) of elemental sulfur per 1 L of ultrapure water. The initial pH value of growth medium was set at 2.5. 2% (vol.) of pre-grown bacterial culture (described above) was inoculated to the batch reactors. Abiotic growth medium supplemented with slag was run as the control. Samples were taken after 1, 2, 3, 6, 9, 14, 21 and 40 days.

### 3.1.3.4.1.1 Activity test for *A. thiooxidans*

At the end of the biotic experiments, an activity test was done in order to confirm the maintenance of living bacterial cells. An aliquot of 2% (*v/v*) of the leachate from each flask was transferred to fresh growth medium (pH 2.5), supplemented with 1% (*wt./v*) of elemental sulfur. Flasks were kept for 10 days at 30°C and observed with respect to sulfur oxidation and compared with experimental controls (bacteria exposed to metal-free solutions). Sulfur oxidation by bacteria could be recognized by changes in solution turbidity and subsequent sulfur settling, whereas in the absence of bacteria, sulfur remained floating on the surface of the medium (Figure S1 Supplementary material).

### 3.1.3.4.2 Bioleaching with *P. fluorescens*

The experimental approach included: i) biotic treatment of slags in the presence of *P. fluorescens* bacteria (GMB) and ii) abiotic treatment with sterile growth medium (GM). The growth medium used in this experiment consists of succinic acid (4 g), ammonium sulfate (1 g), disodium hydrogen phosphate (0.2 g) and Tris buffer (6 g) per 1 L of ultrapure water (Yin et al., 2014). Two percent (*v/v*) of pre-grown bacterial culture (described above) was inoculated to the bioleaching reactors. The initial pH of the medium was adjusted to 7.0 using 5 M NaOH. The experiments were carried out for 40 days, whereas the sampling times were fixed at 3, 7, 14, 21, 30 and 40 days. During each sampling time, 10 mL of supernatant was collected for elemental analysis and the amount of leachate sampled was replaced by the respective volume equivalent of fresh medium. At the end of each experiment, biomass from batch incubations was plated on agar plates (composed of plate counting agar) at aerobic

conditions at 30°C and observed by naked eye with respect to bacterial type purity in order to ensure that no cross contamination in the batch experiments occurred.



**FIGURE 3.11 Schematic picture presenting experimental design for bioleaching experiments.**

# CHAPTER 4

# CHARACTERIZATION AND pH-DEPENDENT LEACHING BEHAVIOUR OF HISTORICAL AND MODERN COPPER SLAGS

# ABSTRACT

A geochemical approach combining chemical and mineralogical studies together with pH-dependent leaching experiments was applied to carry out an environmental risk assessment analysis of copper metallurgical slags. Two groups of Cu-metallurgical slags were investigated: historical (HS) and modern slags including shaft furnace slag (SFS), granulated slag (GS) and lead slag (LS) representing various smelting technologies. The metallic elements composition (Cu, Zn and Pb) of the slags, especially their distribution in mineral phases as well as their leachability at different pH conditions were determined. The slags display different chemical (*e.g.,* Cu; HS: 5657 mg/kg; SFS: 2687 mg/kg; GS: 11425 mg/kg, LS: 10915 mg/kg) and phase composition, with various impurities of metallic elements in different quantities. Consequently, these materials show different leachability of metallic compounds when exposed to various pH conditions (2-13). HS and SFS slags are mainly composed of synthetic analogues of silicates such as fayalite (HS) and diopside (SFS) as well as minor sulfides. GS is an amorphous material composed of glass containing copper droplets, whereas LS is an exceptional slag type corresponding to a matte and characterized by a volumetrically major sulfides and a minor fayalite content. pH-dependent leaching experiments revealed that high concentrations of Cu, Zn and Pb may be released during leaching. Aggressive acidic conditions (pH 2) were found to be the least stable for the analysed materials, *e.g.,* Cu: up to 5873 mg/kg for GS; Zn: up to 8919 mg/kg for LS, Pb: up to 17186 mg/kg for LS. Alkaline pH (12-13), being generally less aggressive for slags than acidic conditions, also showed that significant amounts of metals may be mobilized (*e.g.,* Cu: up to 114 mg/kg for HS; Zn: up to 243 mg/kg for LS; Pb: up to 5539 mg/kg for LS). pH conditions close to neutral (7-8) and those with slightly alkaline pH (10.5) appear to be the most stable for the analysed materials.

**Keywords:** copper slags, primary phases, metal distribution, pH-dependent leaching behaviour (Cu, Zn, Pb)

# 4.1 INTRODUCTION

The continuous demand of society for different metal related products causes rapid expansion of the global industry. Unfortunately, any kind of industrial activity is associated with the generation of by-products, which are a matter of rising concern. Waste materials, especially those containing metallic elements are potential sources of environmental pollution and can cause ecological disturbances when disposed or managed improperly. Therefore, an improvement of storage practices and development of alternative treatment methods is a great challenge in waste management for the years ahead.

One of the processes inherently linked to the generation of wastes containing metals is pyrometallurgy. Copper production constitutes an important part of the global market. However, its significance turns back to early human civilization, when copper utility began (Themelis, 1994; Hong et al., 1996; Radetzki, 2009). Both historical and modern metallurgical processes have generated large quantities of by-products such as ashes, off-gasses and slags, which are important metal-carriers generated by this processing.

Pyrometallurgy of copper is generally accomplished by smelting and fire/electro refining which yield copper with a high grade of purity. However, some metal quantities are lost during processing and remain in the slags. Therefore, concentrations of metallic elements within the slags reflect processing losses (Fernández-Caliani et al., 2012). Additionally, specific pyrometallurgical technologies include variable approaches to the process, applying different initial input products (ores), additives (*e.g.*, siliceous), smelting temperatures and different types of furnaces (*e.g.,* reverberatory, blast, flash, shaft, electric and anode) (Davenport et al., 2002; Moskalyk & Anfantazi, 2003). As a result, slags issued from different pyrometallurgical processes may display various chemical and phase compositions. Moreover, considering developments of pyrometallurgy, historical smelting technologies and their efficiency undoubtedly differ from those applied for present-day smelting. Hence, both the concentration of metals remaining in the waste materials as well as phase composition itself may vary for historical and modern slags. Therefore, geochemical comparison of old wastes with those currently generated is particularly interesting.

Slags are well recognized to be a potential source of metallic pollution of the biosphere. Synthetic analogues of natural mineral phases are the most important compounds of slags. When exposed to environmental conditions, they undergo weathering that often results in the mobilization of the contained metals. Release of these compounds into the environment causes their vertical and horizontal distribution, and consequently has enormous effects on the environment, disturbing its quality and stability.

For this reason, storage of modern industrial wastes is either done according to strict standards or these wastes may be reused for example as additives to building/construction materials (Ettler et al., 2001; Ettler et al., 2003; Shi et al., 2008; Ettler et al., 2009; Piatak &

Seal, 2010; Harish et al., 2011; Chen et al., 2012). Additionally, metal recovery is a promising future direction of slag reuse that would abate their toxicity and improve waste recycling. In contrast, old industrial sites often dumped these materials in the slag heap or sometimes even abandoned them in the places not destined for this purpose. Moreover, at that time it was not known that slags weathering may release metallic contaminants into the surrounding environment. As a consequence, there are many industrial sites where discarded slags have been contributing to contamination of local areas (Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Lottermoser, 2002; Ettler et al., 2003; Ettler et al., 2004; Piatak et al., 2004; Reuter et al., 2004; Ettler et al., 2009; Vítková et al., 2010; Piatak & Seal, 2010; Kierczak et al., 2009; Kierczak et al., 2013; Piatak et al., 2014).

The behaviour of slags under different environmental scenarios should be taken into consideration prior to judging their hazardousness. Leaching tests are useful tools for evaluation of waste material upon exposure to different conditions (Piatak et al., 2014). For example, analysis of the release of inorganic contaminants as a function of pH appears to be important for environmental risk assessment. Therefore, determination of slag behaviour should be done in a wide pH range, from extremely acidic up to strongly alkaline, considering intermediate pH values as well.

The main objective of this paper is a geochemical comparison of two groups of Cu-slags: historical and modern ones each representing various smelting technologies and originating from different time periods of pyrometallurgical activities. During the characterization step that included chemical and phase composition of the slags, relevant attention was given to the abundance and distribution of metallic elements. Additionally, we attempted to answer the question of how these slag materials behave under various pH conditions. Therefore, leaching tests intended to examine leachability of Cu, Zn and Pb as a function of pH (2-13) were performed in order to establish the potential stability of slags at a given range of conditions.

## 4.2 MATERIALS

Metallurgical slag samples derived from historical and modern copper production were selected for this study. Slags originating from former pyrometallurgical process are named 'historical slags', whereas slags collected from present day processing are called 'modern slags' group.

**Historical slag group**. Historical slags analyzed in this study refer to the massive slags described by Kierczak and Pietranik (2011). They were collected from the disposal site located in the Rudawy Janowickie Mountains (south-western Poland) representing a historical mining and smelting site. According to information found in a source material describing the history of the area, industrial activity has been taking place there since the XIVth century up to first decade of XXth century (Kierczak & Pietranik, 2011).

Slags produced as the result of the historical smelting process were not considered at that time as hazardous. Therefore, they have been abandoned and disposed off without any physical barriers separating them from environmental components. Thus, no actions preventing metal migration were implemented. Slags have been present in high quantities on the ground surface, streambeds and soil profiles. Samples for this study were collected from stream beds. Previous studies devoted to their environmental stability pointed out that these slags are not inert, especially within the soil where slags are commonly buried (Kierczak et al., 2013).

**Modern slags group.** This includes three different types of slags: shaft furnace slag (SFS), granulated slag (GS) and lead slag (LS) collected from different stages of technological processes of copper production.

*Shaft furnace slags* are the waste products collected from shaft furnace in which briquette concentrate and converter slag were used as the charge. *Granulated slags* were gathered from a separate copper production process from the electric furnace stage. Previously generated flash furnace slags containing 10-15% of copper were injected in the electric furnace to recover copper. As the result of this processing stage, granulated slag is produced as a by-product. *Lead slags* were issued from the process intended to recover lead. Due to the fact that ore used for copper extraction may contain significant concentrations of lead, by-products such as dusts and slimes obtained during copper production accumulate lead. The name of this slag used in this paper is conventional and relates to a technological process rather than to a compound of interest. Although, the metal of main interest in this process is lead, the initial products include wastes obtained from other cycles of copper production. For this reason, this slag type may be also classified as a copper production by-product.

## 4.3 METHODS

### 4.3.1 Sample preparation

Each slag type was crushed using a steel crusher in order to reduce the fraction size. Fractions were then prepared using a steel sieve to separate the fraction smaller than 0.3 mm. Particles with a size below 0.3 mm were fine enough to be used for the leaching experiments. Several grams of slags were homogenized in an agate mortar for powder X-ray diffraction analyses. Additionally, polished thin sections and polished sections were prepared for phase observations and mineralogical characterization.

For granulated slags, the granulometry (4 mm < f < 0.06 mm) was determined. The material was sieved to separate different grain sizes and fractions were weighed to determine the relative distribution of particular fractions per kilogram of granulated slag.

## 4.3.2 Chemical analyses

Major elements were measured by inductively coupled plasma emission spectrometry (ICP-ES) after fusion of the samples by $LiBO_2/Li_2B_4O_7$ and dissolving the residue with nitric acid in the ACME Analytical Laboratory (Vancouver, Canada). Total sulfur and carbon contents were determined by LECO combustion analysis (ACME Analytical Laboratory). The analytical reproducibility ($2\sigma$), as estimated from replicate analyses of sample LS ranges from 0.5% ($Al_2O_3$) to 4% ($Na_2O$) at 95% confidence limits. The analytical accuracy ($2\sigma$), as estimated from four measurements of standard SO-18, amounted between 0.1 (MgO) to 2.5% ($K_2O$) at 95% confidence limits.

Loss on ignition (LOI) was determined by sintering a sample at 1000°C. Negative loss on ignition values for HS, SFS and GS can be explained by iron oxidation processes leading to the formation of iron ($Fe^{3+}$) oxides as a result of short time ignition at relatively high temperatures (Vandenberghe et al., 2010).

The complete acid digestion procedure was applied for analysis of minor compounds (such as As, Cu, Pb and Zn). Digestion was done in two steps of treatment. The first step followed the total digestion of 0.1 g slag sample using 10 mL 40% HF (hydrofluoric acid) and 0.5 mL concentrated $HClO_4$ (perchloric acid) at 150°C for 2.5 h. Then samples were re-submitted to digestion using 5 mL HF and 0.5 $HClO_4$ for 2 hours. At the end of the digestion procedure, 2% (v/v) $HNO_3$ was added and samples were diluted to 50 mL using distilled water (Tyszka et al. 2012). The concentrations of the minor elements were determined using quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, X Series 2, Thermo Scientific) according to the operating conditions of Mihaljevič et al. (2011). The data concerning quality control of these analyses are presented in Tyszka et al. (2012).

## 4.3.3 Phase determination

Identification of phases present in the slags and determination of their chemical composition were done using optical microscopy, X-ray powder diffraction (XRD), scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS) and electron microprobe analyser (EMPA) at the University Pierre and Marie Curie (Paris, France).

Preliminary observations of polished thin sections were performed with the optical microscope Leica DM2500P in transmitted and reflected light mode. The phase composition was established using powder X-ray diffraction (XRD) analyses. XRD patterns for selected samples were obtained using a Bruker D8 Advance diffractometer (at 40 kV and 40 mA, with CuKα radiation, 2θ range from 2° to 80°, step 0.12° 2θ min$^{-1}$). Results were compared with standard reference patterns. The phase composition was also examined using scanning electron microscope (ZEISS Supra 55) equipped with an X-ray energy dispersive system

(SEM-EDS) at 15 kV working conditions. The chemical composition of the identified phases was determined on a CAMECA SX100 microprobe with two individual analyse programs for silicates and sulfides, respectively. For electron microprobe analysis of silicates and oxides phases, the following conditions were used: accelerating voltage 15 keV, beam current 10 nA, and 5 seconds of counting time and beam diameter of 5 μm, whereas conditions applied for the analysis of sulfides and intermetallic phases were: 15 keV of accelerating voltage, 40 nA of beam current and 3 seconds of counting time.

## 4.3.4 Quantification of metals accommodated in mineral phases

Modal phase composition was estimated by point counting using JMicro Vision 1.2.7 software. Furthermore, the distribution of metals between mineral phases was estimated from modal phase composition and average concentration of metals in individual phases based on microprobe data. Due to proportional variability of mineral phases and the extent to which individual compounds vary in proportions, values present only approximate percentage of metals accommodated in the mineral phases relative to the bulk composition of the materials.

## 4.3.5 Leaching experiments

Leaching tests were performed according to the standard protocol (US EPA 1313) in the pH range of 2-13. For each slag type, a different quantity of water-diluted acid (2 M $HNO_3$) and base (1 M KOH) were prepared depending on the amount required to reach particular pH values. Additionally, extraction with ultrapure water (Milli-Q) was performed to show the slags behaviour at their natural pH. The experiments were carried out with a liquid to solid ratio of 10 using 5 g of slag and 50 mL of solution at a rotation speed of 150 rpm during 24 hours. Afterwards, leachates were filtered using 0.45 μm nitrocellulose syringe filters (GVS filter technology) and acidified using (1% vol.) of concentrated (65%) $HNO_3$. Analyses of leachates were conducted using ICP-OES (Perkin-Elmer Optima 8300). Leaching experiments were done in triplicates. Statistical analysis of triplicates slag samples in individual pH treatments was carried out using t-test in order to assure quality of the results. An assumption made for the t-test was that α=0.05 to judge whether the statistical difference of the replicates was significant at the 95% confidence level.

# 4.4 RESULTS

## 4.4.1 Macroscopic properties of the slags

Historical slag (HS) has a dark grey and/or brownish colour and the size of this type of slag varies from a few centimetres up to several dozen of centimetres (Figure 4.1 A). Generally, it has a massive and aphanitic texture, but locally important porosity is also observed (pore size ranges from several millimetres up to few centimetres). The material is resistant to crushing.

Shaft furnace slag (SFS) has a massive texture and the size of fragments ranges from 10 up to 50 centimetres (Figure 4.1 B1). It has a grey colour and it is not crushed easily. On the slag surface black, shiny glass up to 1 cm thick layer was observed (Figure 4.1 B2). Locally this type of slag is almost devoid of pores, but in some places an important porosity is also observed (pore size ranges from 0.5 - 1.5 cm).

Granulated slag (GS) is a fine-grained material having black-brownish colour and vitreous texture (Figure 4.1 C). Individual grains have sharp edges and do not undergo crushing easily. Moreover, round-shape metallic granules were present among the glassy particles. Analysis of granulometric properties of granulated slag revealed that grains reach a size even finer than 0.06 mm and rarely exceed the size of 4 mm. The fractions 2 - 1 mm and 1 - 0.5 mm constitute 42 wt.% and 39.5 wt.% of granulated slag, respectively. Hence, approximately 80 wt.% of the slag is in the range of 2 - 0.5 mm. The fine fraction less than 0.125 mm in diameter and the coarse fraction greater than 4 mm constitute less than 1 wt.% per kilogram of material. The remaining fractions 4-2 mm and 0.5-0.125 mm occur in the quantities of 8.6 wt.% and 9.6 wt.%, respectively.

Lead slag (LS) is a massive material with a colour approximating black. Individual blocks reach the size from 5 cm up to 50 cm. Locally this type of waste is composed of metallic phases visible even at the surface (Figure 4.1 D) thus it represents a mixture of matte with a silicate slag. It has pores with sizes from 0.5 cm up to 2 cm. This type of slag is generally hard, however for some samples-prominent tendency to crumbling was observed during their preparation.

**FIGURE 4.1 Macroscopic pictures presenting slags selected for this study.**

*A- historical slags found in the field, B1- shaft furnace slag having surface layer of glass (picture B2), C- granulated slag, D- lead slag.*

## 4.4.2  Chemical composition of the slags

### 4.4.2.1   Major compounds

The detailed chemical composition of HS was described elsewhere by Kierczak & Pietranik (2011) and Kierczak et al. (2013). Historical slags are mainly composed of $Fe_2O_3$ (up to 57 wt.%), $SiO_2$ (up to 43 wt.%), $Al_2O_3$ (up to 12 wt.%), whereas other components such as MgO, $K_2O$, CaO remain in concentrations not exceeding 4 wt.% (Kierczak & Pietranik, 2011; Kierczak et al., 2013).

Considering modern slags, each type is characterized by a different chemical composition (Table 4.1). The composition of the SFS is dominated by $SiO_2$, CaO, $Al_2O_3$, $Fe_2O_3$ and MgO

reaching concentrations of 44.9, 17.6, 13.1, 10.7 and 6.3 wt.%, respectively. Other compounds remain in concentrations not exceeding 4 wt.%. Granulated slags display a chemical composition comparable to a shaft furnace slag. This type is also mainly composed of $SiO_2$ (32.6 wt.%), $CaO$ (20.9 wt.%), $Al_2O_3$ (10.1 wt.%), $Fe_2O_3$ (16.4 wt.%) and $MgO$ (5.7 wt.%). Granulated slag is enriched in iron and calcium and impoverished in silica compared to the shaft furnace slag. The concentrations of other compounds in GS are similar to concentrations in the SFS and also do not reach concentrations higher than 4 wt.%. Lead slag shows a definitely different chemical composition. The major compound of lead slag is $Fe_2O_3$ (43.5 wt.%), whereas $SiO_2$ occurs in much lower quantities (4.2 wt.%). This slag is also characterized by a relatively larger abundance of sulfur (22 wt.%) compared to other modern slags having 0.2 wt.% and <0.02 wt.% for SFS and GS, respectively. Other major compounds are present in concentrations lower than 1.5 wt.%.

### 4.4.2.2   Minor compounds

Metallic element concentrations were re-measured to confirm the range of previously reported values for historical slags. Previous results showed that metallic elements in slags reach high values: Cu (up to 8219 mg/kg), Zn (up to 8279 mg/kg), Pb (up to 276 mg/kg), As (up to 315 mg/kg) (Kierczak et al., 2013). Results obtained from our analyses revealed concentrations in the same ranges with values of: Cu (5657 mg/kg), Zn (3962 mg/kg) and Pb (111 mg/kg) (Table 4.1).

Furthermore, all types of studied modern slags display variable concentrations of metallic elements. Comparing modern slags, the SFS contains the lowest concentrations of metallic elements, whereas LS has the highest concentrations of these elements. The granulated slag shows an intermediate composition, having usually slightly higher metal concentrations than SFS and lower than LS.

Concentrations of Zn, Pb and Cu in the LS reach even up to 7.6, 2.6 and 1.1 wt.%, respectively. Besides arsenic (0.3 wt.%), other metallic compounds (Ag, Cd, Co, Hg, Mo, Ni, Sn, Sb, Tl) do not exceed concentrations of 0.1 wt.%. The granulated slag contains significant quantities of Pb (2.1 wt.%), Cu (1.1 wt.%) and Zn (0.7 wt.%), whereas concentrations of other metallic elements remain lower than 0.1 wt.%. The shaft furnace slag contains 0.2 wt.% of Pb, 0.4 wt.% of Zn and 0.3 wt% of Cu and concentrations of other elements do not exceed 0.1 wt.%.

**TABLE 4.1 Chemical composition of copper slags.**

*(HS: historical slag, SFS: shaft furnace slag, GS: granulated slag, LS: lead slag)*

|  | HS | SFS | GS | LS |
|---|---|---|---|---|
| *wt.%* | | *Major elements* | | |
| **SiO$_2$** | 37.6 | 44.87 | 32.6 | 4.18 |
| **TiO$_2$** | 0.45 | 0.70 | 0.58 | 0.06 |
| **Al$_2$O$_3$** | 7.46 | 13.06 | 10.05 | 1.22 |
| **Fe$_2$O$_3$** | 50.7 | 10.69 | 16.42 | 43.51 |
| **MgO** | 2.5 | 6.31 | 5.73 | 1.24 |
| **MnO** | 0.17 | 0.26 | 0.24 | 0.57 |
| **CaO** | 1.1 | 17.6 | 20.93 | 1.48 |
| **Na$_2$O** | 0.27 | 1.54 | 0.79 | 1.48 |
| **K$_2$O** | 1.58 | 3.57 | 3.02 | 1.31 |
| **S tot.** | 0.67 | 0.17 | <0.02 | 22.02 |
| *mg/kg* | | *Minor elements* | | |
| **Ag** | 4.4 | 5.4 | 21.5 | 34.2 |
| **As** | 42.6 | 58.2 | 884 | 3569 |
| **Bi** | 2.3 | 0.1 | 0.6 | 14 |
| **Cd** | 0.5 | 0.8 | 4.55 | 525.6 |
| **Co** | 402 | 345.6 | 963.8 | 42.2 |
| **Cu** | 5657 | 2687 | 11425 | 10915 |
| **Hg** | <0.01 | <0.01 | <0.01 | 0.32 |
| **Mo** | 11.4 | 303.1 | 693.8 | 428.4 |
| **Ni** | 4.2 | 15.8 | 356.7 | 221.9 |
| **Pb** | 111 | 1559 | 21135 | 26125 |
| **Se** | 1.3 | 4.25 | 3.7 | 214.2 |
| **Sn** | 94.3 | 11 | 22 | 762 |
| **Sb** | 0.5 | 9.1 | 39.6 | 122 |
| **Tl** | <0.1 | 0.05 | 3.6 | 41 |
| **Zn** | 3962 | 3832 | 7810 | 76400 |
| **LOI** | -4.7 | -0.6 | -1.1 | 7.1 |

## 4.4.3 Mineralogy and phase composition of slags

The X-ray powder diffraction patterns presented in Figure 4.2 and SEM-EDS spectra (data not shown) of the studied materials showed that slags are composed of various primary phases (Table 4.2). Deliberately, slag samples without any secondary phases were chosen for further study. For modern slags, no secondary phases could be observed. This is due to the fact that fresh samples were collected from the process meaning they have not been exposed to any weathering factors. In contrast, historical slags have been dumped for a long period of time and previously identified secondary phases (e.g., Fe-oxyhydroxides, langite $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$, malachite: $Cu_2CO_3(OH)_2$) present within them have been described elsewhere (Kierczak & Pietranik, 2011; Kierczak et al., 2013).

On the basis of optical microscopic observations, silicates and glass constitute the major phases present in both historical and modern slags (excluding lead slag), whereas sulfides and intermetallic compounds (identified in granulated slag) are minor constituents. Silicate phases as volumetrically major and sulfides as minor phases are in accordance with the analyses performed on any kind of previously studied copper metallurgical slags (Parsons et al., 2001; Manasse et al., 2001; Manasse & Mellini, 2002; Lottermoser, 2002; Sāez et al., 2003; Piatak et al., 2004; Ettler et al., 2009; Álvarez-Valero et al., 2009; Mateus et al., 2011; Vítková et al., 2010; Kierczak & Pietranik, 2011; Kierczak et al., 2013). Exceptionally, lead slag represents a type having much greater volumetric content of sulfides compared to silicate phases clearly visible during microscopic observation and also confirmed by XRD analysis as well as chemical analyses showing low silica and high sulfur concentrations.

### 4.4.3.1 Mineralogy

The historical slags are mainly composed of crystalline phases indicated by XRD analysis. A well-specified phase implied from the XRD patterns is fayalite (Figure 4.2 A), being the most abundant phase composing this material, which was also confirmed by microscopic observations. This slag type also comprises silicate glass as well as volumetrically minor or trace sulfide compounds. Optical microscopic analyses allowed to observe that fayalite occurs as elongated skeletal laths or dendritic crystals surrounded by opaque glass. Fayalite crystals reach lengths from very fine sizes (2 μm) even up to 800 μm (Figures 4.3 A1 and 4.3 A2). Sulfide inclusions (bornite, pyrrhotite and occasionally chalcopyrite with compositions differing from stoichiometry) commonly occur between and on the edge of the fayalite crystals as well as are dispersed within the glassy matrix. Sulfides are present in the form of irregular prills with a fine-grained size smaller than 2 μm and sometimes even up to 700 μm (Figures 4.3 A1 and 4.3 A2).

The shaft furnace slag representing the first type of the modern slag group investigated is mainly composed of pyroxene (diopside) and two types of silicate glass: interstitial glass and surface glass (Figure 4.2 B). Minor and trace phases identified in this type of slag are represented by sulfides such as: bornite, sphalerite and chalcopyrite. Skeletal euhedral and subhedral crystals of pyroxene are embedded within interstitial glass (Figures 4.3 B1 and 4.3 B2). Their length ranges from below 20 μm up to 400 μm. They do not show any preferred orientation. Sulfides occur either as rounded blebs or irregular shaped inclusions dispersed in a glassy matrix. They range in size between 20 - 100 μm in diameter and are sometimes even smaller than 2 μm.

The first observation drawing from optical microscopy analysis of granulated slag is the vitreous texture of this material. It is mainly composed of silicate amorphous glass likely resulting from quick water-quenching of the melt. This material is almost devoid of any crystalline phases. However, hercynite crystals having a size not exceeding 10 μm were rarely observed (Figure 4.3 C1). The compound implied by the XRD diffraction pattern is metallic copper (Figure 4.2 C). These thin metallic droplets were commonly observed and widely dispersed within amorphous glass (Figure 4.3 C1). Metallic droplets occur as very fine or coarse-sized droplets reaching the size from smaller than 2 μm up to 30 μm (Figure 4.3 C2).

Lead slag issued from the process intended to lead recovery represents a mineralogically different slag type. Contrary to previously described slag types, LS mainly comprises sulfides, whereas silicates and glass constitute volumetrically minor components thus this material corresponds to a mixture of matte with subordinate amounts of silicate slag. However, the term "lead slag" is used for descriptive purposes of this material. Sulfides occur in the form of approximately rounded, sometimes slightly irregular shaped inclusions between fayalite and the glassy matrix (Figure 4.3 D1) and more often as gathered groups (Figure 4.3 D2). Sphalerite is the most commonly observed sulfide occurring as volumetrically major sulfide component confirmed by XRD analysis (Figure 4.2 D). Furthermore, other sulfides such as bornite, chalcopyrite and pyrrhotite were also identified. They reach a size from smaller than 2 μm up to 200 μm. Fayalite being the minor constituent occurs in the form of elongated crystals usually presenting a preferred orientation of parallel growth and having a length up to 1800 μm (Figure 4.3 D2).
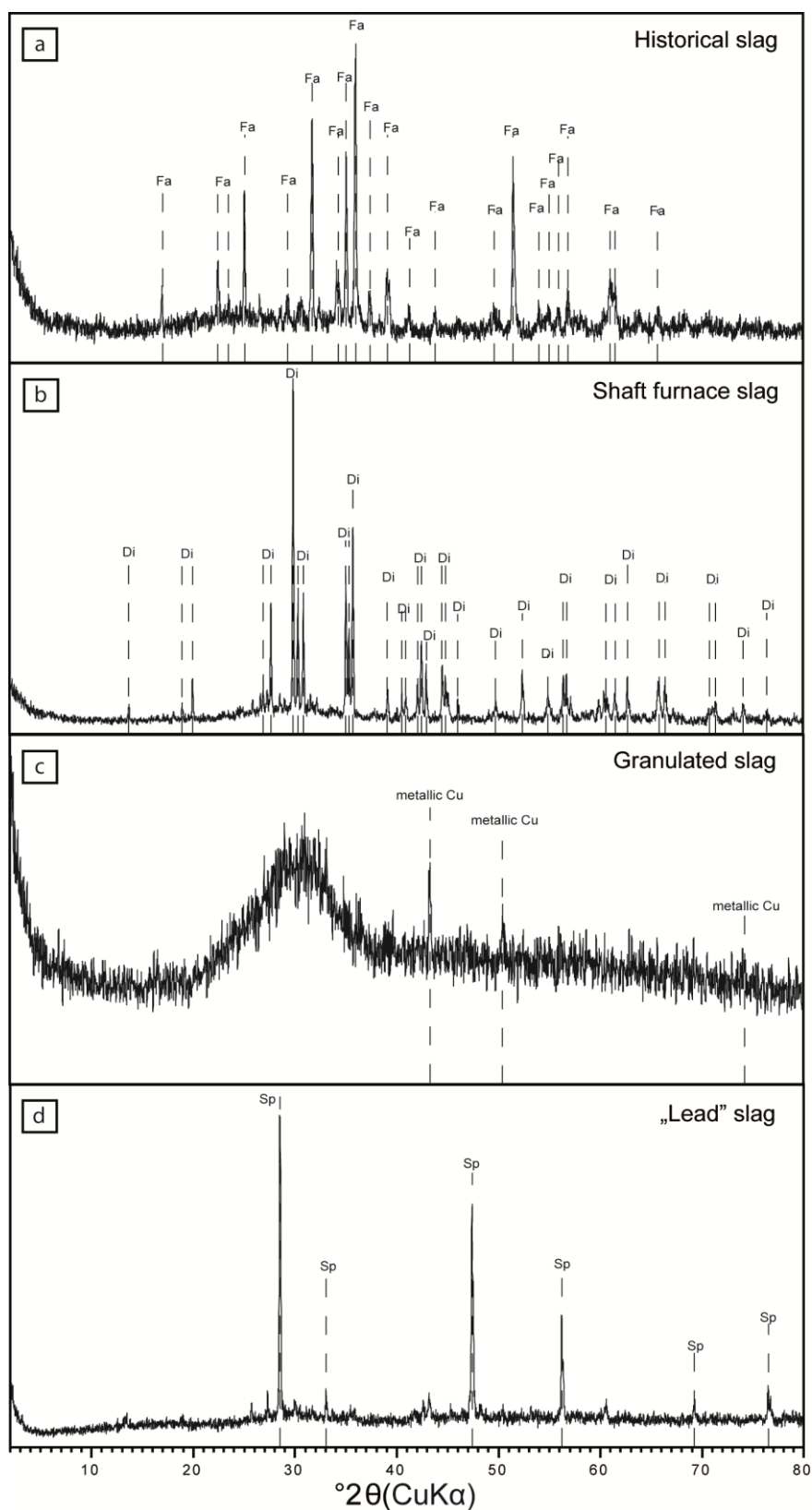
**FIGURE 4.2 X-RAY powder diffraction patterns of copper slags.**

(Mineral names abbreviations after Whitney and Evans (2010):
*Fa: fayalite, Di: diopside, Sp: sphalerite*)
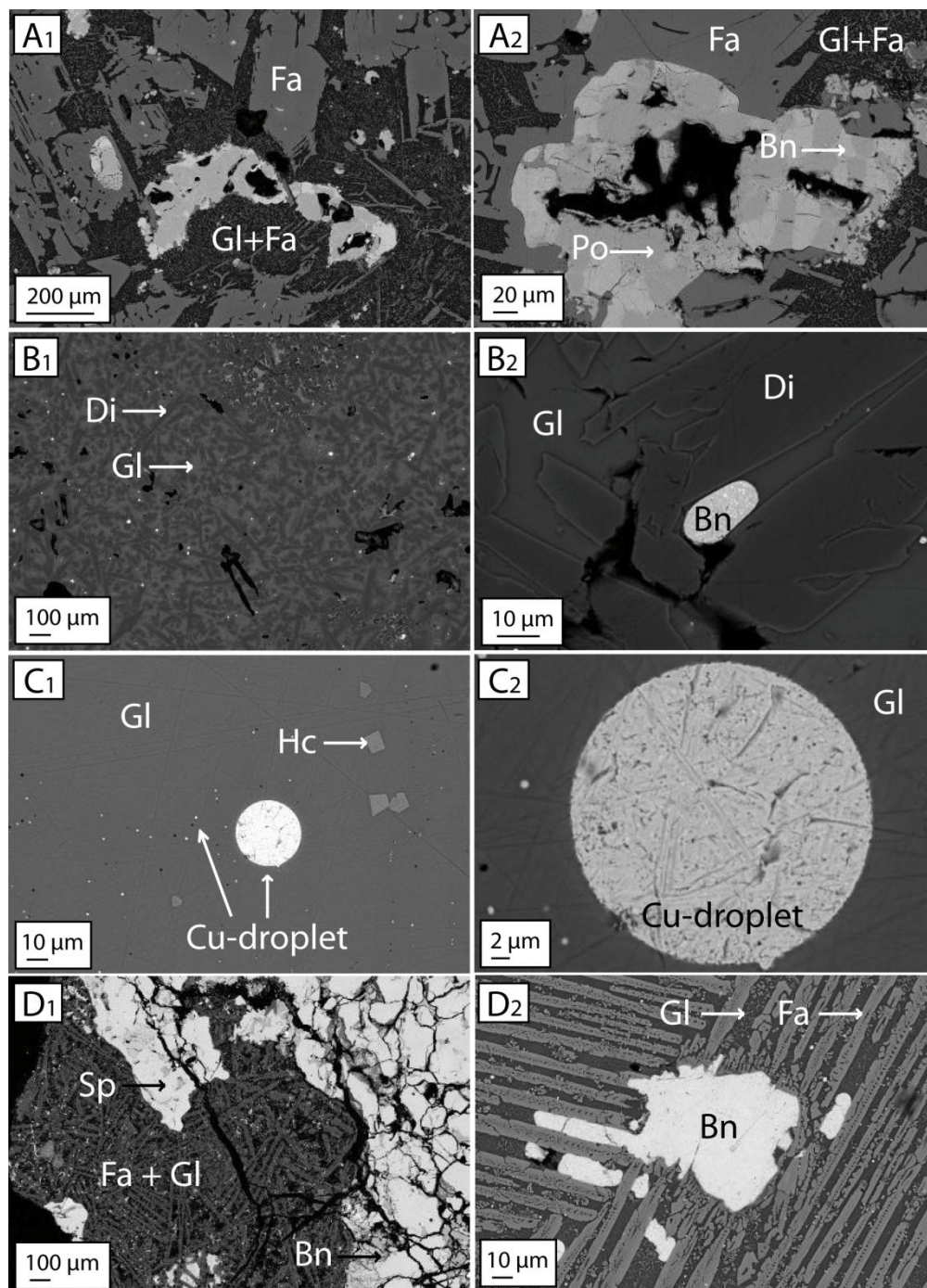
**FIGURE 4.3 Scanning electron microscope images of the phases identified in the copper slags.**

Presenting: A1 and A2- Historical slags (A1- Fayalite embedded in silicate glass and commonly occurring sulfides, A2- pyrrhotite and bornite growing between the crystal of fayalite), B1 and B2- Shaft furnace slag (B1- Pyroxene: diopside crystals surrounded by glassy matrix, B2- bornite embedded between diopside crystals) C1 and C2- Granulated slag (C1- amorphous glass with widely dispersed copper droplets and occasionally identified crystals of hercynite, C2- copper droplets reaching the size of 17 μm), D1 and D2- Lead slag (D1- Elongated fayalite crystals present within glassy matrix and sulfides: sphalerite occurring as volumetrically major phase and bornite, D2- Bornite occurring between elongated fayalite crystals).

**TABLE 4.2 Primary (formed during slag solidification) phases identified in the studied slags.**

| Name | Formula | HS | SFS | GS | LS |
|---|---|---|---|---|---|
| *Glass and synthetic equivalents of silicates* | | | | | |
| Interstitial glass[a] | | ++ (n=13) | ++ (n=22) | ++ (n=29) | + (n=10) |
| Surface glass[a] | | - | ++ (n=20) | | |
| Pyroxene (diopside)[a, b] | $CaMgSi_2O_6$ | - | ++ (n=9) | - | - |
| Olivine (fayalite) [a, b] | $Fe^{2+}_2SiO_4$ | ++ (n=21) | - | - | + (n=9) |
| | | | | | |
| *Sulfides and intermetallic compounds* | | | | | |
| Bornite[a] | $Cu_5FeS_4$ | + (n=10) | + (n=13) | - | + (n=16) |
| Chalcopyrite [a] | $CuFeS_2$ | (+)(n=10) | (+)(n=6) | - | + (n=27) |
| Pyrrhotite [a] | $Fe_{(1-X)}S$ | + (n=13) | - | - | + (n=3) |
| Sphalerite (*marmatite*)[a, b] | (Zn,Fe)S | - | + (n=5) | - | ++ (n=17) |
| Metallic Cu [a, b] | | - | - | + (n=6) | - |
| Metallic Pb [a] | | | | | + (n=4) |
| | | | | | |
| *Oxides* | | | | | |
| Spinel (hercynite)[a] | $Fe^{2+}Al_2O_4$ | - | - | (+) (n=2) | - |

++ - major, + - minor, (+) – traces, [a] – phases inferred on the basis of SEM-EDS and microprobe analyses, [b]- phases identified by XRD, *n*- number of chemical analyses

(*HS: historical slag; SFS: shaft furnace slag, GS: granulated slag, LS: lead slag*)

## 4.4.3.2  Chemical composition of slag phases

### 4.4.3.2.1  Silicates

**Glass**

Silicate glass is found to be an ubiquitous phase in HS, SFS and GS, whereas it is present in much lower quantities in LS. A variability of chemical composition of glass is presented in Table 4.3. The glass displays a common chemistry observed for silicate phases and it mainly contains $SiO_2$, FeO and $Al_2O_3$. It is also composed of various alkali compounds such as CaO, MgO, $Na_2O$ and $K_2O$ and demonstrates significant distribution of metallic elements such as ZnO, CuO and PbO (Table 4.3).

Chemical components of glass present in HS and LS achieve comparable average quantities, however a slightly higher content of $K_2O$ and lower content of CaO is observed in HS compared to LS. The glasses in SFS and GS are impoverished in FeO and richer in CaO relative to HS and LS (Table 4.3). The SFS contains two types of glass: a surface and an interstitial one. These types of glass display slightly a different composition, however both of them contain compounds with the following relations of concentrations: Si>>Ca>Al>Fe>Mg>K>Na (Table 4.3). The proportions of metallic components in glasses vary from one slag to another. The glass in GS contains even up to: 4.77 wt.% of Pb, 3.70 wt.% of Cu and 1.90 wt.% of Zn. Although glasses in other slags (HS, SFS, LS) reach average metals content one order of magnitude lower, they should be considered as important metal carriers as well.

**TABLE 4.3 Glass composition determined for studied slags.**

| Chemical compounds wt% | Glass HS | | | Glass SFS | | | Glass (surface) SFS | | | Glass GS | | | Glass LS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | max. | min. | ave. | max. | min. | aver. | max. | min. | aver. | max. | min. | aver. | max. | min. | aver. |
| SiO$_2$ | 59.77 | 39.23 | 48.15 | 44.57 | 38.15 | 42.42 | 45.45 | 42.28 | 43.58 | 38.04 | 29.41 | 33.82 | 50.12 | 40.59 | 44.78 |
| Al$_2$O$_3$ | 24.68 | 4.83 | 16.14 | 19.44 | 12.50 | 13.91 | 13.72 | 13.06 | 13.43 | 12.10 | 9.63 | 10.90 | 19.34 | 15.47 | 16.94 |
| TiO$_2$ | 1.67 | 0.23 | 1.01 | 0.87 | 0.16 | 0.60 | 0.84 | 0.55 | 0.70 | 0.70 | 0.31 | 0.48 | 1.01 | 0.36 | 0.66 |
| FeO | 52.75 | 12.39 | 27.15 | 24.84 | 8.13 | 12.90 | 9.58 | 9.01 | 9.28 | 14.93 | 10.63 | 12.93 | 31.72 | 22.43 | 27.51 |
| MnO | 0.20 | < d.l | 0.08 | 0.48 | 0.15 | 0.30 | 0.31 | 0.14 | 0.24 | 0.29 | 0.11 | 0.20 | 0.18 | 0.12 | 0.15 |
| MgO | 0.85 | 0.06 | 0.33 | 8.37 | 0.35 | 4.84 | 6.62 | 6.35 | 6.48 | 6.15 | 5.41 | 5.77 | 0.88 | 0.38 | 0.56 |
| CaO | 4.61 | 0.79 | 1.69 | 18.75 | 6.30 | 14.52 | 17.02 | 16.54 | 16.82 | 20.76 | 18.05 | 19.47 | 4.14 | 1.92 | 2.98 |
| Na$_2$O | 0.39 | 0.16 | 0.29 | 5.03 | 0.79 | 2.15 | 1.65 | 1.48 | 1.55 | 1.37 | 0.56 | 0.91 | 0.39 | 0.20 | 0.30 |
| K$_2$O | 4.80 | 1.63 | 3.61 | 8.62 | 2.70 | 4.42 | 3.31 | 3.11 | 3.23 | 2.80 | 2.47 | 2.65 | 2.82 | 1.82 | 2.38 |
| ZnO | 0.74 | 0.17 | 0.45 | 1.51 | 0.49 | 0.89 | 0.70 | 0.63 | 0.67 | 1.90 | 0.88 | 1.45 | 0.55 | 0.41 | 0.47 |
| CuO | 0.83 | 0.09 | 0.25 | 0.45 | 0.01 | 0.08 | 1.24 | 0.05 | 0.14 | 3.70 | 1.96 | 2.89 | 0.44 | 0.16 | 0.30 |
| PbO | 0.04 | < d.l | 0.02 | 0.39 | 0.09 | 0.16 | 0.46 | 0.13 | 0.16 | 4.77 | 3.97 | 4.47 | 0.07 | 0.04 | 0.06 |

*d.l: detection limits, (HS: historical slag; SFS: shaft furnace slag, GS: granulated slag, LS: lead slag)*

**Olivine and pyroxene**

The chemical composition of olivine identified in HS and LS corresponds to this of fayalite ($Fe_2SiO_4$), an iron-rich end-member of the forsterite-fayalite solid solution group. The average fayalite content is higher in olivine from HS (Fa: 86.5%) than this from olivine analysed in the LS (Fa 81.9%). Furthermore, the chemical composition of fayalite (Table 4.4) suggests a variable distribution of metallic elements within its crystal structure. Some enrichments of ZnO, CuO and PbO are observed probably substituting $Fe^{2+}$ in the octahedral position of olivine. The average content of ZnO is maintained on a quite high level of 0.33 wt.% and 0.41 wt.% for HS and LS, respectively (Table 4.4). This high concentration of Zn may refer to its atomic radius which is nearer to that of $Fe^{2+}$, hence can easier replace $Fe^{2+}$ in the octahedral sites of fayalite.

Pyroxene is found only in SFS and is determined as major crystalline compound of this slag. It has a chemical composition close to diopside ($(Ca,Mg)Si_2O_6$; Table 4.4). Metallic elements such as Zn, Pb and Cu are distributed within crystals of diopside probably substituting to Mg and Ca in octahedral position with maximum values up to: 1.0, 0.5, 0.2 wt.% for ZnO, PbO and CuO, respectively (Table 4.4).

**TABLE 4.4 Silicates (fayalite and pyroxene) identified in the studied slags.**

| | Fayalite | | | Fayalite | | | Diopside | | |
|---|---|---|---|---|---|---|---|---|---|
| Chemical | HS | | | LS | | | SFS | | |
| compounds *wt.%* | max. | min. | aver. | max. | min. | aver. | max. | min. | aver. |
| $SiO_2$ | 32.28 | 29.30 | 31.01 | 31.75 | 29.04 | 30.38 | 47.57 | 42.85 | 44.95 |
| $Al_2O_3$ | 0.37 | 0.03 | 0.09 | 2.02 | 0.06 | 1.03 | 12.92 | 8.19 | 10.18 |
| $TiO_2$ | 0.15 | < d.l | 0.03 | 0.15 | < d.l | 0.07 | 1.23 | 0.64 | 0.96 |
| FeO | 69.75 | 58.42 | 61.93 | 61.30 | 54.76 | 57.11 | 11.05 | 5.53 | 7.68 |
| MnO | 0.27 | 0.02 | 0.17 | 0.29 | 0.22 | 0.25 | 0.3 | 0.1 | 0.18 |
| MgO | 9.59 | 0.48 | 6.68 | 13.37 | 4.64 | 8.80 | 12.17 | 7.11 | 9.91 |
| CaO | 0.10 | 0.02 | 0.07 | 0.41 | 0.05 | 0.24 | 23.78 | 18.5 | 21.75 |
| $Na_2O$ | 0.05 | < d.l | 0.02 | 0.06 | < d.l | 0.02 | 1.61 | 0.13 | 0.67 |
| $K_2O$ | 0.08 | < d.l | 0.01 | 0.39 | 0.01 | 0.17 | 2.99 | 0.06 | 1.1 |
| ZnO | 0.44 | 0.14 | 0.33 | 0.51 | 0.32 | 0.41 | 1.02 | 0.31 | 0.63 |
| CuO | 0.42 | < d.l | 0.03 | 0.28 | 0.02 | 0.13 | 0.22 | 0.02 | 0.06 |
| PbO | 0.13 | < d.l | 0.01 | 0.05 | < d.l | 0.02 | 0.45 | 0.06 | 0.15 |
| Si (a.p.f.u) | 1.072 | 0.981 | 1.002 | 1.056 | 0.961 | 0.995 | 1.789 | 1.678 | 1.729 |
| Al | 0.016 | 0.001 | 0.004 | 0.237 | 0.002 | 0.098 | 0.595 | 0.363 | 0.462 |
| Ti | 0.003 | 0.000 | 0.001 | 0.008 | 0.000 | 0.003 | 0.036 | 0.018 | 0.028 |
| Fe | 1.948 | 1.556 | 1.707 | 1.656 | 1.319 | 1.471 | 0.369 | 0.174 | 0.248 |
| Mn | 0.007 | 0.001 | 0.004 | 0.008 | 0.004 | 0.006 | 0.010 | 0.003 | 0.006 |
| Mg | 0.420 | 0.026 | 0.267 | 0.600 | 0.120 | 0.325 | 0.682 | 0.411 | 0.568 |
| Ca | 0.003 | 0.002 | 0.003 | 0.047 | 0.002 | 0.017 | 0.982 | 0.774 | 0.897 |
| Na | 0.003 | 0.000 | 0.001 | 0.012 | 0.000 | 0.004 | 0.121 | 0.010 | 0.050 |
| K | 0.004 | 0.000 | 0.001 | 0.041 | 0.000 | 0.017 | 0.149 | 0.003 | 0.054 |
| Zn | 0.009 | 0.004 | 0.007 | 0.012 | 0.007 | 0.010 | 0.028 | 0.009 | 0.018 |
| Cu | 0.011 | 0.000 | 0.002 | 0.008 | 0.001 | 0.004 | 0.006 | 0.001 | 0.002 |
| Pb | 0.001 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.005 | 0.001 | 0.002 |

*a.p.f.u. = atoms per formula unit, d.l. = detection limit*

*(HS: historical slag; SFS: shaft furnace slag, LS: lead slag)*

#### 4.4.3.2.2 Sulfides and intermetalic compounds

**Bornite ($Cu_5FeS_4$).** One of the most commonly identified sulfides in the studied slags (HS, SFS, LS) is the phase with a stoichiometric composition close to bornite (Table 4.5). It has been detected in HS as well as in two types of modern slags: SFS and LS. Chemical composition of bornite identified in the slags is variable but it always places within the stability field of bornite on the ternary diagram presenting atomic proportions of Cu, Fe and S (Figure 4.4). This variability can be explained by some important impurities of other metallic compounds within bornite (Table 4.5).

**Chalcopyrite ($CuFeS_2$)** present in HS and LS occurs less frequently compared to bornite and is hardly ever identified as a mineral phase in SFS. Only several crystals were found during analyses. Chalcopyrite identified in SFS and LS are located close to its stability field, whereas chalcopyrite present in HS strays towards intermediate solid field. The chemical composition of chalcopyrite (Table 4.5) shows that some impurities of metallic compounds are also present. Chalcopyrite in HS and LS has important concentrations of Zn and Pb with an average content of 0.1 wt.% (Zn), 0.2 wt.% (Pb) and 0.4 wt.% (Zn), 0.8 wt.% (Pb) for HS and LS, respectively. Moreover, it is observed that the Zn concentration is extremely high in chalcopyrite in SFS and elevates as high as 15 wt.%. It may be due to the presence of zinc microinclusions observed within chalcopyrite. Additionally, relatively high concentrations of As (1.6 wt.%) and Co (1.1 wt.%) were also noted that may occur due to the same reason.

**Pyrrhotite ($Fe_{1-x}S$)** is a frequently observed sulfide in HS as well as in one sample representing modern slag, i.e. LS. The chemical composition presented on the ternary diagram shows that pyrrhotite determined for LS lies very close to its stoichiometric field, whereas this observed in HS, slightly strays towards pyrite field (Figure 4.4). Regarding its composition determined for HS, pyrrhotite contains an important distribution of Cu which reaches even a value as high as 14.0 wt.% and an average concentration of 5.2 wt.% (Table 4.5). This may be due to the presence of chalcopyrite microinclusions within crystals of this mineral that occur frequently, even for naturally formed pyrrhotite as it has been shown experimentally (Lynton et al., 1993; Elliot and Watling, 2011).
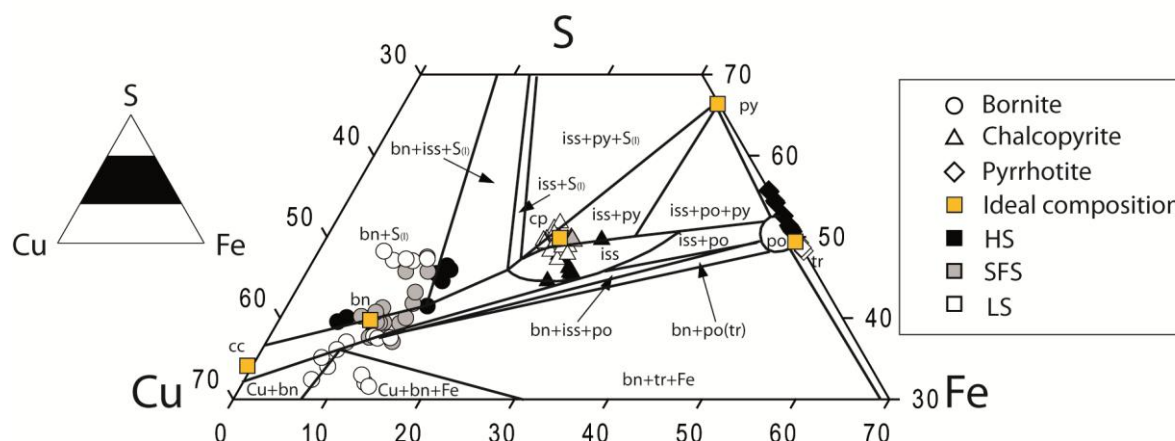
**FIGURE 4.4 Variability of the chemical composition (at.%) of main sulfides in slags presented in the Cu-Fe-S isothermal section at 600°C.**

Diagram redrawn from Cabri (1972) and Piatak et al. (2004).
*Abbreviations: (cc) chalcocite, (bn) bornite, (cp) chalcopyrite, (py) pyrite, (tr) troilite, HS: historical slag, SFS: shaft furnace slag, GS: granulated slag, LS: lead slag.*

**Sphalerite (ZnS)** was identified only in SFS and LS. It demonstrates a relatively high content of Fe, up to 31 wt.% that would qualify this sphalerite to marmatite (Fe-rich variety of sphalerite). Sphalerite present in SFS contains relatively high impurities of Cu elevating up to 5.9 wt.%. It suggests a relatively even distribution of this element. It may be also due to the presence of chalcopyrite inclusions that are also common in naturally formed sphalerite (Kojima, 1992). Sphalerite (marmatite) identified in LS displays a higher content of Zn (up to 43.58 wt.%) and slightly less important impurities of metallic elements such as Cu and Pb relative to sphalerite examined in SFS.

**Intermetallic phases** accommodating metals and their admixtures, which do not correspond to any known minerals were identified only in the GS and LS. Copper droplets commonly occur in the amorphous glass of the GS. Due to the small size of these droplets, their electron microprobe analysis could not be performed. For this reason, quantitative analyses of copper droplets were performed using SEM-EDS (Table 4.5). Analysis of droplets distributed within the glass shows that Cu has a content ranging from 86.7 up to 92.6%, but some other metals also occur as impurities. Droplets contain relatively high concentrations of Pb and As that reach even up to 6.0-7.0 wt.% (Table 4.5). The intermetallic phase identified in LS contains up to 91.4 wt.% of Pb and 4.52 % of Fe (Table 4.5). Although, its occurrence was rarely observed and the number of analyses was limited, it appears to be the most important Pb-carrier responsible for a high bulk Pb content in this material.

**TABLE 4.5 Sulfides and intermetallic phases identified in the studied slags.**

| Chemical compounds | BORNITE | | | | | | | | | SPHALERITE | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | HS | | | SFS | | | LS | | | SFS | | | LS | | |
| *wt.%* | max. | min. | ave. | max. | min. | ave. | max. | min. | ave. | max. | min. | ave. | max. | min. | ave. |
| **S** | 29.95 | 23.80 | 27.51 | 30.91 | 22.70 | 25.00 | 31.28 | 19.38 | 25.99 | 35.18 | 32.24 | 33.35 | 33.98 | 32.99 | 33.63 |
| **Mn** | 0.02 | < d.l | <0.01 | 0.22 | < d.l | 0.06 | 0.07 | < d.l | 0.02 | 0.30 | 0.08 | 0.2 | 0.54 | 0.46 | 0.51 |
| **Fe** | 17.16 | 6.88 | 14.14 | 14.32 | 9.02 | 12.26 | 14.77 | 7.29 | 11.07 | 31.38 | 27.39 | 29.95 | 31.21 | 22.31 | 26.69 |
| **Co** | 0.03 | < d.l | 0.01 | 1.87 | < d.l | 0.28 | 0.03 | < d.l | 0.01 | - | - | - | 0.01 | < d.l | <0.01 |
| **Ni** | 0.03 | < d.l | 0.01 | 1.09 | < d.l | 0.10 | 0.02 | < d.l | <0.01 | 0.03 | < d.l | <0.01 | 0.05 | < d.l | <0.01 |
| **Cu** | 66.32 | 49.75 | 54.97 | 63.43 | 52.55 | 57.68 | 76.07 | 59.88 | 63.46 | 5.89 | 1.22 | 4.33 | 1.77 | 0.03 | 0.63 |
| **Zn** | < d.l | < d.l | < d.l | 0.38 | < d.l | 0.10 | 0.93 | < d.l | 0.27 | 29.84 | 26.42 | 27.87 | 43.58 | 33.34 | 38.78 |
| **As** | 2.87 | 0.11 | 0.57 | 2.88 | < d.l | 0.19 | 0.53 | < d.l | 0.09 | 0.06 | < d.l | 0.01 | 0.06 | < d.l | <0.01 |
| **Pb** | < d.l | < d.l | < d.l | 1.57 | < d.l | 0.52 | 0.25 | < d.l | 0.13 | 1.62 | 0.04 | 0.77 | 0.74 | 0.18 | 0.25 |

| Chemical compound | CHALCOPYRITE | | | | | | | | | PYRRHOTITE | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | HS | | | SFS | | | LS | | | HS | | | LS | | |
| *wt.%* | max. | min. | ave. | max. | min. | ave. | max. | min. | ave. | max. | min. | ave. | max. | min. | ave. |
| **S** | 33.32 | 29.86 | 31.75 | 26.54 | 26.07 | 26.32 | 36.54 | 32.24 | 33.35 | 36.77 | 34.85 | 35.52 | 35.55 | 34.39 | 34.82 |
| **Mn** | <0.01 | < d.l | <0.01 | 0.29 | 0.26 | 0.28 | 0.30 | 0.08 | 0.20 | 0.03 | < d.l | 0.01 | 0.51 | < d.l | 0.17 |
| **Fe** | 34.49 | 30.31 | 32.20 | 24.47 | 24.16 | 24.28 | 31.38 | 27.39 | 29.95 | 60.95 | 48.36 | 56.12 | 64.12 | 63.36 | 63.74 |
| **Co** | 0.13 | < d.l | 0.02 | 1.15 | 1.10 | 1.13 | n.a | n.a | n.a | 0.76 | < d.l | 0.17 | 0.01 | < d.l | <0.01 |
| **Ni** | < d.l | < d.l | < d.l | 0.56 | 0.52 | 0.54 | 0.03 | < d.l | <0.01 | 0.10 | < d.l | 0.02 | < d.l | < d.l | < d.l |
| **Cu** | 38.75 | 27.74 | 34.81 | 25.26 | 24.99 | 25.15 | 36.37 | 33.09 | 34.89 | 13.99 | 1.25 | 5.19 | 9.94 | < d.l | 3.32 |
| **Zn** | 0.57 | < d.l | 0.12 | 14.99 | 13.80 | 14.28 | 0.77 | 0.02 | 0.36 | 0.44 | < d.l | 0.08 | 0.71 | < d.l | 0.24 |
| **As** | 0.10 | < d.l | 0.06 | 1.64 | 1.54 | 1.59 | 0.06 | < d.l | 0.01 | 1.49 | 0.01 | 0.17 | 0.68 | 0.17 | 0.43 |
| **Pb** | 0.59 | < d.l | 0.21 | 2.58 | 2.13 | 2.37 | 1.62 | 0.04 | 0.77 | 0.31 | < d.l | 0.08 | 0.29 | < d.l | 0.10 |

| Chemical compound | COPPER DROPLETS GS | | | METALLIC Pb LS | | |
| --- | --- | --- | --- | --- | --- | --- |
| *wt.%* | max. | min. | ave. | max. | min. | ave. |
| **Cu** | 92.56 | 86.71 | 90.19 | 0.53 | 0.13 | 0.31 |
| **Zn** | 0.27 | < d.l | 0.14 | 3.17 | 0.02 | 0.86 |
| **Fe** | 0.80 | 0.42 | 0.65 | 4.52 | 0.22 | 1.37 |
| **Cr** | 0.07 | < d.l | 0.02 | n.a | n.a | n.a |
| **Ni** | 0.24 | < d.l | 0.08 | < d.l | < d.l | < d.l |
| **Pb** | 6.98 | 1.57 | 3.25 | 91.41 | 89.12 | 90.49 |
| **As** | 6.13 | 4.98 | 5.67 | 0.07 | < d.l | 0.03 |

*(HS: historical slag; SFS: shaft furnace slag, GS: granulated slag, LS: lead slag) < d.l.: below detection limit, n.a.: not analysed)*

### 4.4.3.3 Quantification of metals accommodated in mineral phases

The approximate distribution of metals between individual mineral phases is presented in Table 4.6. According to the mineral quantification coupled with microprobe data, both major and minor phases accommodate significant amounts of metals relative to their bulk content in slags. Glass and fayalite were found to carry significant quantities of Zn and Pb (over 76%) in the HS, whereas over 90% of Cu was distributed in sulfides. The same general relation was observed in the SFS, however with greater contribution of sulfides to the bulk metal content compared to sulfides from the HS. Over 60% of the metals are incorporated in the glass matrix of the GS. Although Cu-droplets are modally minor components, they carry up to 37% of Cu. Metals present in the LS are mainly accommodated in sulfides. Despite metallic Pb occurs in very low volumetric proportions, the contribution of this phase to the bulk Pb content of LS lies in 80%.

**TABLE 4.6 Approximate distribution of metals between mineral phases.**

Values expressed in percentages of elements accommodated in individual mineral phases relative to bulk composition *(HS: historical slag; SFS: shaft furnace slag, GS: granulated slag, LS: lead slag).*

| | HS | | | SFS | | | GS | | | LS | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cu | Zn | Pb | Cu | Zn | Pb | Cu | Zn | Pb |
| *Glass and synthetic equivalents of silicates* | | | | | | | | | | | | |
| Interstitial glass | 6.9 | 56.2 | 50.6 | 1.7 | 34.1 | 34.3 | 62.2 | 99.8 | 98.8 | 2.9 | 0.3 | 0.7 |
| Surface glass | | | | 0.1 | 0.6 | 0.9 | | | | | | |
| Pyroxene (diopside) | | | | 1.6 | 34.5 | 45.7 | | | | | | |
| Olivine (fayalite) | 1.0 | 42.6 | 25.6 | | | | | | | 1.4 | 0.2 | 0.3 |
| | | | | | | | | | | | | |
| *Sulfides and intermetallic compounds* | | | | | | | | | | | | |
| Bornite | 58.3 | 0 | 0 | 78.4 | 0.2 | 5.9 | | | | 12.5 | 0 | 0 |
| Chalcopyrite | 21.2 | 0.3 | 9.4 | 17.1 | 16.6 | 13.3 | | | | 39.5 | 0 | 1.1 |
| Pyrrhotite | 12.6 | 0.9 | 14.3 | | | | | | | 16.2 | 0.1 | 0.6 |
| Sphalerite (*marmatite*) | | | | 1.3 | 13.9 | 0 | | | | 27.4 | 99.4 | 13.5 |
| Metallic Cu | | | | | | | 37.8 | 0.2 | 1.2 | | | |
| Metallic Pb | | | | | | | | | | 0.2 | 0 | 83.7 |

### 4.4.3.4   Leaching experiment

Results of the leaching tests (Figures 4.5 and 4.6) revealed that slags display a different behaviour under various pH conditions. Susceptibility of slags to leaching was defined by calculation of relative values of metals released from the material. Raw results represent only quantities of metals leached out from slags without any reference to the bulk content of metals in slags (Figure 4.5), whereas calculated relative values corresponding to the percentage of leached elements define either slag susceptibility to leaching (high percentage) or its resistance (low percentage) (Figure 4.6). Analytical errors calculated from replicate analyses, were below 5% RSD (relative standard deviation). Statistical analysis of data revealed that differences between replicates in individual pH treatments of slag samples were on the level of 95% confidence limits.

A common trend implying from the leaching test is that a maximum concentration of leached contaminants occurs at strongly acidic conditions (pH- 2-4), significantly decreasing towards natural pH and slightly increasing at highly alkaline conditions. The natural pH of the analysed slags is a: HS: 6.2, SFS: 9.2, GS: 8.1, LS: 7.8, therefore the conventional name of "natural" pH is introduced to present extraction when ultrapure water (milli-Q) is used as extractant.

Under the experimental conditions applied, at pH 2, copper may be mobilized from slags in quantities even up to 5873 mg/kg (GS), 1710 (HS), 348.8 mg/kg (SFS) and 346.6 mg/kg (LS). At pH 4 and 5.5, Cu leaching is lower, but still important, especially for the GS (1752.7 and 517.9 mg/kg), whereas the LS under exposure to pH 4 and 5.5 shows concentrations below detection limit. Slags when exposed to alkaline conditions behave much more stable compared to acidic pHs and display a leachability not higher than 114.0 mg/kg (HS).

Zinc leachability shows a similar general trend of intense leaching under acidic pH values (2-4) and its less important release under alkaline conditions. The LS is the material giving the highest concentrations of Zn (up to 8919 mg/kg), whereas GS shows especially great leaching (3693.5 mg/kg) at pH of 2. For other materials (HS and SFS), release of Zn is maintained at the level of one order of magnitude lower compared to the cases mentioned above and elevates not higher than 493.9 mg/kg. In the case of the HS and the GS values of leached metal at alkaline pHs were below detection limit, whereas up to 242.6 mg/kg was released from LS (pH 12 – 13) and negligible quantities of 1.4-1.7 mg/kg from the SFS.

Regarding Pb leachability from the analysed slags, results show highly comparable trends with those observed for Zn leaching. However, higher quantities are leached at pH 13. Under strongly acidic conditions (pH 2) 17186 mg/kg (LS), 6293.8 mg/kg (GS), 393.6 mg/kg (SFS) and 36.3 mg/kg (HS) of Pb were leached. Lead concentrations are also considerable in the case of the LS at strong alkaline conditions reaching even values of 5538.5 mg/kg at pH 13. The shaft furnace slag shows as high leached concentrations: 390.0-446.3 mg/kg at pH 13 and

12, whereas the value of leached Pb elevates not higher than 42.5 mg/kg in the case of the GS (Figure 4.5 C).

The pH conditions of 10.5 seems not to have any effect on stability of the HS, SFS and GS, because concentrations of all the metals in leachates were below detection limits. Only in case of the LS values 9.5 mg/kg of Cu and 18.5 mg/kg of Pb were achieved.
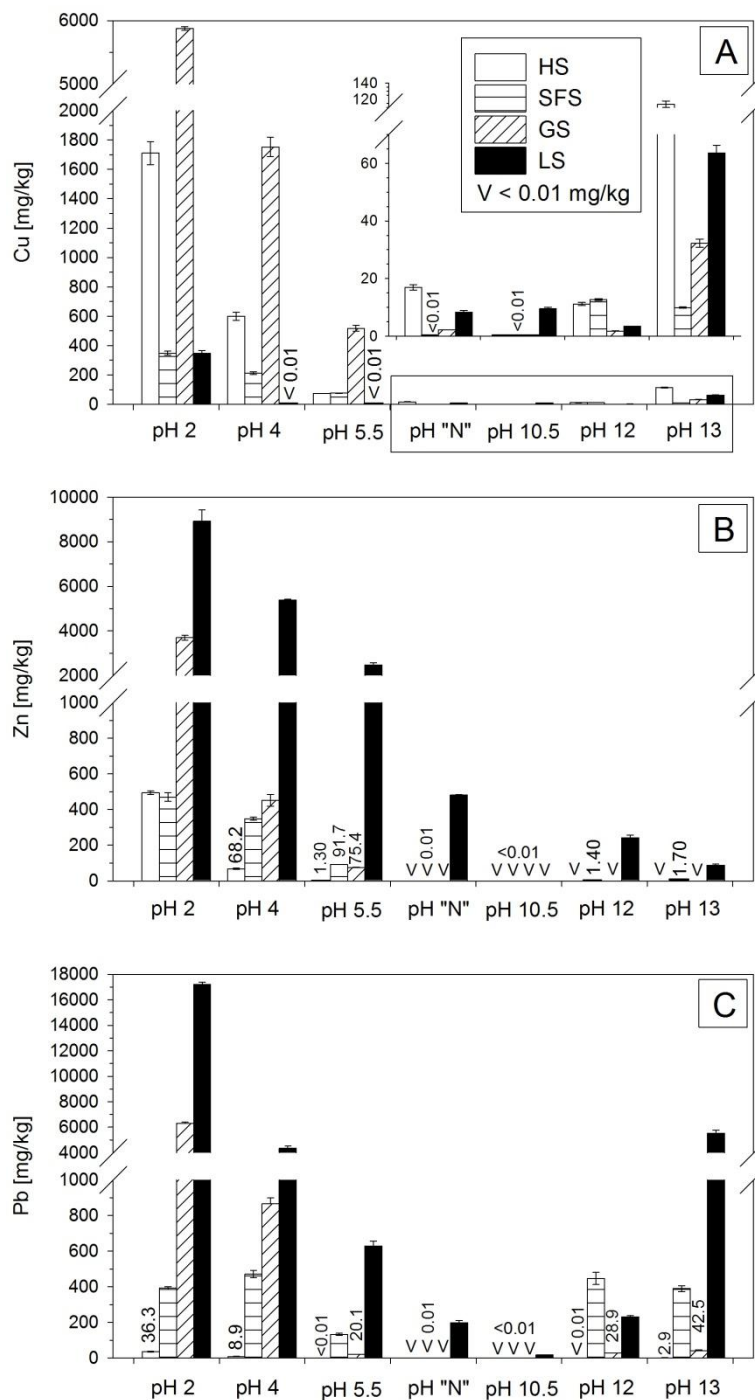


**FIGURE 4.5 Diagrams presenting leaching of metals (Cu, Zn, Pb) versus pH (± 0.1).**

*(HS: historical slag, SFS: shaft furnace slag, GS: granulated slag, LS: lead slag,*
*pH "N": natural sample's pH)*
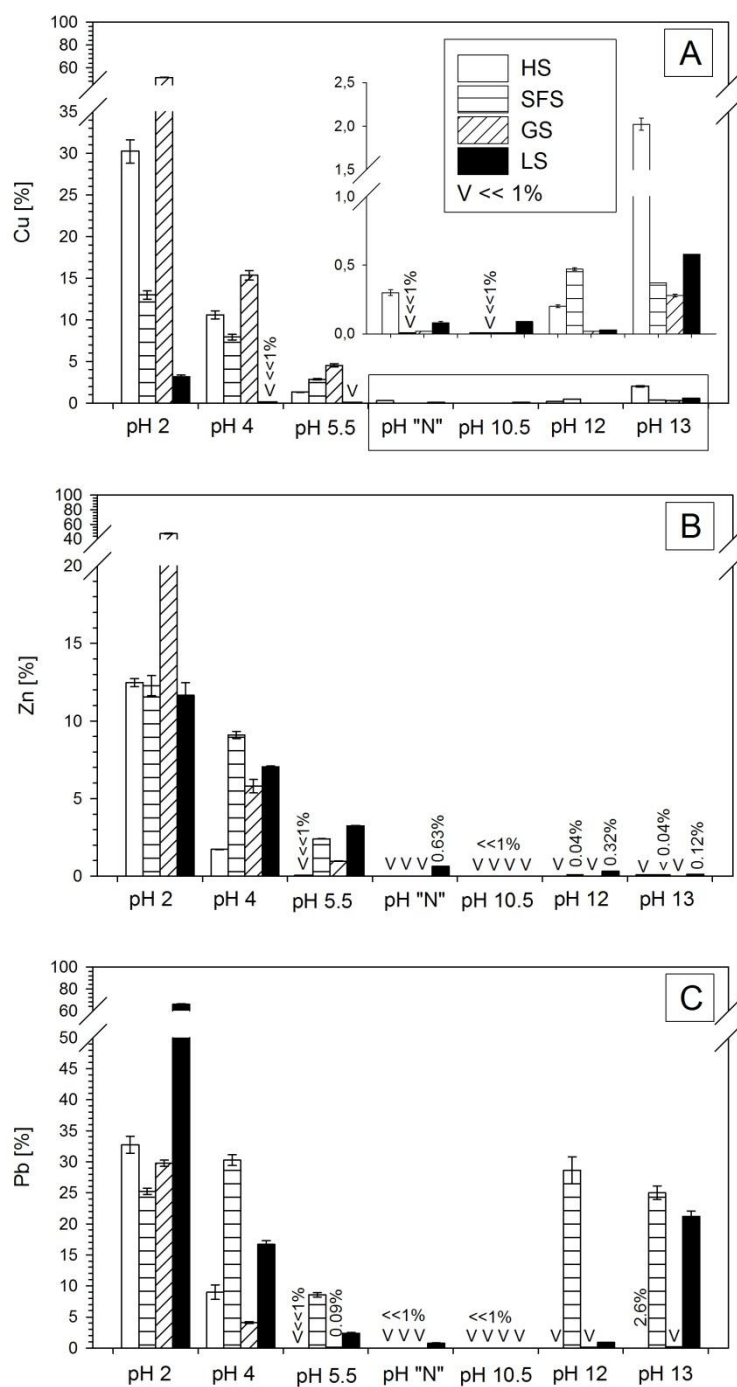
**FIGURE 4.6 Diagrams presenting relative values of leached metals versus pH (± 0.1).**

*(HS: historical slag, SFS: shaft furnace slag, GS: granulated slag, LS: lead slag, pH "N": natural sample's pH)*

# 4.5 DISCUSSION

## 4.5.1 Bulk composition of copper slags

Chemical analyses of Cu-slags discharged in two different periods of pyrometallurgical activities revealed that historical and modern slags display a different chemical composition. Bulk chemistry of slags varies from one type of slag to another (Table 4.1). Although modern slags are resulting from improved industrial processes, they still contain considerable concentrations of metallic elements, unexpectedly even higher than those observed in historical slags. It suggests that not only historical slags, but also those originating from nowadays production should be considered as substantial waste materials. It may appear surprising that historical slags show lower concentrations of metallic elements compared to those issued from nowadays processing. Nevertheless, it does not have to mean a lower efficiency of nowadays processing.

Modern pyrometallurgical industry likely generates lesser quantities of slags compared to historical ones. Therefore, it may be assumed that metallic elements unrecovered during modern processing are concentrated in wastes giving a higher metal content, whereas historical slags were produced in larger quantities and the distribution of these metallic compounds could have been dispersed in larger quantities of these materials giving their final lower concentration. Furthermore, it has to be noticed that ores mined in historical times contained comparable Cu concentration (1.2-3.8%) to those mined nowadays (for the process where the investigated slags originate from: 1.3-2.6%). However, modern pyrometallurgy applies enriched concentrate (up to 30% of Cu) as the initial input to the process, whereas in historical times pyrometallurgical technology was not as much developed and ore was directly submitted to processing. Therefore, the most probable reason of the higher metal concentration in modern slags is the fact of its higher content in the initial processing product. The bulk chemistry of modern slags distinctly indicates them as the materials with potential for further industrial processing such as metal recovery which attracts scientific attention lately.

The comparison of slags bulk chemistry with other previously examined copper slags is listed in the Table 4.7. The bulk content of metallic elements in HS does not exceed 1% for individual elements, whereas previous studies demonstrated that metal quantities may reach even up to 28.06 wt.% of Cu, 12.09 wt.% of Zn and 18.38 wt.% of Pb as shown in slags from Tsumeb in Namibia (Ettler et al., 2009). Furthermore, the GS and LS predominantly owe their high metal concentrations to their phase composition.

The lead slag is an exceptional material (mixture of matte and silicate slag) that has an extremely high sulfide content. These phases are considered as important metal carriers, hence the bulk concentration of metallic elements for this slag is also very high (Table 4.7).

Additionally, it has to be highlighted that volumetrically minor metallic Pb was found to be the most important Pb carrier. Therefore, not only major phases, but also the minor ones have an important relation with the bulk chemistry of slags. The granulated slag has a high metal content due to the presence of Cu-droplets distributed within the glass and important distribution of metals in glass itself. The zinc content in the GS is almost ten times lower compared to that in LS indicating sphalerite as the most important Zn carrier. Nevertheless, its concentration within glass and silicates may be also considered as significant.

**TABLE 4.7 The range of content of Cu, Zn and Pb in copper slags.**

| SLAG | Cu wt. % | Zn wt. % | Pb wt. % | References |
|---|---|---|---|---|
| **Slags from this study** | | | | |
| Historical (massive) slag POLAND | up to 0.82 | up to 0.83 | up to 0.03 | Kierczak & Pietranik (2011) Kierczak et al., (2013) |
| Shaft furnace slag | 0.27 | 0.38 | 0.16 | - |
| Granulated slag | 1.14 | 0.78 | 2.11 | - |
| Lead slag | 1.09 | 7.64 | 2.61 | - |
| **Literature data** | | | | |
| ITALY Campigilia Marittima district: Capattoli Valley | 0.22-0.31 | 1.62-6.07 | 0.53-3.40 | Manasse et al., (2001) |
| ITALY Massa Marittima district | 0.07-1.23 | 0.31- 5.26 | 0.01-1.95 | Manasse & Mellini, (2002) |
| AUSTRALIA North Queensland | 0.14-0.86 | up to 5.86 | up to 5.16 | Lottermoser, (2002) |
| SPAIN Huelva Province, Cabezo Jure | 0.14-28.06 | up to 0.14 | up to 0.46 | Sāez et al. (2003) |
| USA Vermont/Tennessee | 0.19-1.35 | 0.23-1.02 | 0.0047 | Piatak et al., (2004) |
| NAMIBIA Tsumeb | 0.49-12.19 | 2.8-12.09 | 0.98-18.38 | Ettler et al., (2009) |
| PORTUGAL Sao Domingos District | | | | Alvarez-Valero et al., (2009) |
| Historical | 0.1 | 0.03 | 0.05 | |
| Modern | 0.27 | 0.89 | 0.51 | |
| ZAMBIA Copperbelt Province | <2 wt.% (few samples 8.6-35 wt.%) | up to 0.23 | up to 0.11 | Vítková et al., (2010) |

## 4.5.2 Phase composition

For both the HS and SFS, silicates and glass were the major components, what is congruent with data obtained for other metallurgical slags having these phases as major components (Parsons et al., 2001; Manasse et al., 2001; Manasse & Mellini, 2002; Lottermoser, 2002; Sāez et al., 2003; Piatak et al., 2004; Ettler et al., 2009; Álvarez-Valero et al., 2009; Mateus et al., 2011; Vítková et al., 2010; Kierczak & Pietranik, 2011; Kierczak et al., 2013; Piatak et al., 2014). The granulated slag exhibits a different phase composition and represents amorphous material resulting from fast cooling using water. The lead slag presents various characteristics due to the fact that it represents a mixture of matte and silicate slag and sulfides are significantly more abundant than silicate phases. Fayalite is a commonly identified phase in metallurgical slags (Mihailova & Mehandrejiev, 2010). The presence of fayalite in studied slags (HS and LS) may be attributed to the melt composition impoverished in CaO (Ettler et al., 2001). Furthermore, it carries significant concentrations of ZnO that are due to its substitution for $Fe^{2+}$ in the olivine crystal structure (Ettler et al., 2001).

The chemical composition of glass present in historical (HS) and modern slags (SFS and LS) was found to contain important quantities of metallic elements.

Comparing the distribution of metals of interest (Cu, Zn, Pb) in glass to these observed in other copper slags (Table 4.8), it may be noticed that previously investigated copper slags may have similar or even higher concentrations of these metals. It has been shown previously that glass can entrap even as much as 6.9 wt.% of Cu (Vítková et al., 2010), 17.8 wt.% of Zn (Manasse & Mellini, 2002) and 11.80 wt.% of Pb (Ettler et al., 2009).

**TABLE 4.8 Distribution of metallic elements within glasses analysed for different Cu-slags.**

| SLAG | CuO | ZnO [wt.%] | PbO | References |
|---|---|---|---|---|
| **Slags from this study** | | | | |
| Historical slag POLAND | 0.09-0.83 | 0.17-0.74 | up to 0.04 | - |
| Shaft furnace slag | Bulk glass 0.01-0.45 | Bulk glass 0.49-1.51 | Bulk glass 0.09-0.39 | - |
| | Surface glass 0.05-1.24 | Surface glass 0.63-0.70 | Surface glass 0.13-0.46 | |
| Granulated slag | 1.96-3.70 | 0.88-1.90 | 3.97-4.77 | - |
| Lead slag | 0.16-0.44 | 0.41-0.55 | 0.04-0.07 | - |

| Literature data | | | | |
|---|---|---|---|---|
| ITALY<br>Massa Marittima district | n.d | 0.96-17.83 | n.d. | Manasse & Mellini, (2002) |
| AUSTRALIA<br>North Queensland | 0.06 | 4.69 | 0.43 | Lottermoser, (2002) |
| USA<br>Vermont/Tennessee | Bulk glass<br>0.03-1.43 | Bulk glass<br>0.35-2.17 | Bulk glass<br>up to 0.14 | Piatak et al., (2004) |
| | Int. glass<br>up to 1.24 | Int. glass<br>0.18- 1.14 | Int. glass<br>up to 0.08 | |
| NAMIBIA<br>Tsumeb | up to 1.78<br>mean 0.15 | 2.42-16.21<br>mean 9.29 | up to 11.80<br>mean 2.29 | Ettler et al., (2009) |
| ZAMBIA<br>Copperbelt Province | up to 6.90<br>mean 0.08-0.77 | up to 0.44 | n.d. | Vítková et al., (2010) |

Sulfides are considered as the most important metal bearing-phases in metallurgical slags and they are of particular importance because they easily undergo weathering (Piatak & Seal, 2010; Vítková et al., 2010). Concerning sulfide phases, those having a composition close to chalcopyrite and bornite are present in both slag types (historical and modern ones), whereas sphalerite was observed only in SFS and LS. Moreover, pyrrhotite was found in LS and HS. These sulfide phases were also commonly observed in different previously studied copper slags (Lottermoser, 2002; Piatak et al., 2004; Ettler et al., 2009; Álvarez-Valero et al., 2009; Mateus et al., 2011). According to microprobe data significant quantities of metallic impurities have been incorporated in sulfide structures. As a result of their compositional variability, sulfides often stray from their stoichiometrical fields as shown at the ternary diagram (Figure 4.4). Such variations are attributed to accommodation of atomic substitutions (e.g. Zn, Pb, As) in sulfides structure as well as may result from high temperature quenching (Vítková et al., 2010). Furthermore, some microinclusions of metallic Pb have been observed in bornite of SFS (Figure 4.7 A).
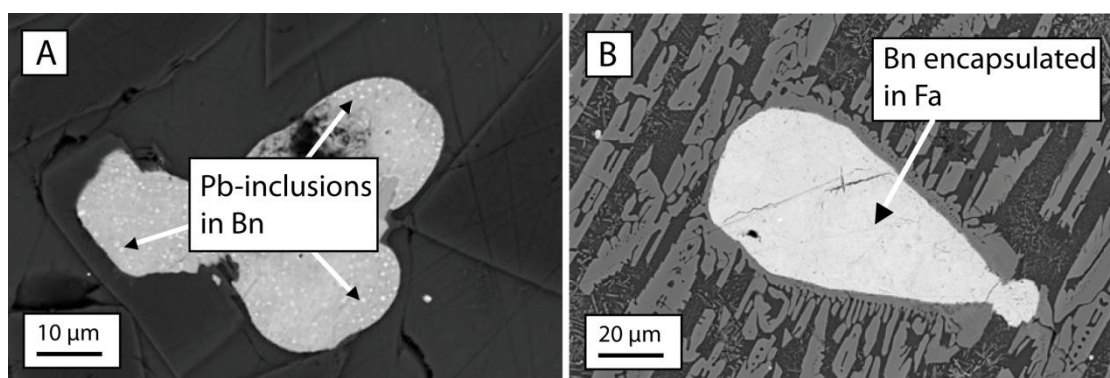


**FIGURE 4.7 Scanning electron microscope images presenting Pb-inclusions in bornite of SFS (a) and bornite encapsulated in fayalite crystals of LS (b).**

*(LS: lead slag, SFS: shaft furnace slag, Bn: bornite, Fa: fayalite)*

## 4.5.3 Leaching behaviour

A common trend resulting from leaching test experiments is the maximum concentration of leached contaminants under strongly acidic conditions (pH 2-4). Subsequently, a significant decrease of metal leachability is observed towards the sample's natural pH and finally a slight increase in metal concentrations in the leachate is noticed under highly alkaline conditions (Figures 4.5 and 4.6). Low quantities of detected metals at near neutral pH may be due to metal precipitation (*e.g.,* as oxy-hydroxides), whereas at higher pH values (> 10), the solubility of these elements slightly increases.

Considering results obtained from pH-dependent leaching experiments, it may be noted that the mineralogy and bulk chemistry are principal factors that affect the preference of the metals that are leached.

Comparing results of tests done for all studied slag types, it is important to notice that slags show a different leaching susceptibility. Analysing the relative values of metals, results indicate that GS undergoes efficient leaching at strongly acidic conditions for all metals analysed. As much as 51.4, 47.3 and 29.8% of Cu, Zn and Pb is leached out (Figure 4.6).

The lead slag has a very high Pb leachability at extreme pH values (2 and 13), reaching values as high as 65.8 and 21.2%, respectively (Figure 4.5 C). The historical slag shows a maximum susceptibility to leaching out metals (32.7% of Pb) when exposed to a pH of 2, whereas important leachability of the SFS is observed at the pH range 2-4.

Based on the results of pH-dependent leaching experiments, it can be concluded that slag are not completely inert materials, because their exposition to different pH conditions may lead to significant metal release. Leachability of metals is especially high under strongly acidic conditions and much more important compared to highly alkaline ones. This point is significant for environmental considerations, but on the other hand such aggressive conditions (pH=2) do not occur abundantly in nature. Low pH related extreme scenarios may nevertheless occur on the dumping sites. Both, slags and waste rocks undergo weathering that may result in acid generation, especially when sulfides are being dissolved (Jamieson, 2011; Piatak et al., 2014). Subsequent exposure of wastes to acid leachate attack may facilitate their further weathering, leading to dispersal of the metal bearing leachate and bringing undesirable environmental consequences (Lottermoser, 2011). Alkali conditions are much more stable for slags. The granulated slag should be managed with a special caution only if exposed to strongly acidic conditions, whereas alkaline conditions should also be avoided in order to prevent Pb leaching from the SFS and LS. Our findings suggest that slags are stable materials in the sample natural pH and they have even better stability at slightly alkaline conditions (pH

10.5). Thus any kind of management ensuring stable pH in the range mentioned above is required to minimise metal release from the slags.

The granulated slag is a material with an amorphous structure (Figure 4.2 C). A previous study revealed that the susceptibility of amorphous slags to be leached under exposure to acid leaching is lower compared to slags with a crystalline structure (Kuo et al., 2008). This is not congruent with our results, giving usually more important leaching from amorphous materials, especially at strong acidic conditions. Nevertheless, our result is in accordance with Maweja et al. (2010), who concluded that breaking of amorphous silicate structures may result in stronger metals (Cu, Zn, Pb) dissolution when exposed to nitric acid leaching. On the other hand, the high content of metals in our leachate may also be due to the presence Cu-droplets which are the most important Cu-carriers responsible for ~38% of Cu in the GS. Therefore, glass dissolution theoretically did not have to appear. Nevertheless, easier decomposition of this material was observed during leaching experiments and particle dissolution was easily visible as colloid matter suspended in the leachate proving partial decomposition of the material. Additionally, a high leaching of Zn and Pb which are mainly accommodated in glass (~99%) would suggest that not only Cu-droplets, but also glass releases metals to the solution. In other words, Cu-droplets carry less than 1.5% of the bulk content of Zn and Pb (Table 4.6), while over 30% of these metals were released from slags (Figure 4.6), hence these metals were partially liberated from glass as well. Glass dissolution should thus also be considered in case of the HS and SFS as this phase is an important metal carrier (up to ~56%) in these materials (Table 4.6).

The high quantity of Zn leached from the LS may refer to dissolution of sphalerite identified as a major constituent of this type of slag, responsible in ~99.4% for the bulk content of Zn in this material. It is also confirmed by the relatively high Zn concentrations present in SFS also composed of sphalerite. Although, sphalerite occurs in much lower volumetric proportions in the SFS compared to the LS, it carries ~14% of bulk Zn content. Additionally, even a higher content of bulk Zn (16.6%) is accommodated in chalcopyrite in the SFS (Table 4.6) and could also liberate this element. Nevertheless, the bulk chemistry of these materials seems to be important. The shaft furnace slag, having a 20 times lower Zn content than LS, shows this relation for acidic leaching and gave an almost 20 times lower content of zinc in the leachate at pH of 2 and 15 times lower at pH 4. Lead slag having the highest bulk content of Pb easily releases this element to the leaching solution. High quantities of Pb released from the LS may be due to dissolution of the Pb phase which carries over 80% of bulk Pb, although it is present in minor volumetric proportions. Surprisingly, the LS reveals a low Cu release (maximal 3.17%) and preferential release of other metallic compounds. That may be due to two reasons. Firstly, sphalerite dissolved only partially. This phase carries up to ~99% of Zn, while only 11.7% was released. When we consider Cu (3% of the total Cu concentration is released) and compared to the quantity accommodated in sphalerite, it is seen that approximately 9 times less Zn than sphalerite carries is released. A similar correlation is noticed for Cu. Secondly,

Cu-bearing sulfides are also encapsulated in a fayalite structure that could imply relatively good prevention of these phases against the leaching solution (Figure 4.7 B).

Furthermore, an interesting observation implying from the diagram presenting leaching of Pb (Fig. 5 C) is the great leachability of Pb from the SFS under alkaline (12-13) conditions, which is much higher compared to the HS. These materials mainly owe their bulk Pb content to glass and crystalline silicates (fayalite in the HS and diopside in the SFS). General rates of silicate dissolution (Figure 4.8) show that they drop gradually along with pH for fayalite, whereas a steady state is being achieved for diopside. That indicates that Pb release may be related to diopside dissolution. Additionally, under extremely acidic conditions, a similar Pb liberation (SFS) is observed and fits the trend of diopside dissolution. Release of Cu and Zn from the HS and SFS also fits the theoretical curves of silicates dissolution. However, liberation of these elements from sulfides and glass should not be neglected as they exhibit even greater susceptibility to release metals relative to crystalline silicates (Parsons et al., 2001). Moreover, important quantities of Cu released from the HS (up to 30%) and the SFS (up to 13%) demonstrate sulfide dissolution as only up to ~7% of the bulk Cu is accommodated in silicate phases. In turn, Pb released from the SFS reached even 25%, while less than ~20% is accommodated in sulfides.
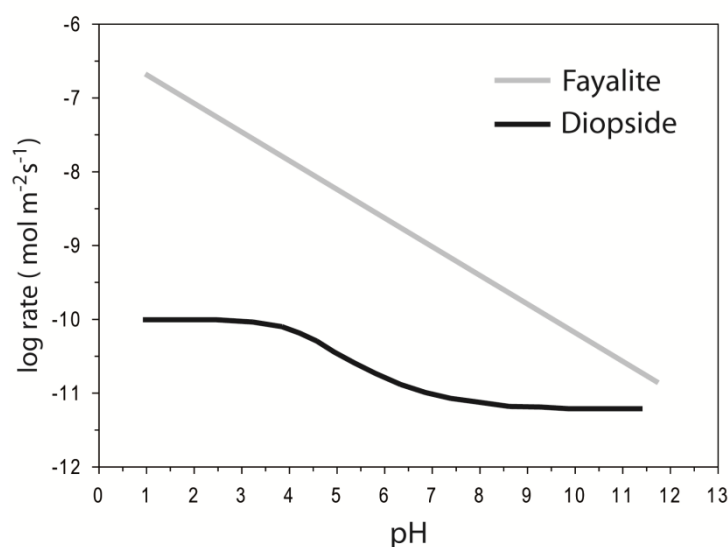


**FIGURE 4.8 Estimated dissolution rates of fayalite and diopside as a function of pH.**

Graph redrawn from Haustrath et al. (2008).

Our observations imply that the leaching behaviour of slags depends not only on their bulk chemistry, but also on the slag phase composition. Although in some cases the relation between bulk slag composition is reflected by the leachate chemistry, the mineralogy seems to have a superior importance in the leaching of metals. Furthermore, results of these leaching experiments show that separate considerations of the behaviour of individual slags is important for their hazard assessment.

Considering the future fate of these materials it has to be stressed that when chemical leaching is aimed to be applied for metal extraction, adaptation of the leaching conditions has to be taken into account. The leaching behaviour of both modern and historical slags suggests a greater performance of acidic solutions over alkaline ones if potential recovery of the contained metallic constituents is intended. The fact of a maximum metal dissolution as high as 50 and 60% for Cu and Pb, respectively, suggests that either higher acid concentration or another leaching solution should be used in order to achieve greater metal recovery. Additionally, extension of leaching time, increase of the temperature or different liquid to solid ratio should be also considered.

## 4.6  CONCLUSIONS

This study confirmed that differences in pyrometallurgical technologies have a significant impact on the slag chemistry and mineralogy. Unexpectedly, some of modern slags display a higher residual content of metallic elements compared to those observed in historical slags. This finding suggests their potential to be considered as materials useful for further processing. Results of the leaching tests demonstrated a higher metal release in strong acidic conditions, whereas leachability at alkaline conditions revealed a lower importance. A slightly alkaline pH of 10.5 was found to be optimal for any slag management strategy due to the low susceptibility of slags to release the contained metals. The high resistance of historical slags to alkaline conditions indicates that reusing them as *e.g.,* cement additives could be better than their disposal.

According to the leaching results the slags susceptibility to be leached depends on both their bulk chemistry and mineralogy. However, the factor playing the superior role in metal leachability is the mineral phase. Therefore, separate consideration of the behaviour of individual slags is important in order to prevent potential contamination of the environment.

# REFERENCES

1. **Álvarez-Valero A., Pérez-López R., Nieto J.M. (2009):** „*Prediction of the environmental impact of modern slags: A petrological and chemical comparative study with Roman age slags".* American Mineralogist 94, 1417-1427.

2. **Chen M., Han Z., Wang L. (2012):** „*Recovery of valuable metals from copper slags by hydrometallurgy".* Advanced Material Research 402. 35-40.

3. **Davenport W.G., King M., Schlesinger M., Biswas A.K. (2002):** „*Extractive metallurgy of copper".* Fourth edition/Pergamon 1-417.

4. **Elliot A.D. & Watling, H.R. (2011):** „*Chalcopyrite formation through the metathesis of pyrrhotite with aqueous copper".* Geochimica et Cosmochimica Acta 75 (8), 2103-2118.

5. **Ettler V., Johan Z., Křríbek B., Šebek O., Michaljevič M. (2009):** „*Mineralogy and environmental stability of slags from Tsumeb smelter. Namibia".* Applied Geochemistry 24. 1-15.

6. **Ettler V., Komarková 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.

7. **Ettler V., Legendre O., Bodénan F., Touray J.C. (2001):** „*Primary phases and natural weathering of old lead-zinc pyrometallurgical slag from Pribram. Czech Republic".* Canadian Mineralogist 39. 873-888.

8. **Ettler V., Piantone P., Touray J.C. (2003):** „*Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long-term assessment".* Mineralogical Magazine 67 (6). 1269-1283.

9. **Fernández-Caliani J.C., Ríos G., Martínez J., Jiménez F. (2012):** „*Occurrence and speciation of copper in slags obtained during the pyrometallurgical processing of chalcopyrite concentrates at the Huelva smelter (Spain)".* Journal of Mining and Metallurgy 48 (2). 161-171.

10. **Gee C., Ramsey M.H., Maskall J., Thornton I. (1997):** „*Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead".* Journal of Geochemical Exploration 58 (2), 249-257.

11. **Harish V., Sreepada R.A., Suryavanshi U., Shanmuganthan P., Sumathy A. (2011):** „*Assessing the effect of leachate of copper slag from the ISASMELT process on cell growth and proximate components in microalgae Chlorella vulgaris (Beijerinck)".* Toxicological and environmental chemistry 93 (7),1399-1412.

12. **Hausrath E.M., Navarre-Sitchler A.K., Sak P.B., Steefel C.I., Brantley S.L. (2008):** „*Basalt weathering rates on Earth and the duration of liquid water on the plains of Gusev Crater, Mars".* Geology 36 (1), 67-70.

13. **Hong S., Candelone J.P., Soutif M. Boutron C.F (1996):** „*A reconstruction of changes in copper production and copper emissions to the atmosphere during the past 7000 years".* Science of The Total Environment 188 (2-3), 183-193.

14. **Jamieson H.E. (2011):** „*Geochemistry and mineralogy of solid mine wastes: Essential knowledge for predicting environmental impact".* Elements magazine 7 (6), 381-386.

15. **Kierczak J. & Pietranik A. (2011):** „*Mineralogy and composition of historical Cu Slags from the Rudawy Janowickie Mountains. Southwestern Poland".* Canadian Mineralogist 49(5), 1281-1296.

16. **Kierczak J. Neel C., Puziewicz J., Bril H. (2009):** „*The mineralogy and weathering of slag produced by the smelting of Ni-ores. Szklary. Southwestern Poland.* The Canadian Mineralogist 47 (3), 557-572.

17. **Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Néel C., Ettler V., Mihaljevič M. (2013) :** „*Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland).* Journal of Geochemical Exploration 124, 183-194.

18. **Kojima S. (1992):** „*The nature of chalcopyrite inclusions in sphalerite: exsolution, coprecipitation or "disease"? a discussion",* Economic Geology 87 (4), 1191-119.

19. **Kuo Y-M., Wang J-W., Wang Ch-T., Tsai Ch-H. (2008):** „*Effect of water quenching and $SiO_2$ addition during vitrification of fly ash Part 1: On the crystalline characteristics of slags".* Journal of Hazardous Materials 152, 994-1001.

20. **Lottermoser B.G. (2002)**: „*Mobilization of heavy metals from historical smelting slag dumps. North Queensland. Australia".* Mineralogical Magazine 66(4), 475-490.

21. **Lottermoser B.G. (2011) :** „*Recycling, reuse and rehabilitation of mine wastes"* Elements magazine 7 (6), 405-410.

22. **Lynton S.J., Candela P.A., Piccoli P.M.(1993):** *„An experimental study of the partitioning of copper between pyrrhotite and a high silica rhyolitic melt".* Economic Geology 88 (4), 901-915.

23. **Manase A. & Mellini M. (2002):** *„Chemical and textural characterization of medieval slags from the Massa Marittima smelting sites (Tuscany. Italy).* Journal of Cultural Heritage 3, 187-198.

24. **Manasse A., Mellini M., Viti C. (2001):** *„The copper slags of the Capattoli Valley. Campiglia Marittima. Italy".* European Journal of Mineralogy 13, 949-960.

25. **Manz M. & Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District. Mexico".* Environmental Pollution 98(1), 7-13.

26. **Mateus A., Pinto A, Alves L.C., Matos J.X., Figueiras J., Neng N.R. (2011):** *„Roman and modern slag at S. Domingos mine (IPB, Portugal): Compositional features and implications for their long-term stability and potential reuse".* Int. Journal of Environment and Waste Management 8, 133-159.

27. **Maweja K., Mukongo T., Mbaya R.K., Mochubele E.A. (2010):** *„Effect of annealing treatment on the crystallisation and leaching of dumped base metal smelter slags".* Journal of Hazardous Materials 183, 294-300.

28. **Mihailova I. & Mehandrejiev D. (2010):** *„Characterization of fayalite from copper slags".* Journal of University of Chemical Technology and Metallurgy 45, 317-326.

29. **Mihaljevič, M., Ettler, V., Šebek, O., Sracek, O., Kříbek, B., Kyncl, T., Majer, V., Veselovský , F. (2011):** *„Lead isotopic and metallic pollution record in tree rings from the Copperbelt mining–smelting area, Zambia".* Water Air Soil Pollution 216, 657–668.

30. **Moskalyk R.R. & Alfantazi A.M (2003):** *„Review of copper pyrometallurgical practice: today and tomorrow".* Minerals Engineering 16, 893–919.

31. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California".* Applied Geochemistry 16, 1567–1593.

32. **Piatak N.M. & Seal II R.R. (2010):** *„Mineralogy and the release of elements from slag from the Hegeler Zinc smelter. Illinois (USA)".* Applied Geochemistry 25. 302-320.

33. **Piatak N.M., Parsons M. B., Seal R.R. (2014):** *„Characteristics and Environmental Aspects of Slags: A review".* Applied Geochemistry 57, 236-266.

34. **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".* Applied Geochemistry 19, 1039-1064.

35. **Radetzki M. (2009):** *„Seven thousand years in the service of humanity-the history of copper the red metal".* Resources Policy 34, 176-184.

36. **Reuter M., Xiao Y., Boin U. (2004):** *„Recycling and environmental issues of metallurgical slags and salt fluxes". VII International Conference on Molten Slags Fluxes and Salts.* The South African Institute of Mining and Metallurgy.

37. **Sāez R., Nocete F., Nieto J.M., Capitān M.A., Rovira S. (2003):** *„The extractive metallurgy of copper from Cabezo Jurē. Huelva. Spain: Chemical and mineralogical study of slags dated to the third millennium b.c.".* The Canadian Mineralogist 41, 627-638.

38. **Shi C., Meyer Ch., Behnood A. (2008):** *„Utilization of copper slag in cement and concrete".* Resources. Conservation and Recycling 52 (10), 1115–1120

39. **Sobanska S., Ledésert B., Deneele D., Laboudigue A. (2000):** *„Alteration in soils of slag particles resulting from lead smelting".* Earth and Planetary Sciences 331, 271-278.

40. **Themelis M.J. (1994):** *„Pyrometallurgy near the end of 20th century".* Industrial Insight 46 (8), 51-57.

41. **Tyszka R., Pietranik A., Kierczak J., Ettler V., Mihaljevič M., Weber J. (2012):** *„Anthropogenic and lithogenic sources of lead in Lower Silesia (Southwest Poland): An isotope study of soils, basement rocks and anthropogenic materials".* Applied Geochemistry 27, 1089-1100.

42. **US EPA 1313** "*Liquid-solid partitioning as a function of extract pH using parallel batch extraction procedure".* United States Environmental Protection Agency 2012, 1-28.

43. **Vandenberghe R.E., de Resende V.G., da Costa G.M., De Grave E. (2010):** *„Study of loss-on-ignition anomalies found in ashes from combustion of iron-rich coal".* Fuel 89, 2405-2410.

44. **Vítková M., Ettler V., Johan Z., Kribek B., Sebek O., Mihaljevic M. (2010):** *„Primary and secondary phases in copper-cobalt smelting slags from the Copperbelt Province. Zambia".* Mineralogical Magazine 74(4), 581-600.

**45. Whitney D.L. & Evans B.W. (2010):** *„Abbreviations for names of rock-forming minerals".* American Mineralogist 95, 185-187.

# Preface to Chapter 5

Chapter 4 presented a detailed characterization of Cu-slags that is recommended study stage prior to environmental risk assessment. According to the collected data, slags exhibit different chemical and mineralogical compositions which results in their various behavior at pH-stat conditions. Thus, an assumption about various environmental behaviors of these slags and potentially high metal release can be speculated. However, a deeper study reflecting conditions closely simulating environmental situation that might be encountered in reality is needed to confirm the given hypothesis. Even though modern slags are not disposed, there are many places across the world where slags owing similar compositions have been disposed in the past. For this reason, next stages of the work consider these slags as model samples rather than real scenario that they may be exposed to. The study considering behavior of these slags is nonetheless relevant for the improvement of general knowledge about alteration of mineral phases that Cu-slags are composed of. In contrast, environmental studies devoted to stability of historical slag represent the situation that may go on in the disposal site where these slags have been left unattended by long period of time.

It is worth to point out that former dumping sites are characterized by no or very poor prevention against weathering and consequently these processes are scarcely preventable. Slags are especially exposed to interact with soil and in turn surrounding soil is also endangered to chemical changes brought by metals input of slags weathering. However, complexity and number of factors and variables that play a role on this scale is large. First of all, different soils display various chemical compositions, hence the weathering scenario might vary from one dumping site to another. For this reason designing the experimental set-up that could represent global problem is difficult. The next stage of work will consider therefore general effect of common soil components such as humic and fulvic acids and other organics related to root exudation. In spite of wide range of concentrations of these organics found in different soils, the question of how do they affect slags stability remains to be answered. In these regards, previously characterized Cu-slags will be subjected to preliminary risk assessment through simulating soil weathering scenario. The study will especially be focused on mobilization of metals such as Cu, Zn and Pb as well as alteration of mineral phases present in slags. More detailed information concerning interactions of organic acids with slags and justification of their choice might be found in the introduction section of Chapter 5.

Preceding next chapter it is also worth to give a more extended explanation of *why is evaluation of metals release so much relevant for environmental research?*

The importance of studies considering metal release into the environment lies in toxicity effect that metals can cause on various members of food chain. Abnormal excessive concentrations of metals are usually the result of anthropogenic input into the environment. As the result of intensification of industrial activity the concentrations of metals in soils are currently even by 1000 fold higher as compared to soils with natural metal content (Faucon et al., 2012). The presence of metals in water column is usually lower due to on-going natural purification processes such as complexation, precipitation and adsorption, where sediments play a crucial sinking role (Flemming & Trevors, 1989). The toxic concentration refers to metal whose load exceeds metabolic requirement of living organism (Giller et al., 1998). Among the metals of interest Cu and Zn are essential, whereas Pb is prime

example of metal lacking any biological function (Emamverdian et al., 2015). Metal toxicity depends not only on its total concentration, but also on bioavailability which is governed by species that metal forms. The most available forms of metals are (in decreasing order): cationic form, inorganic complexes (*e.g.* $SO_4^{2-}$, $Cl^-$, $CO_3^{2-}$) and organic complexes. Likewise, metal mobility in the environment is also driven by its speciation. Dissolved forms of metals exhibit high mobility; those associated with organic matter are classified as moderately mobile, but might become highly mobile in the result of decomposition or oxidation of organic matter (John & Leventhal, 1995). The least available metals are those associated with crystalline mineral phases, however might turn into mobile form after release from weathered mineral (John & Leventhal, 1995). Furthermore, surrounding conditions are important variables affecting behavior and toxicity of metal. For example, pH declination favors occurrence of metal in cationic form, hence increases its toxicity (Wang et al., 2016).

The occurrence of metals at toxic levels might lead to undesirable effect to organisms. For example, when microorganisms exposed to high metal concentrations, their activity might decrease disturbing environmental balance. Detrimental effects on plants might result in changes of metabolic processes such as: respiration, photosynthesis, $CO_2$ fixation and gas exchange (Hossain et al., 2012). However, organisms are capable to survive even at critical concentrations levels due to adaptation mechanisms that enable them to overcome the problem of metal excess and toxicity. Beginning from the very micro scale of intake, defensive mechanisms utilized by microorganisms include: biomethylation, complexation, activation of efflux pump, binding on cell surface or metal removal via precipitation (Chapter 2). When the metal content in the plant tissue reaches critical level, different counteracting mechanisms are activated. The latter evolve: intracellular vacuolar sequestration, excretion of intracellular detoxification enzymes such as metallothionein or phytochelatins, symbiotic association with fungi (Emamverdian et al., 2015). The tolerance to metals rises along food chain. For example, Cu tolerance of mammals is even up to 100 fold greater as compared to fish or 1000-fold higher as compared to algae (Flemming & Trevors, 1989). Furthermore, accumulation of metals at any level of food chain carries the risk of acquisition by higher organisms that can consequently result in human (*e.g.* dietary) intake and undesirable chronic effects.

Metals play an important role in geochemical and biological cycles, however their critical concentrations might lead to undesirable consequences. For this reason, estimating different industrial and anthropogenic metal inputs into the environment are needed for predicting their detrimental impacts.

**John D.A. & Leventhal J.S. (1995):** „*Bioavailability of metals*". Preliminary compilation of descriptive geoenvironmental mineral deposit models, 10-18.

**Emamverdian A., Ding Y., Mokhberdoran F., Xie Y. (2015):** „*Heavy Metal Stress and Some Mechanisms of Plant Defense Response*". The Scientific World Journal, 2015.

**Flemming C.A. & Trevors J.T. (1989):** „*Copper toxicity and chemistry in the environment: a review*". Water Air & Soil Pollution 44 (1), 143-158.

**Giller K.E., Witter E., Mcgrath, S.P. (1998):** „*Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review*". Soil Biology and Biochemistry 30 (10), 1389-1414.

**Hossain M.A., Piyatida P., da Silva J.A.T., Fujita M. (2012):** „*Molecular mechanism of heavy metal toxicity and tolerance in plants: central role of glutathione in detoxification of reactive oxygen species and methylglyoxal and in heavy metal chelation*". Journal of Botany, 2012.

**Wang Z., Meador J.P., Leung K.M. (2016):** „*Metal toxicity to freshwater organisms as a function of pH: A meta-analysis*". Chemosphere 144, 1544-1552.

# CHAPTER 5

# METAL MOBILIZATION FROM Cu-SLAGS BY SOIL ORGANIC ACIDS

# ABSTRACT

Four types of Cu-slags (historical (HS), shaft furnace (SFS), granulated (GS) and lead slag (LS)) differing in chemical and phase composition were studied with respect to their susceptibility to release metallic elements (Cu, Zn, Pb) under exposure to various soil organic acids. Incubations (24-960 hours) were conducted with: i) humic acid (HA: 20 mg/L) at pH (4.4), ii) fulvic acid (FA: 20 mg/L) at pH (4.4), iii) an artificial root exudates (ARE) solution at pH (4.4), iv) ARE solution at pH (2.9) and v) ultrapure water (UPW). The results demonstrated that artificial root exudates contribute the most to the mobilization of metals from all slags analysed, regardless of the initial pH value of the solution. For example, even up to 803 mg/kg (14%), 810 mg/kg (30%), 2729 mg/kg (24%) and 565 mg/kg (5%) of Cu could be released within 960 h from HS, SFS, GS and LS, respectively when exposed to ARE (2.9). Humic and fulvic acids were found to have the highest impact on GS and SFS as compared to UPW control and increased the release of metals by a factor up to 37.5 (Pb) and 20.5 (Cu) for GS and SFS, respectively. HA/FA amplified mobilization of metals by a maximal factor of 13.6 (Pb) and 12.1 (Pb) for HS and LS, respectively. Various factors such as chemical and mineralogical characteristic of slags, solution acidity and affinity of organic molecules to metals contributed to the different behavior of individual slags under the conditions tested.

**Keywords:** Cu-slags, soil organic matter, artificial root exudates, humic/fulvic acids, metal mobilization

# 5.1  INTRODUCTION

Copper has been an essential metal for human civilization since ancient times and remains indispensable for modern day culture. Subsequently, its pyrometallurgical processing is currently well developed worldwide (Radetzki, 2009). Unfortunately, smelting industry generates waste slags that are unavoidable even at a very high level of process efficiency. Slags are important by-products in terms of production volume and the residual metal content resulting from smelting process loses (Ettler et al., 2009; Fernández-Caliani et al., 2012; Potysz et al., 2015). Currently Cu-slags are used for civil and hydraulic engineering applications (Shi et al., 2008; Schmukat et al., 2012). However, appropriate slag management requires the evaluation of potential release of metallic contaminants from the slags (Schmukat et al., 2013).

Due to lack of environmental awareness in the past, slags were considered to be non-hazardous materials and their "life cycle" was limited to two stages: production and disposal. A long-term exposure of these wastes to biogeochemical weathering led to mobilization of metals and undesirable effects on soil, sediment and water contamination which is experienced nowadays (*e.g.* Manz & Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2004; Piatak et al., 2004; Kierczak et al., 2013). In spite of playing essential biological functions, metals can accumulate in living organisms (*e.g.* plants) or even have a toxicological effect if concentrations exceed toxicity thresholds (Nederlof et al., 1993). Furthermore, the transfer of metals to soil or surface water and their subsequent passage into higher levels of the food chain might be a great concern too. For this reason, an evaluation of slags weathering and metal release under different environmental conditions/scenarios is important for existing dumping sites at which remediation operations might be of strong need in order to comply with regulatory requirements of environmental quality.

The soluble organic acids in soils are very complex and represent a large spectrum of polymers consisting of specific low- and high-molecular weight compounds varying in chemical composition, aromaticity and functional groups (Chin et al., 1994; Fu et al., 2006; Sposito, 2008; Güngör & Bekbölet, 2010). Due to specific properties, soluble organic acids affect directly and/or indirectly the weathering rate of minerals (Drever and Stillings, 1997; Jones et al., 1998). By adsorption onto mineral surfaces, formation of aqueous complexes with dissolving cations or changing pH of the solution, organic acids influence the thermodynamic equilibria and/or locally weak the chemical bounds of the dissolving mineral structure (Lawrence et al., 2014; Drever & Stilling, 1997; Oelkers and Schott, 1998; Welch & Ulman, 1993; Li et al., 2006; Ganor et al., 2009; Jahnson et al., 2005). Moreover, metal complexation with dissolved organic compounds may control metal speciation, toxicity and bioavailability as well as facilitate its migration or transport (Rashid, 1971; Hinsinger, 2001;

Mostofa et al., 2013). The predominant input of soluble organic acids to the soil environment is decaying plants and microbial decomposition products as well as roots exudates (Jones, 1998; Wu et al. 2002), even if some organic compounds may be deposited onto soil by winds or rainwater (Millet et al., 1997). The most common components of soluble organic acids are humic substances (humic and fulvic acids), although other biomolecules such as lipids, amino acids, organic acids and carbohydrates are frequently present as well (Jones & Darrah, 1994). In the majority of soils, the highest concentrations of organic compounds are found in a near surface soil horizon and particularly in the rhizosphere (Drever & Vance, 1994; van Hees et al., 2000; Degryse et al., 2008). Non humified organic acids in soils are typically present at micro-molar concentrations, however those at mili-molar ranges have also been reported (Jones, 1998; Strobel et al., 2001). The content might vary depending on plant species growing and its age as well type of soil and environmental conditions (*e.g.* moisture content) (Jones, 1998; Strobel et al., 2001). Humified organic acids usually contribute in 10-50% to soil organic matter whose concentration might be estimated out of organic carbon content by multiplying its value by approximate factor of 2 (Pribyl, 2010). Thus, slag weathering enhanced by humic substances and root exudates is especially relevant because disposed slags are often in direct contact with soil. Moreover, vegetation cover developing on the dump surface might serve not only as protective layer minimizing erosion (Roy et al., 2002), but might also supply organic compounds derived from root exudation (Houben et al., 2013). A possible weathering scenario which may be encountered in soil and rhizosphere environments is presented in Figure 5.1.

Soluble organic acids affect even highly insoluble mineral phases (Jones and Darrah, 1994; Bennett, 1991). The interactions of organic compounds with silicate minerals may enhance their weathering due to intensification of breaking Si-O-Si bonds (Bennett, 1991). The disturbance of metal bearing mineral phases might result in release of important quantities of elements including toxic ones (Baker, 1973). In turn, plant uptake of metals in excess might lead to (i) $H^+$ exudation as charge balancing reaction, hence local acidification (Dakora & Phillips, 2002) or (ii) metal transfer on the top of dumps through leaf deposition at the end of the vegetation cycle (Figure 5.1).

A number of studies on industrial wastes *e.g.* fly ashes and mine tailings, has examined leaching of metals under exposure to simple organic acids. Banks et al. (1994) observed enhanced mobilization of Zn from mine tailings under exposure to succinic, acetic and formic acid (50-1000 μM). Likewise, Burckhard et al. (1995) observed a similar effect and noted greater Zn complexation by citric acid as compared to formic, succinic and oxalic acids (1000-10000 μM). Ettler et al. (2009) reported enhanced release of Zn and Pb from fly ashes when exposed to acetic, oxalic and citric acid (500 μM). Despite the fact that several studies have already proven mobilization of metals by simple organic acids, a more complex composition of root exudates or humic substances would be required to represent more specific rhizosphere and soil conditions.

This study has been undertaken in order to compare the leaching behavior of four chemically and mineralogically different slags under exposure to organic components commonly present in soil and rhizosphere. Humic and fulvic acids solutions used in the leaching experiments represented dissolved soil humic substances, while a mixture of low molecular weight organic acids, sugars and amino acids represented root exudates of the rhizosphere. Ultrapure water was used as experimental control.
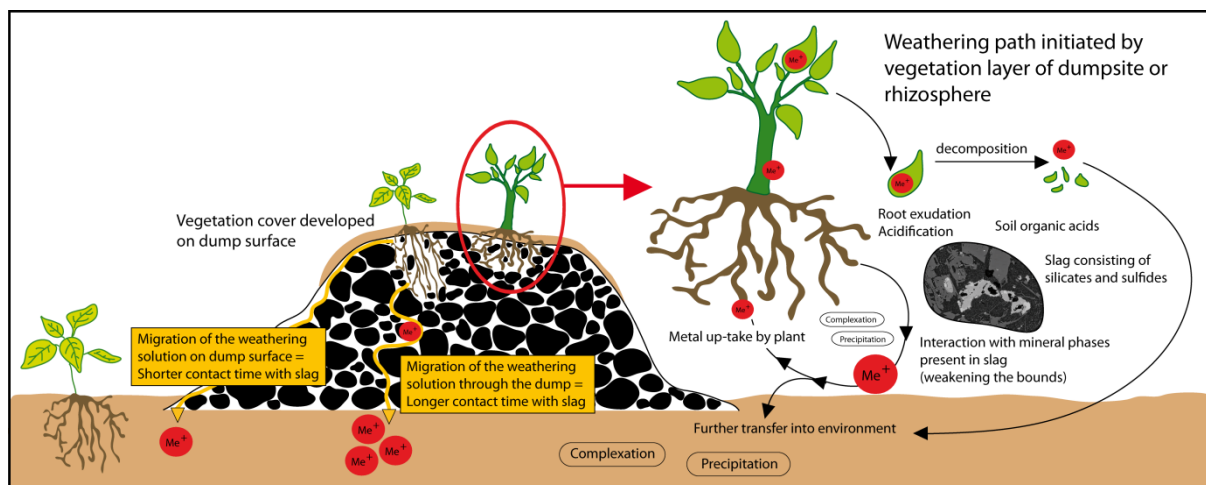


**FIGURE 5.1 Weathering scenarios that may occur at slag dumping sites.**

## 5.2 MATERIALS AND METHODS

### 5.2.1 Materials

Four types of Cu-slags representing materials from different time periods of industrial activities (historical and modern-day production) and different smelting technologies were evaluated in this study. Slags exhibit various chemical and mineralogical characteristics: i) historical slag (HS) is crystalline and consists mostly of fayalite, ii) modern shaft furnace slag (SFS) is principally composed of diopside, iii) modern granulated slag (GS) represents amorphous glassy material and iv) modern "lead" slag (LS) is a sulfide matte with admixtures of silicate (fayalite-rich) slag. An overview of slags chemical composition is listed in Table 5.1, whereas detailed information concerning their characteristics can be found elsewhere (Chapter 4: Potysz et al., 2016a).

**TABLE 5.1 Chemical composition of slags.**

|     |         | HS   | SFS  | GS    | LS    |
|-----|---------|------|------|-------|-------|
| *Cu* | [mg/kg] | 5657 | 2687 | 11425 | 10915 |
| *Zn* | [mg/kg] | 3962 | 3832 | 7810  | 76400 |
| *Pb* | [mg/kg] | 111  | 1559 | 21135 | 26125 |

*(HS: historical slag, SFS: shaft furnace slag, GS: granulated slag, LS: lead slag)*

### 5.2.2 Leaching solutions

Leaching experiments were performed using humic (HA) and fulvic acids (FA) as well as artificial root exudates (ARE). The HA and FA solutions were prepared by dissolving 20 mg of commercial (Suwannee River, International Humic Substances Society) humic (HA) or fulvic acid (FA) in 1 L of MilliQ water (20 mg/L) and were pre-set at initial pH of 4.4.

The ARE solution corresponded to the rhizosphere composition described by Baudoin et al. (2003) and contained: glucose (3.31 g/L), fructose (3.31 g/L), sucrose (3.15 g/L), citric acid (1.77 g/L), lactic acid (1.66 g/L), succinic acid (1.63 g/L), alanine (0.74 g/L), serine (0.97 g/L) and glutamic acid (0.81 g/L). The initial pH of ARE solution was 2.9 and 4.4 for two different treatments. The pH value of the solutions was adjusted using $HNO_3$ or NaOH.

The ARE solution is composed of simple, low molecular weight organic acids, whereas HA/FA are characterized by a more complex structure and higher molecular weight (Schulten & Schnitzer, 1993).

### 5.2.3  Batch-leaching experiments

The leaching experiments included five approaches at which each slag was submitted to leaching tests with: i) humic acid at pH $t_0$= 4.4, ii) fulvic acid at pH $t_0$= 4.4, iii) artificial root exudates solution at pH $t_0$= 4.4, iv) artificial root exudates solution at pH $t_0$= 2.9 and v) ultrapure water. The slags were crushed to reduce the particle size below 0.3 mm. The use of smaller slag particle size aimed at demonstrating "the worst case metal leaching scenario". A mass of 3 g of each slag was placed into batches and 30 mL of leaching solutions were added to maintain liquid to solid ratio of 10. Independent batches in triplicates were accompanied by procedural blanks. The batches were wrapped up in aluminium paper in order to avoid photo-oxidation of organic compounds, kept at ambient temperature (21±1°C) on a table shaker continuously agitated at 150 rpm. Leaching solutions with slags were left at free pH drift. The leachates were sampled after 24, 48, 72, 168 and 960 hours. At each sampling time, the pH of the leaching solution was measured, solutions were filtered using 0.45 µm nitrocellulose filters (Whatman), immediately acidified using suprapure $HNO_3$ (2% v/v) to prevent precipitate formation and stored at 4°C until analysis.

### 5.2.4  Metals measurements

The leachates were analysed for their Cu, Zn and Pb content using ICP-MS (Agilent 7700x) with [45]Sc and [115]In as internal standards. Quality control included systematic analysis of certified reference materials (SLRS-5 standard). The detection limits were typically 0.04, 0.4 and 0.05 µg/L for Cu, Zn and Pb, respectively. Additionally, some samples were measured using an atomic absorption spectrometer (AAS). The detection limits for AAS measurements were 0.01 mg/L (10 µg/L), 0.02 mg/L (20 µg/L) and 0.1 mg/L (100 µg/L) for Cu, Zn and Pb respectively.

### 5.2.5  Scanning electron microscope (SEM) observations

Slag samples resulting from long-term (960 h) treatments with the organic solutions were observed by SEM with respect to presence of weathering features. At the end of the experiments, grains were dried, coated with Au and placed on conductive tape. Microscopic observations of slags were conducted using SEM (JEOL JSM-601OA) coupled with an Energy Dispersive Spectrometer at high vacuum and 15-20 kV working mode.

# 5.3 RESULTS

## 5.3.1 pH evolution

During the experiments, the pH of the leachates shifted from the pre-set value to higher pH values due to neutralization potential of the slags. The pH change varied depending on slag and solution used (Figures 5.2-5.4). A more significant neutralization of pH occurred in case of GS and SFS, whereas HS and LS revealed slightly acidic pH.

## 5.3.2 Metal release

The concentrations of metals in the leachates (24, 48, 72, 168 and 960 hours) are plotted as a function of final solution pH (Figures 5.2-5.4) and data from the individual sampling points is presented in Table 5.2.

### 5.3.2.1 Historical slag

The amount of Cu leached within 24 h was 214.7 mg/kg and 83.7 mg/kg for ARE at an initial pH 2.9 and 4.4, respectively (Table 5.2, Figure 5.2). A prolongation of the leaching time up to 960 h led to mobilization up to 803.1 mg/kg and 302.0 mg/kg of Cu for ARE (pH 2.9) and ARE (pH 4.4), respectively. The amounts of Cu leached out from HS under exposure to HA and FA were similar to values extracted by ultrapure water. As much as 41.9 mg/kg (HA), 55.4 mg/kg (FA) and 37.5 mg/kg of Cu (UPW) was mobilized within 24 h and rose up to 126.7 mg/kg, 130.0 mg/kg and 97.7 mg/kg after 960 h of leaching (Table 5.2, Figure 5.2). Similar trends of HS behavior could be observed for Zn and Pb. The quantity of Zn mobilized within 24 h was 118.6 mg/kg (ARE pH 2.9), 61.5 mg/kg (ARE pH 4.4), 7.6 mg/kg (HA) and 9.3 mg/kg (FA). An extension of the leaching time up to the 960 h led to release of 79.6 mg/kg (ARE 2.9), 90.3 (ARE 4.4), 13.7 mg/kg (HA) and 11.7 mg/kg (FA). Amount of Zn leached out by UPW did not exceed 14.0 mg/kg throughout the experiment. The amount of Pb extracted by ARE over 24 h-960 h was maximally 23.0 mg/kg and 4.9 mg/kg for 2.9 and 4.4 initial solution pH, respectively. The amount of Pb released under exposure to HA, FA and UPW did not reach values higher than 0.4 mg/kg (Table 5.2).

### 5.3.2.2 Shaft furnace slag

The amount of Cu leached out under SFS exposure to ARE reached 300.2 mg/kg (pH 2.9) and 90.5 mg/kg (pH 4.4) within 24 h and increased up to 810.2 mg/kg and 219.4 mg/kg after 960 h of leaching. A lower release of Cu was observed in the presence of HA and FA, with a

maximum mobilization (2.0 mg/kg) after 48-168 h of leaching. The Cu concentrations in the leachates were lower (1.2-0.8 mg/kg) at the end of HA and FA experiments probably due to formation of secondary phases and subsequent metal trapping. Humic acid/fulvic acid/UPW leached out up to 0.7/1.7/0.2 mg/kg and 5.6/5.3/0.7 mg/kg for Zn and Pb, respectively. ARE (pH 2.9) solution mobilized up to 587.7 mg/kg (72 h) and 756.2 mg/kg (72 h) of Zn and Pb, respectively (Table 5.2).

### 5.3.2.3  Granulated slag

Granulated slag exposed to the ARE solutions was found to release important quantities of Cu. As much as 2127.9 mg/kg (pH 2.9) and 1387.2 mg/kg (pH 4.4) of Cu were released after 24 h of the experiments. The values reached after 960 h leaching increased slightly and comparable values (2728.7 and 1919.6 mg/kg) of Cu were determined in the leachates (ARE). Similarly, the most significant release of Zn and Pb occurred within 960 h and did not exceed the quantities of 910.5 mg/kg and 2505.9 mg/kg throughout the experiments. The maximum amount of Cu released under exposure to HA and FA was 13.6 mg/kg (960 h) and 9.9 mg/kg (72 h), whereas Cu extracted by UPW was not higher than 2.2 mg/kg (24 h). The Zn and Pb quantities extracted by HA and FA were up to 2.0 mg/kg and 1.5 mg/kg, respectively. GS exposed to UPW leaching released not more than 0.2 mg/kg of Zn and Pb (Table 5.2).

### 5.3.2.4  Lead slag

The significant release of Cu from LS occurred after 960 h of leaching (565.0 mg/kg) with ARE (pH 2.9), while concentrations at the early stage of the experiments were much lower (7.8 mg/kg). In contrast, very high quantities of Zn were released: 2767.4 mg/kg (pH 2.9) and 1307.1 mg/kg (pH 4.4) after 24 h of leaching. Zn concentrations noted after 960 h were 6462.3 and 1537.1 mg/kg for ARE pH 2.9 and pH 4.4, respectively. Similarly, the Pb content in the ARE leachates was very high and reached up to 11529.4 mg/kg (168 h). The quantity of Zn released from LS exposed to HA and FA was 692.1-1329.9 mg/kg and 494.8-2243.5 mg/kg respectively. The amount of Pb leached out was 62.3-168.3 mg/kg (HA) and 57.9-514.7 mg/kg (FA). An exposure of LS to UPW leaching extracted even up to 1015.0 (48 h) and 96.5 mg/kg (48 h) of Zn and Pb, respectively (Table 5.2).
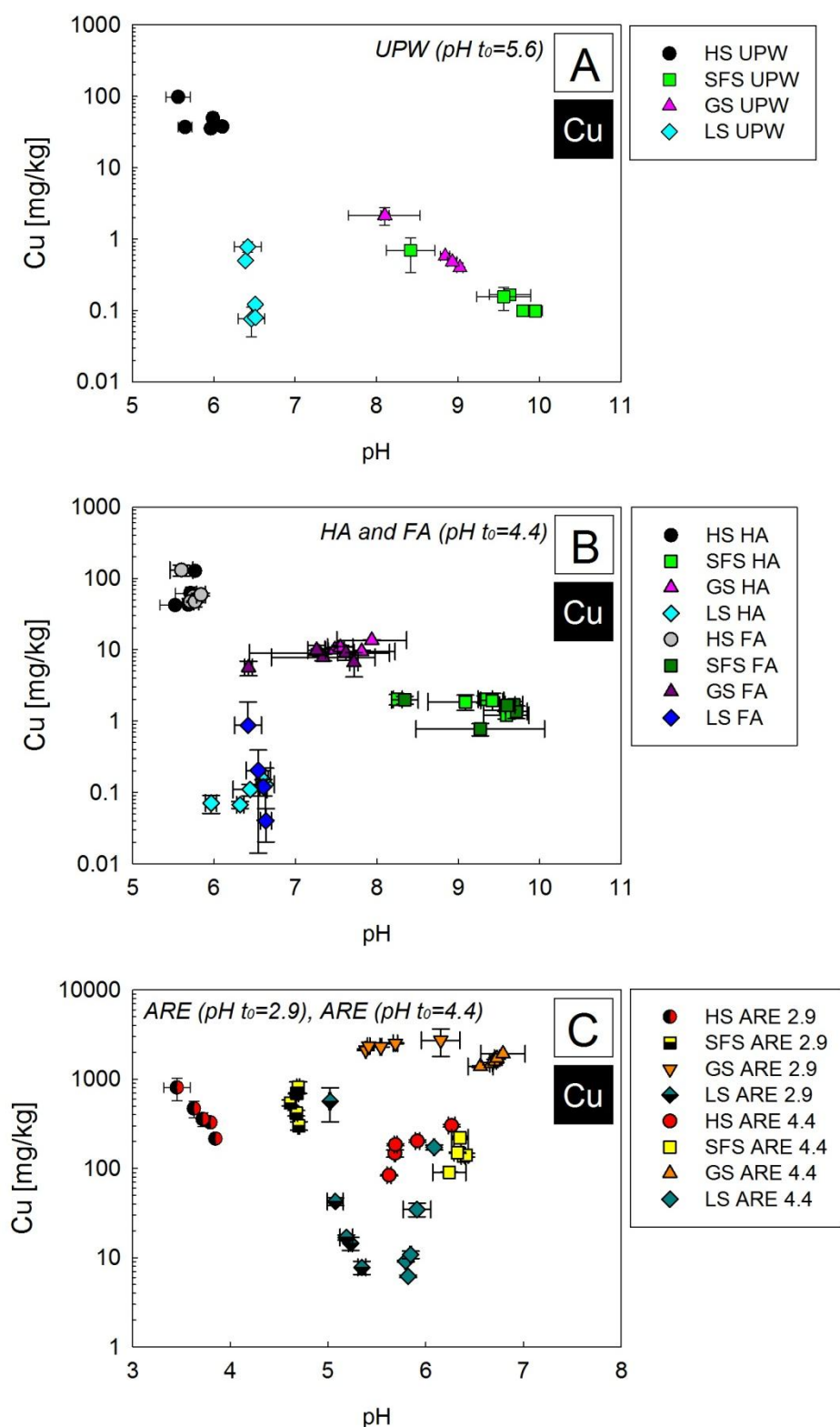
**FIGURE 5.2 The release of Cu under slags exposure to UPW (A), HA, FA (B) and ARE (pH 2.9 and 4.4) (C).**

*(HS: historical slag, SFS, shaft furnace slag, GS: granulated slag, LS: lead slag, UPW: ultrapure water, HA: humic acid, FA: fulvic acid, ARE: artificial root exudates)*
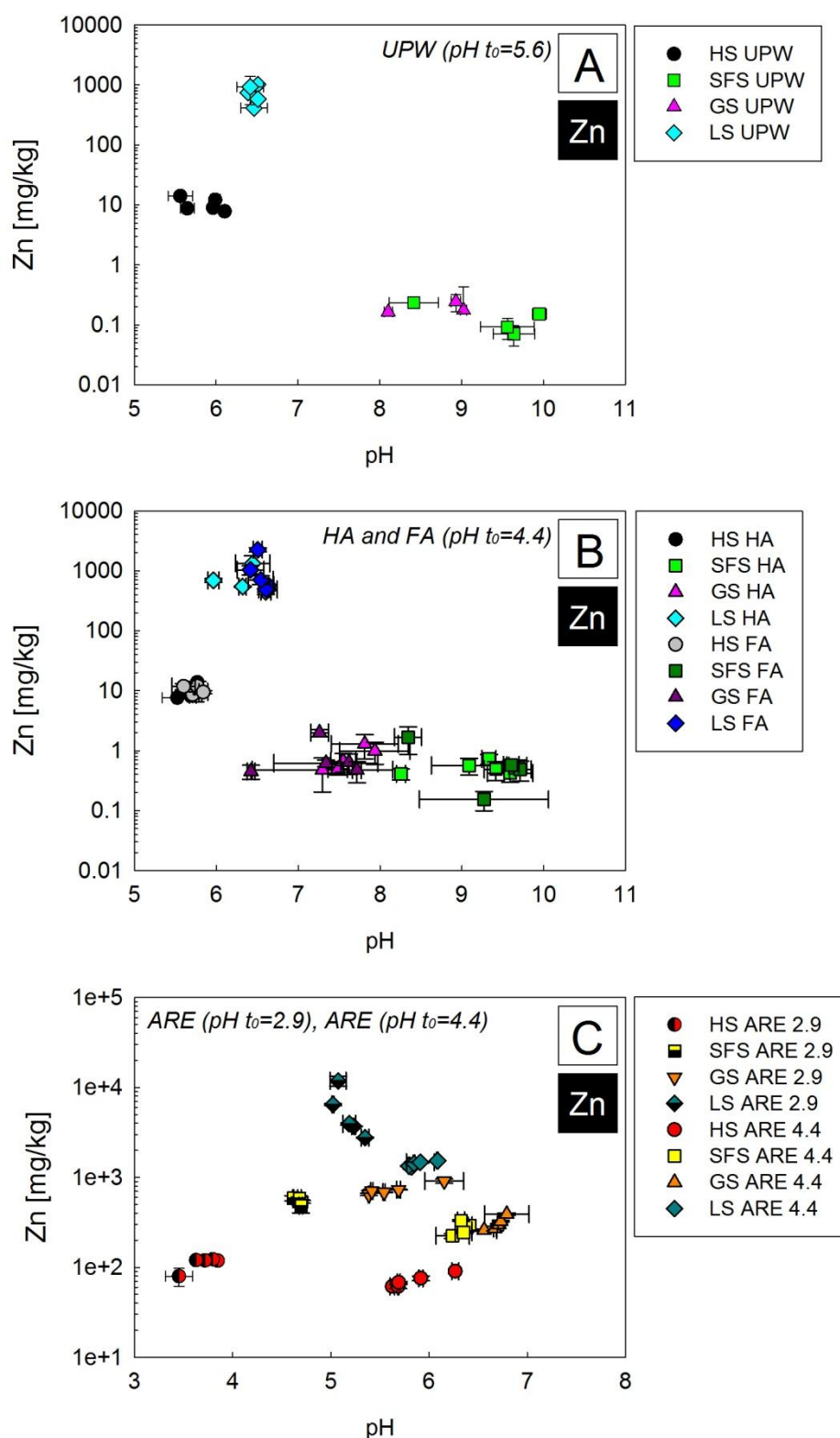
**FIGURE 5.3 The release of Zn under slags exposure to UPW (A), HA, FA (B) and ARE (pH 2.9 and 4.4) (C).**

*(HS: historical slag, SFS, shaft furnace slag, GS: granulated slag, LS: lead slag, UPW: ultrapure water, HA: humic acid, FA: fulvic acid, ARE: artificial root exudates)*
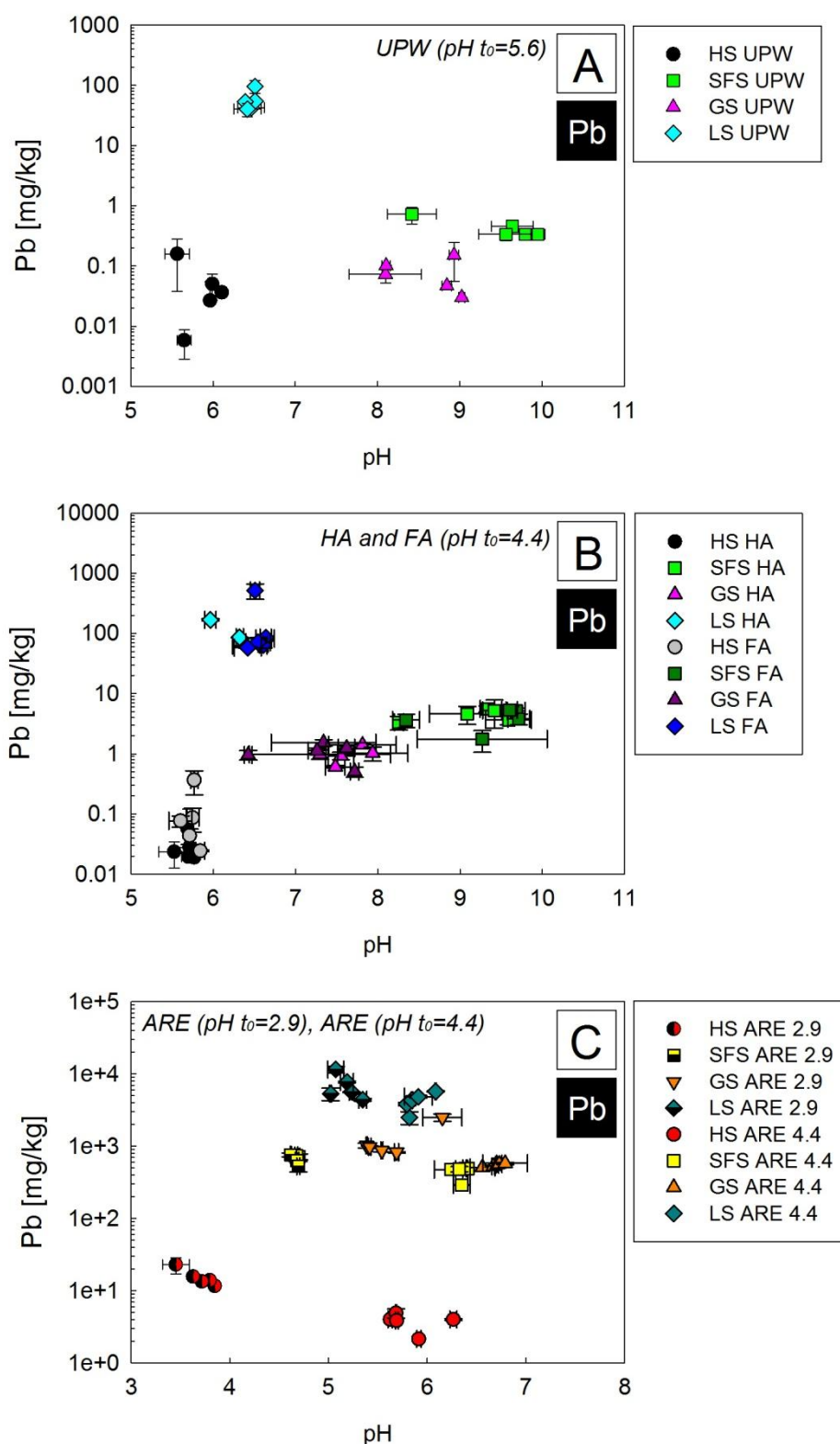
**FIGURE 5.4 The release of Pb under slags exposure to UPW (A), HA, FA (B) and ARE (pH 2.9 and 4.4) (C).**

*(HS: historical slag, SFS, shaft furnace slag, GS: granulated slag, LS: lead slag, UPW: ultrapure water, HA: humic acid, FA: fulvic acid, ARE: artificial root exudates)*

**TABLE 5.2 Amounts [mg/kg] of metals leached out from individual slags after 24 h, 48 h, 72 h, 168 h and 960 h.**

*(HS: historical slag, SFS, shaft furnace slag, GS: granulated slag, LS: lead slag, ARE: artificial root exudates, HA: humic acid, FA: fulvic acid, UPW: ultrapure water).*

**HS**

| **Cu** | **24 h** | RDS | **48 h** | RDS | **72 h** | RDS | **168 h** | RDS | **960 h** | RDS |
|---|---|---|---|---|---|---|---|---|---|---|
| ARE (pH 2.9) | 214.7 | (±18.9) | 326.2 | (±4.7) | 357.3 | (±63.2) | 468.1 | (±99.5) | 803.1 | (± 226.0) |
| ARE (pH 4.4) | 83.7 | (± 1.5) | 147.2 | (±13.5) | 184.4 | (±4.5) | 203.0 | (±6.0) | 302.0 | (± 10.1) |
| HA (pH 4.4) | 41.9 | (± 2.5) | 42.5 | (±4.3) | 45.2 | (±0.9) | 61.9 | (±13.4) | 126.7 | (± 4.6) |
| FA (pH 4.4) | 55.4 | (± 15.9) | 47.2 | (±4.6) | 47.2 | (±1.1) | 59.0 | (±2.4) | 130.0 | (± 22.4) |
| UPW (pH 5.6) | 37.5 | (± 2.5) | 49.5 | (±9.6) | 35.4 | (±4.5) | 37.0 | (±1.8) | 97.7 | (± 3.9) |
| **Zn** | | | | | | | | | | |
| ARE (pH 2.9) | 118.6 | (± 7.1) | 122.8 | (±3.8) | 119.0 | (±5.0) | 120.4 | (±3.0) | 79.6 | (± 18.0) |
| ARE (pH 4.4) | 61.5 | (± 0.5) | 61.3 | (±3.0) | 67.8 | (±1.5) | 75.6 | (±4.5) | 90.3 | (± 0.4) |
| HA (pH 4.4) | 7.6 | (± 0.8) | 8.3 | (±0.5) | 9.3 | (±2.1) | 11.1 | (±2.5) | 13.7 | (± 0.7) |
| FA (pH 4.4) | 9.3 | (± 2.8) | 8.6 | (±0.6) | 11.9 | (±2.4) | 9.5 | (±0.5) | 11.7 | (± 1.3) |
| UPW (pH 5.6) | 7.8 | (± 0.4) | 12.1 | (±2.8) | 8.9 | (±1.2) | 8.8 | (±0.4) | 14.0 | (± 1.5) |
| **Pb** | | | | | | | | | | |
| ARE (pH 2.9) | 11.6 | (± 0.5) | 13.9 | (±0.7) | 13.4 | (±1.3) | 15.6 | (±1.6) | 23.0 | (± 5.8) |
| ARE (pH 4.4) | 4.00 | (± 0.02) | 4.9 | (±0.7) | 3.85 | (±0) | 2.15 | (±0) | 4.00 | (± 0.1) |
| HA (pH 4.4) | 0.02 | (± 0.01) | 0.06 | (±0.06) | 0.02 | (±0.02) | 0.03 | (±0.01) | 0.02 | (± 0.00) |
| FA (pH 4.4) | 0.09 | (± 0.04) | 0.04 | (±0.01) | 0.36 | (±0.16) | 0.02 | (±0.00) | 0.08 | (± 0.02) |
| UPW (pH 5.6) | 0.04 | (± 0.01) | 0.05 | (±0.02) | 0.03 | (±0.03) | 0.01 | (±0.00) | 0.2 | (± 0.1) |

**SFS**

| **Cu** | **24 h** | RDS | **48 h** | RDS | **72 h** | RDS | **168 h** | RDS | **960 h** | RDS |
|---|---|---|---|---|---|---|---|---|---|---|
| ARE (pH 2.9) | 300.2 | (± 32.9) | 416.6 | (±28.9) | 541.8 | (±43.1) | 693.5 | (±8.7) | 810.2 | (± 120.5) |
| ARE (pH 4.4) | 90.5 | (± 0.8) | 137.8 | (±3.1) | 141.2 | (±7.1) | 149.9 | (±2.4) | 219.4 | (±4.0) |
| HA (pH 4.4) | 1.9 | (± 0.4) | 2.0 | (±0.2) | 1.9 | (±0.5) | 2.0 | (±0.3) | 1.2 | (± 0.1) |
| FA (pH 4.4) | 1.7 | (± 0.2) | 1.4 | (±0.3) | 2.0 | (±0.3) | 1.7 | (±0.2) | 0.8 | (± 0.2) |
| UPW (pH 5.6) | 0.1 | (± 0.0) | 0.2 | (±0.0) | 0.2 | (±0.1) | 0.1 | (±0.0) | 0.7 | (± 0.3) |
| **Zn** | | | | | | | | | | |
| ARE (pH 2.9) | 533.5 | (± 19.0) | 535.7 | (±29.7) | 587.7 | (±39.8) | 584.0 | (±18.6) | 485.6 | (± 82.1) |
| ARE (pH 4.4) | 224.4 | (± 14.4) | 277.4 | (±0) | 292.7 | (±0) | 332.5 | (±7.2) | 245.4 | (± 8.9) |
| HA (pH 4.4) | 0.6 | (± 0.2) | 0.7 | (±0.1) | 0.5 | (±0.2) | 0.4 | (±0.1) | 0.4 | (± 0.1) |
| FA (pH 4.4) | 0.6 | (± 0.1) | 0.5 | (±0.2) | 1.7 | (±0.8) | 0.6 | (±0.1) | 0.2 | (± 0.1) |
| UPW (pH 5.6) | 0.0 | (± 0.0) | 0.07 | (±0.03) | 0.09 | (±0.03) | 0.15 | (±0.02) | 0.2 | (± 0.04) |
| **Pb** | | | | | | | | | | |
| ARE (pH 2.9) | 712.0 | (± 67.5) | 740.6 | (±37.7) | 756.2 | (±48.3) | 629.6 | (±13.0) | 525.7 | (± 85.7) |
| ARE (pH 4.4) | 477.3 | (± 0.0) | 491.7 | (±0.0) | 492.0 | (±15.7) | 481.7 | (±39.2) | 290.6 | (± 3.5) |
| HA (pH 4.4) | 4.6 | (± 1.5) | 5.6 | (±0.7) | 5.2 | (±2.6) | 3.3 | (±0.9) | 3.6 | (± 0.6) |
| FA (pH 4.4) | 5.2 | (± 0.5) | 3.8 | (±0.8) | 3.6 | (±0.9) | 5.3 | (±0.7) | 1.8 | (± 0.7) |
| UPW (pH 5.6) | 0.3 | (± 0.0) | 0.5 | (±0.0) | 0.3 | (±0.1) | 0.3 | (±0.0) | 0.7 | (± 0.2) |

**GS**

| **Cu** | **24 h** | RDS | **48 h** | RDS | **72 h** | RDS | **168 h** | RDS | **960 h** | RDS |
|---|---|---|---|---|---|---|---|---|---|---|
| ARE (pH 2.9) | 2127.9 | (± 44.1) | 2345.8 | (±17.3) | 2298.6 | (±0.3) | 2526.6 | (±21.8) | 2728.7 | (± 931.5) |
| ARE (pH 4.4) | 1387.2 | (± 28.8) | 1495.3 | (±43.3) | 1595.3 | (±79.3) | 1717.2 | (±36.1) | 1919.6 | (± 7.2) |
| HA (pH 4.4) | 9.0 | (± 1.3) | 9.4 | (±0.4) | 10.1 | (±0.6) | 10.8 | (±0.8) | 13.6 | (± 0.1) |
| FA (pH 4.4) | 5.6 | (± 1.3) | 7.8 | (±0.8) | 9.9 | (±1.5) | 9.0 | (±2.0) | 6.6 | (± 2.5) |
| UPW (pH 5.6) | 2.2 | (±0.2) | 0.6 | (±0.1) | 0.4 | (±0.0) | 0.5 | (±0.1) | 2.1 | (± 0.1) |
| **Zn** | | | | | | | | | | |
| ARE (pH 2.9) | 646.5 | (± 16.9) | 705.8 | (±33.2) | 683.6 | (±3.3) | 730.1 | (±6.9) | 910.4 | (± 51.3) |
| ARE (pH 4.4) | 260.1 | (± 7.2) | 270.8 | (±14.4) | 300.4 | (±7.2) | 325.4 | (±7.2) | 391.2 | (± 10.0) |
| HA (pH 4.4) | 0.5 | (± 0.3) | 1.3 | (±0.6) | 0.5 | (±0.1) | 0.7 | (±0.2) | 1.0 | (± 0.4) |
| FA (pH 4.4) | 0.5 | (± 0.1) | 0.6 | (±0.1) | 2.0 | (±0.3) | 0.6 | (±0.2) | 0.5 | (± 0.2) |
| UPW (pH 5.6) | 0.00 | (± 0.0) | 0.00 | (± 0.0) | 0.2 | (±0.2) | 0.2 | (±0.1) | 0.2 | (± 0.01) |

| *Pb* | 24 h | RDS | 48 h | RDS | 72 h | RDS | 168 h | RDS | 960 h | RDS |
|---|---|---|---|---|---|---|---|---|---|---|
| *ARE (pH 2.9)* | 1021.9 | (± 76.4) | 979.4 | (±26.5) | 875.4 | (±45.7) | 822.0 | (±14.1) | 2505.9 | (± 292.0) |
| *ARE (pH 4.4)* | 508.8 | (± 0.9) | 527.9 | (±15.0) | 554.4 | (±15.0) | 568.2 | (±30.0) | 580.1 | (± 20.0) |
| *HA (pH 4.4)* | 1.0 | (± 0.2) | 1.4 | (±0.1) | 0.6 | (±0.0) | 0.9 | (±0.1) | 1.0 | (± 0.3) |
| *FA (pH 4.4)* | 1.0 | (± 0.2) | 1.5 | (±0.2) | 1.1 | (±0.1) | 1.2 | (±0.1) | 0.5 | (± 0.1) |
| *UPW (pH 5.6)* | 0.1 | (± 0.02) | 0.05 | (±0.00) | 0.03 | (±0.00) | 0.15 | (±0.10) | 0.1 | (± 0.0) |

**LS**

| *Cu* | 24 h | RDS | 48 h | RDS | 72 h | RDS | 168 h | RDS | 960 h | RDS |
|---|---|---|---|---|---|---|---|---|---|---|
| *ARE (pH 2.9)* | 7.8 | (±1.3) | 14.5 | (±2.4) | 16.8 | (±1.1) | 42.5 | (±4.3) | 565.0 | (± 13.0) |
| *ARE (pH 4.4)* | 6.7 | (±0.8) | 9.2 | (±0.2) | 10.8 | (±1.0) | 34.7 | (±6.0) | 172.0 | (±10.0) |
| *HA (pH 4.4)* | 0.07 | (±0.02) | 0.07 | (±0.01) | 0.13 | (±0.09) | 0.15 | (±0.00) | 0.11 | (± 0.02) |
| *FA (pH 4.4)* | 0.04 | (±0.02) | 0.04 | (±0.02) | 0.12 | (±0.03) | 0.20 | (±0.19) | 0.32 | (± 0.18) |
| *UPW (pH 5.6)* | 0.08 | (±0.03) | 0.1 | (±0.02) | 0.1 | (±0.0) | 0.5 | (±0.02) | 0.80 | (± 0.1) |
| *Zn* | | | | | | | | | | |
| *ARE (pH 2.9)* | 2767.4 | (± 41.5) | 3700.7 | (±26.4) | 3932.7 | (±137.0) | 11825.5 | (±1459.3) | 6462.3 | (± 154.1) |
| *ARE (pH 4.4)* | 1307.1 | (± 70.7) | 1345.0 | (±20.2) | 1430.7 | (±30.3) | 1470.0 | (±20.2) | 1537.1 | (±10.4) |
| *HA (pH 4.4)* | 692.1 | (± 51.5) | 544.0 | (±12.1) | 488.8 | (±25.4) | 445.7 | (±42.0) | 1329.9 | (± 454.9) |
| *FA (pH 4.4)* | 2243.5 | (±177.5) | 573.9 | (±19.3) | 494.8 | (±18.3) | 704.9 | (±115.5) | 1032.5 | (± 184.5) |
| *UPW (pH 5.6)* | 413.5 | (± 37.5) | 1015.0 | (±136.4) | 581.8 | (±25.4) | 744.0 | (±54.8) | 926.5 | (± 457.5) |
| *Pb* | | | | | | | | | | |
| *ARE (pH 2.9)* | 4391.6 | (±187.6) | 5631.9 | (±50.1) | 7735.9 | (±216.4) | 11529.4 | (±1239.1) | 5323.6 | (± 1031.7) |
| *ARE (pH 4.4)* | 2500.0 | (±505.1) | 3821.4 | (±202.0) | 4321.4 | (±0.0) | 4835.7 | (±202.0) | 5721.4 | (± 101.0) |
| *HA (pH 4.4)* | 168.3 | (± 6.6) | 85.7 | (±0.2) | 82.2 | (±7.2) | 67.0 | (±7.1) | 62.3 | (± 4.8) |
| *FA (pH 4.4)* | 514.7 | (± 146) | 85.0 | (±5.1) | 64.4 | (±6.9) | 70.8 | (±14.0) | 57.9 | (± 1.4) |
| *UPW (pH 5.6)* | 42.6 | (± 5.2) | 96.5 | (±22.4) | 54.9 | (±3.9) | 53.8 | (±2.7) | 40.3 | (± 10.2) |

### 5.3.3  SEM observations

#### 5.3.3.1   Weathering with artificial root exudates

Historical slag immersed in the ARE solution was found to have erosion features on fayalite and glass (Figure 5.5 A1) as well as important changes on sulfides structures (Figure 5.5 A2). Alteration of fayalite was similar to previously observed microbial dissolution (Chapter 5: Potysz et al., 2016b). The changes associated with exposure of SFS to the ARE solution mainly resulted in the presence of glass alteration (Figure 5.5 B1) and dissolution of sulfides (Figure 5.5 B2), however to lesser extend as compared to HS. The alterations noted on the GS surface were principally present in the form of glass fractures and removal of Cu-blebs present in glass (Figure 5.5 C1 and 5.5 C2). Weathering signatures similar to those were also observed in our previous study considering abiotic and biotic alterations (Chapter 5: Potysz et al., 2015b). Lead slag immersed in the ARE solution was found to exhibit disruption of gathered sulfide groups, especially sphalerite and pyrrhotite (Figure 5.5 D1 and 5.5 D2).

#### 5.3.3.2   Weathering with humic and fulvic acids

HA and FA were found to break-down the mineral phases present in slags (Figure 5.6), however to a lesser degree as compared to weathering features observed after ARE attack. Historical slag exhibited some signs of dissolution on metal bearing sulfides, whereas glass and fayalite remained poorly affected (Figure 5.6 A1 and A2). Likewise, SFS weathering was mainly limited to sulfide phases (Figure 5.6 B1 and B2). A modest alteration of these slags was also reflected by solution chemistry which yielded lower concentrations of metals as compared to those of ARE. Granulated slag did not show any prominent alteration features. Removal of Cu-blebs was observed (Figure 5.6 C), however their dissolution was less advanced as shown by the Cu concentration in HA/FA solutions. Etched particle surface was observed too (Figure 5.6 C). Lead slag displayed some signs of alteration primarily present as locally dissolved sulfides. Silicates such as fayalite and glass remained undisturbed (Figure 5.6 D1 and D2).
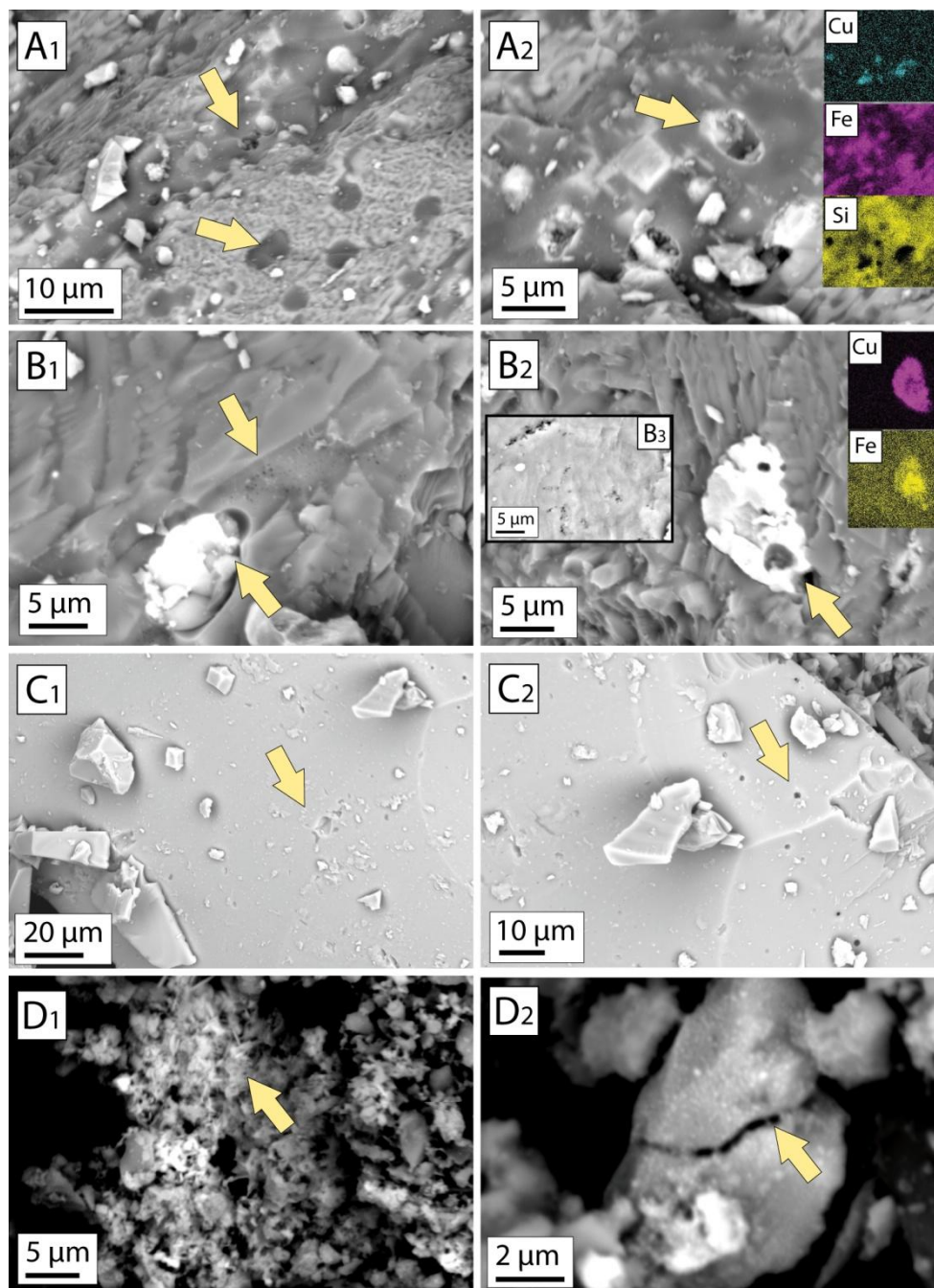
**FIGURE 5.5 Scanning electron microscopic images presenting weathering features of slags exposed to artificial root exudates solution for 960 h.**

*(A: HS, B: SFS, C: GS, D: LS)*

*Arrows indicate: A1: Glass and fayalite alteration, A2: Cu-sulfides dissolution, B1: glass alteration, B2: Cu-sulfides dissolution, B3: diopside alteration, C1: glass dissolution, C2: Cu-droplets removal, D1: fragmentation of gathered groups of sulfides, D2: Zn-sulfide break.*

**FIGURE 5.6 Scanning electron microscope images presenting weathering features of slags exposed to humic acid solution for 960 h.**

*(A: HS, B: SFS, C: GS, D: LS).*

*Arrows indicate: A1: Lack of alteration features, A2 and A3: Cu-sulfides dissolution, B1: insignificant sulfide alteration, B2 and B3: Cu-sulfides dissolution, C1: Cu-droplets removal, C2: partial dissolution of glass, D1: sulfides dissolution, D2: sulfides removal.*

# 5.4 DISCUSSION

## 5.4.1 Slags behavior under exposure to soil organic acids

The results of this study demonstrated that the behavior of metallurgical slags under exposure to organic compounds depends on their chemical and mineralogical properties and environmental conditions affecting their stability which jointly determine the weathering paths. Interactions of slags with organic acids present in soil will be driven by its acidity, binding affinity of organic molecules to metals (Figures 5.2-5.4) and susceptibility of mineral phases to alteration (Figures 5.5 and 5.6).

One of the processes responsible for slags weathering and thus metal release from mineral lattices in a soil and rhizosphere environment is the attack of mineral surfaces by dissolved organic acids. Being an important source of protons and/or complexing agents, dissolved organic acids induce mineral dissolution by proton-promoted (acidolysis) or ligands-promoted (complexolysis) mechanisms (Figure 5.1). The experimental data demonstrated various behavior of individual slags in term of pH neutralization capacity and the amounts of metals released (Figures 5.2-5.4).

The pH of the leachates shifted rapidly within 24 h and reached different values depending on slag and leaching solution used (Figure 5.2). Likewise, the most significant metal release occurred within 24 h. The concentrations changed slightly in case of humic and fulvic acids, whereas more significant changes in metal concentrations were observed when ARE was used as leaching solution. Furthermore, HA and FA had a comparable effect on metal mobilization, varied however for each slag types (Figures 5.2-5.4).

The differences in the metal leachability observed among the studied slags might be firstly ascribed to the variation of solution pH as this factor strongly governs the mobilization of metals in the environment (Ganne et al., 2006; Cappuyns & Swennen, 2008). As shown in Figures 5.2-5.4, neutralization capacity of the slags caused the increase of the pre-set solution pH. The more important pH rise was observed for SFS and GS and the lower for HS and LS. A higher increase of pH value in the solution supplemented with SFS and GS probably resulted from glass hydrolysis and proton replacement of cations entrapped in Si network (Eq. 1 and 2) (Yin et al., 2014; Potysz et al., 2016b), whereas the lower pH increase in HS- and LS- containing solution might be due to additional simultaneous sulfides dissolution and subsequent proton release (Eq. 3) (Ettler et al., 2003). Due to lack of sulfides in case of granulated slag and their low volumetric proportion in case of shaft furnace slag, acid producing reaction does not occur. In contrast a higher volumetric proportion of sulfides in the case of historical and "lead" slags make acid producing reaction likely to happen.

Moreover, sulfides dissolution is thought to proceed faster than the neutralizing reaction of silicates.

$$- Si - O - M_{(glass)} + H^+ \leftrightarrow - Si - OH_{(glass)} + M^+_{(aq)} \qquad \text{Eq. n°1}$$

$$Si - O - Si + H_2O \leftrightarrow - Si - OH + - Si - OH \qquad \text{Eq. n°2}$$

$$MS_2 + 7/2\ O_2 + H_2O \rightarrow M^{2+} + 2\ SO_4^{2-}{}_{(aq)} + 2\ H^+ \qquad \text{Eq. n°3}$$
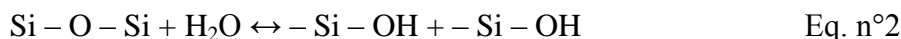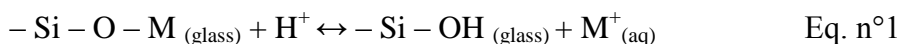
Furthermore, the variation of pH observed for slags further entails two other issues. First, the leaching of metals from slags is expected to be higher under acidic conditions. On the other hand, the complexation ability of fulvic and humic acids towards dissolved metals is higher when the pH rises (Ong et al., 1970; Spark et al., 1997). According to the literature, the formation of aqueous complexes impacts the thermodynamic equilibrium and/or locally weaken the chemical bounds of the dissolving mineral structure (Lawrence et al., 2014; Drever & Stilling, 1997; Oelkers and Schott, 1998; Welch & Ulman, 1993; Li et al., 2006; Ganor et al., 2009; Jahnson et al., 2005). That could be a reason of higher effect of HA and FA under alkaline conditions respective to the UPW control as shown for GS and SFS and their lower effect under acidic conditions demonstrated for HS and LS. A strong acidity of the ARE solution and elevated content of organic molecules consequently led to a higher reactivity of the slags under exposure to both, ARE at $t_0=4.4$ and ARE at $t_0=2.9$

## 5.4.2 Effect of humic and fulvic acids

Historical slag revealed a similar behavior in terms of Cu, Zn and Pb release when exposed to HA/FA solutions and UPW. These organic acids were found to enhance mobilization of metals by a maximal factor of 13.6 (Pb). The behavior of humic substances might be assigned to natural slag pH which was slightly acidic and thus the final pH solution of HA and FA did not go beyond 5.8. Moreover, the general susceptibility of slag to leach out the metals under the conditions tested was generally high even under exposure to UPW due to its slightly acidic natural pH. Similar observation applies to LS, which released similar quantities of metals under exposure to HA/FA and UPW. In case of LS, HA/FA increased the metal release by the maximal factor of 1.6 (Cu), 5.4 (Zn) and 12.1 (Pb), while the values obtained for HS did not exceed 1.7 (Cu), 1.3 (Zn) and 13.6 (Pb). It has to be emphasized that the pH neutralization capacity of these materials (HS and LS) was less pronounced as compared to two other slags (*i.e.* GS and SFS). GS and SFS readily served as pH neutralizers which resulted in final alkaline conditions already within 24 h.

The leaching of metals was generally lower for SFS and GS as compared to HS and LS. However, the impact of humic and fulvic acids on metal release from SFS and GS was higher compared to UPW. HA/FA amplified the release of metals even by a factor of 20.5 (Cu), 18.1

(Zn), 15.8 (Pb) in the case of SFS and 25.4 (Cu), 11.3 (Zn), 37.5 (Pb) in the case of GS, respectively. A larger difference between UPW and organic acids leaching observed for SFS and GS than that for HS and LS could be due to the higher HA and FA affinity to metals under alkaline conditions (Ong et al., 1970; Spark et al., 1997). That statement is in agreement with Wang and Mulligan (2009) who demonstrated enhanced mobilization of metals (*e.g.* Cu, Pb, Zn) from mine tailings under alkaline conditions.

Wu et al. (2002) pointed out that Cu -humate and -fulvate complexes are the only dissolved Cu species at pH above 8. A similar observation has been done by Spark et al. (1997) who pointed out that the presence of HA at high pH prevents precipitation of metals with salts and forms soluble humate complexes. Furthermore, Güngör & Bekbölet (2010) stated that the effect of HA on Zn release at pH 5 is attributed to acidity effect, whereas increase of pH, which led to an increase of Zn release might be related to the contribution of other functional groups (*e.g.* phenolic) enhancing metal mobilization process. Furthermore, various behaviours of metals might also be due the competition of individual metals for different functional groups of organic ligands (Kerndorff & Schnitzer, 1980) as well as binding strength (Güngör & Bekbölet, 2010). Competitive interactions might occur when only a restricted number of active sites is available for complex formation and depends on the pH conditions which strongly influence the stability of formed complexes (Kerndorff & Schnitzer, 1980; Güngör & Bekbölet, 2010). In general, the effect of HA/FA on metal mobilization in this study was comparable that is in accordance with the study of Alberts and Filip (2010) showing a comparable effect of HA/FA on Cu binding.

In this study, the effect of major cations on the complexation with HA/FA (20 mg/L) was not taken into account. However, as indicated by Reuter & Perdue (1977), the humic acid concentration at the level of 10 mg/L has a significant contribution towards metals complexation even when major cations occur. Nevertheless, the competition of major cations could likely take place in such systems whereby alkaline earth elements such as Ca and Mg would have an important competing behavior (Tipping, 1993). Furthermore, cations such as Fe and Al can also be involved in competing reaction and affect complexation of trace metals (Tipping et al., 1992).

## 5.4.3  Effect of artificial root exudates

Artificial root exudates (pH 2.9 and 4.4) enhanced the metals release from all studied slags. A higher release of metals in ARE solution pre-set at pH of 2.9 as compared to ARE pre-set at pH 4.4 may surely be due to the strong solution acidity. Lower pH led to more extensive dissolution of slags and metal release (Figures 5.2-5.4). Consequently, the surface area exposed to further attack of ARE solutions undoubtedly increased. For example, Fedje et al. (2010) demonstrated that more aggressive leaching solutions (*e.g.* pH~0) could increase fly

ash particle surface size even by a factor 4 up to 6 due to greater dissolution and subsequent increase of reactive surface of the solid material.

Even though the initial ARE pH was adjusted to the same value (4.4) as HA and FA, ARE were still found to have a much greater impact on metal release than HA and FA. It relates to the more complex composition of the ARE solution, which contained a number of metal complexing molecules (*e.g.* citric, lactic, succinic acids) and additionally at higher concentration level (g/L) compared to this of HA/FA (mg/L). Citric acid has been previously reported as a strong Zn complexing agent (Burckhard et al., 1995; Ettler et al., 2009). Fedje et al. (2010) demonstrated that lactic acid shows a greater affinity to form complexes with Cu and Pb compared to Zn. Likewise, Mench & Martin (1991) revealed increased Cu solubility by root exudates, while lacking effect on Zn. In contrast, Treeby et al. (1989) demonstrated that root exudates increase the metal mobilization with a higher effect observed for Zn as compared to Cu. As shown by Mench et al. (1988), complexation of metals with root exudates at pH 5 corresponds to the order of Cu>Pb>Zn. In our study, the effect of root exudates was different for individual slags due to different chemical and mineralogical composition and various slag susceptibilities to dissolution (discussed below). However, the presence of various complexing compounds exhibiting high affinity towards different metals collectively contributed to a larger metal extraction as compared to effects of HA and FA.

## 5.4.4 Effect of phase composition on slag alteration

An exposure of slags to organic solutions resulted in different proportions of leached metals for individual slags. Therefore, besides the factor of affinity of organic acids to metals, slags phase composition also determined the variability in metal extraction. As shown in Figure 5.5, historical slag was found to exhibit dissolution features on fayalite ($Fe^{2+}_2SiO_4$) and sulfides under exposure to ARE solutions. Dissolution of olivine [$(Mg^{2+}, Fe^{2+})_2SiO_4$] by organic ligand complexation and acid attack (*e.g.* citric, oxalic) has been already reported (Siever & Woodford, 1979; Barman et al., 1992; Wogelius & Walther, 1992). The weathering record shown by SEM revealed alteration features on HS and SFS sulfides for all the organic solutions tested. The effect of HA on the stability of Cu-bearing sulfides such as chalcopyrite and chalcocite has been already shown by Baker (1973). The author demonstrated that HA mobilizes up to 220 times higher amounts of metals compared to water within 24 h of contact time. In contrast, the effect of HA on the dissolution of the studied slags was lower, likely due to encapsulation of principal metal carriers (e.g. sulfides) within silicate matrix (i.e. glass and fayalite) restricting their exposure to leaching agent.

An alteration of diopside ($FeCaSi_2O_6$) was solely observed when ARE was used as solution. That is in accordance with Sergey et al. (2006) who pointed out that diopside displays a low susceptibility to organic ligands, unless they are present in high concentrations. For GS the removal of Cu-blebs accounted the most to release important quantities of Cu, whereas glass

dissolution likely contributed to the release of other metals (i.e. Zn and Pb). Dissolution of silicate glass has previously been demonstrated by Welch & Ulman (1996). Lead slag was found to be more affected by the ARE solution than HA/FA. Partial decomposition of sphalerite [(Zn,Fe)S] yielded a high Zn content in the leachates. Furthermore, metallic lead present in fresh samples (Chapter 4: Potysz et al., 2016a) was hardly found in LS exposed to HA/FA and ARE, thus the contribution of this metal by Pb-bearing intermetallic phases is assumed to be important. In contrast, LS exhibit very low leaching of Cu. As stated by Cao et al. (1995) excess of Pb might decrease Cu complexation. On the other hand, general susceptibility of LS to leach out Cu is low as demonstrated under pH-stat conditions (Chapter 4: Potysz et al., 2016a).

## 5.4.5 Environmental considerations and perspectives

The weathering case considered in this study included only impact of organic acids on mobilization of metals from the slags. Mobilization of metals from mineral phases present in slag is driven by prevailing pH variations, however it has to be emphasized that a real dumping scenario would involve many other factors including activity of microbial organisms, sorption of metals on soil particles as well as precipitation of secondary phases. All of these processes acting together would undoubtedly modify the real weathering rates through hindering or facilitating migration of elements depending on the actual conditions faced. For example, the activity of microorganisms (not considered in this study) could affect slag dissolution in double way. First, organic acids could serve for microorganisms as energy source which could further lead to mineralization of organic compounds or decomposition of soil organic matter (Jones, 1998). For example, Banks et al. (1994) demonstrated that the release of Zn from mine tailings was inversely proportional to the acid concentration due to organic acid degradation by microorganisms. On the other hand, microbial activity, related metabolites as well as the presence of the multi-species communities in the soil and rhizosphere environment could increase degradation of mineral phases present in slags at various pH, Eh conditions and thus enhance the release of elements. As shown by previous studies, the presence of bacteria (*e.g. Pseudomonas aeruginosa*) significantly contributed to alteration of the mineral phases in slags (Yin et al., 2014; van Hullebusch et al., 2015; Potysz et al., 2016b). Therefore, a deeper study including the presence of microbial organisms would be required in order to separate the effect of organic acids themselves and microbial activity. Furthermore, a comparison of slags behavior under pH-stat conditions could be done in order to separate the effect of acidolysis and complexolysis, while column tests could be useful to represent a scenario closer to what is occurring in the field (Seignez et al., 2008). The precipitation of secondary phases such as Fe-oxyhydroxides, carbonates, sulfates in the field conditions could also serve as sorbent for metals and thus hinder their mobility (Lottermoser, 2002; Ettler et al., 2004). Therefore, a detailed analysis of secondary phases formation is

further required to complete the study of the fate of the released metals from the weathered slags in dump sites. In addition, a consideration of redox potential in such environmental systems would be interesting since conditional changes might affect metal speciation, hence its mobility and bioavailability. Most of mineral phases present in slag would rather be expected to exhibit low solubility under reductive conditions, nevertheless metal sorbed on secondarily formed Fe and Mn-oxides might become mobile. Therefore, redox potential is relevant for assessing the mobility of metals resulting from slags weathering when considering soil system as a whole.

It is noteworthy that the vegetation cover of slag dumps which are good prevention for erosion and particle dispersion by wind, may not always be a good remediation solution for the dual reason of root exudation and possibly insufficient metal uptake and/or toxic effects on plants growing there (Houben et al., 2013; Bunzl et al., 2001). Therefore, potential counterbalance between metal mobilization by root exudates as well as accumulation dynamic and capacity of plants need to be estimated. Additionally, the factors such as plant species diversity, the growth density and uptake capacity are also decisive. Therefore, all these aspects should be considered when designing a remediation strategy for slag dumping sites.

## 5.5  CONCLUSIONS

The study demonstrated that Cu-slags originating from different time periods of industrial activities (historical and modern) and smelting technologies are susceptible to dissolution in the presence of soil organic acids (artificial root exudates, humic and fulvic acids). The artificial root exudates, composed of low molecular weight organic acids have a higher impact on Cu, Zn and Pb mobilization regardless of initial solution pH compared to the more complex, larger humic and fulvic acids. Furthermore, humic and fulvic acids were found to have a comparable impact on the mobilization of metals from slags. Under alkaline conditions, weak organic acids were found to have a higher impact on metal mobilization as compared to effect of ultrapure water. Clear differences in terms of metal release were noted for the four types of Cu-slags studied. Different behavior of these materials is strictly related to their characteristics (chemical and phase composition) reflecting various susceptibilities to dissolution under the investigated conditions. Therefore, our study highlighted the need of detailed material characterization in order to predict the environmental risks related with the release of metals from pyrometallurgical slags subjected to weathering in soils or covered dumps.

## ACKNOWLEDGEMENTS

# REFERENCES

1.  **Alberts J.J. & Filip Z. (1998):** *„Metal binding in estuarine humic and fulvic acids: FTIR analysis of humic acid-metal complexes"*. Environmental Technology 19 (9), 923-931.

2.  **Baker W.E. (1973):** *„The role of humic acids from Tasmanian podzolic soils in mineral degradation and metal mobilization".* Geochimica et Cosmochimica Acta 37 (2), 269-281.

3.  **Banks M.K., Waters C.Y., Schwab A.P. (1994):** *„*Influence of organic acids on leaching of heavy metals from contaminated mine tailings". Journal of Environmental Science & Health Part A 29 (5), 1045-1056.

4.  **Barman A.K., Varadachari C., Ghosh K. (1992):** *„Weathering of silicate minerals by organic acids. I. Nature of cation solubilisation".* Geoderma 53 (1), 45-63.

5.  **Baudoin E., Benizri E., Guckert A. (2003):** *„Impact of artificial root exudates on the bacterial community structure in bulk soil and maize rhizosphere".* Soil Biology and Biochemistry 35 (9), 1183-1192.

6.  **Bennett P.C. (1991):** *„Quartz dissolution in organic-rich aqueous systems".* Geochimica et Cosmochimica Acta 55 (7), 1781–1797.

7.  **Bunzl K., Trautmannsheimer M., Schramel P., Reifenhäuser W. (2001):** *„Availability of arsenic, copper, lead, thallium, and zinc to various vegetables grown in slag-contaminated soils".* Journal of Environmental Quality 30 (3), 934-939.

8.  **Burckhard S.R., Schwab, A.P., Banks, M.K. (1995):** *„The effects of organic acids on the leaching of heavy metals from mine tailings".* Journal of Hazardous materials 41 (2), 135-145.

9.  **Cao Y., Conklin M., Betterton E. (1995).** *„Competitive complexation of trace metals with dissolved humic acid".* Environmental Health Perspectives 103 (1), 29.

10. **Cappuyns V. & Swennen R. (2008):** *„The application of pH stat leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials".* Journal of Hazardous Materials 158 (1), 185-195.

11. **Chin Y.P., Aiken G., O'Loughlin E. (1994):** *„Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances".* Environmental Science & Technology 28 (11), 1853-1858.

12. **Dakora F.D. & Phillips D.A. (2002):** *„Root exudates as mediators of mineral acquisition in low-nutrient environments".* Plant and Soil 245 (1), 35-47.

13. **Degryse F., Verma V.K., Smolders E. (2008):** *„Mobilization of Cu and Zn by root exudates of dicotyledonous plants in resin-buffered solutions and in soil".* Plant and Soil 306 (1), 69-84.

14. **Derver J.I. & Stillings L.L. (1997):** *„The role of organic acids in mineral weathering".* Colloids and Surfaces A: Physicochemical and Engineering Aspects 120 (1), 167-181.

15. **Drever J.I. & Vance G.F. (1994):** *„Role of Soil Organic Acids in Mineral Weathering Processes".* Organic Acids in Geological Processes Chapter 6, 138-161.

16. **Ettler V., Johan Z., Kříbek B., Šebek O., Michaljevič M. (2009):** *„Mineralogy and environmental stability of slags from Tsumeb smelter. Namibia".* Applied Geochemistry 24 (1), 1-15.

17. **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 (7), 567- 577.

18. **Ettler V., Piantone P., Touray J.C. (2003):** *„Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long- term assessment".* Mineralogical Magazine 67 (6), 1269-1283.

19. **Fedje K.K., Ekberg, C., Skarnemark, G., Steenari, B.M. (2010):** *„Removal of hazardous metals from MSW fly ash—an evaluation of ash leaching methods".* Journal of Hazardous Materials 173 (1), 310-317.

20. **Fernández-Caliani J.C., Ríos G., Martínez J., Jiménez F. (2012):** *„Occurrence and speciation of copper in slags obtained during the pyrometallurgical processing of chalcopyrite concentrates at the Huelva smelter (Spain)".* Journal of Mining and Metallurgy 48 (2), 161-171.

21. **Fu P., Wu F., Liu C.Q., Wei Z., Bai Y., Liao H. (2006):** *„Spectroscopic characterization and molecular weight distribution of dissolved organic matter in sediment porewaters from Lake Erhai, Southwest China".* Biogeochemistry 81 (2), 179-189.

22. **Ganne P., Cappuyns V., Vervoort A., Buvé L., Swennen R. (2006):** *„Leachability of heavy metals and arsenic from slags of metal extraction industry at Angleur (eastern Belgium)".* Science of The Total Environment 356 (1), 69-85

23. **Ganor J., Reznik I.J., Rosenberg Y.O. (2009)**: *„Organics in Water-Rock Interactions*. In: *Thermodynamics and Kinetics of Water-Rock Interaction"*. (Eds. E. H. Oelkers and J. Schott). Springer–Verlag. pp. 259–369.

24. **Güngör E.B.Ö. & Bekbölet M. (2010):** *„Zinc release by humic and fulvic acid as influenced by pH, complexation and DOC sorption"*. Geoderma 159 (1), 131-138.

25. **Hinsinger P. (2001):** *„Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review"*. Plant and Soil 237 (2), 173-195.

26. **Houben D., Couder E., Sonnet P. (2013):** *„Leachability of cadmium, lead, and zinc in a long-term spontaneously revegetated slag heap: implications for phytostabilization"*. Journal of Soils and Sediments 13 (3), 543-554.

27. **Jahnson S.B., Yoon T.H., Brown G.E. (2005):** *„Adsorption of organic matter at mineral/water interfaces: 5. Effects of adsorbed natural organic matter analogues on mineral dissolution"*. Langmuir 21 (7), 2811–2821.

28. **Jones D.L. & Darrah P.R. (1994):** *„Role of root derived organic acids in the mobilization of nutrients from the rhizosphere"*. Plant and Soil 166 (2)**,** 247-257.

29. **Jones L.D. (1998):** *„Organics acids in the rhizosphere-a critical review"*. Plant and Soil 205 (1)**,** 1849-1859.

30. **Kerndorff H. & Schnitzer M. (1980):** *„Sorption of metals on humic acid"*. Geochimica et Cosmochimica Acta 44 (11), 1701-1708.

31. **Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Neel C., Ettler V., Mihaljevic M. (2013):** *„Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland).* Journal of Geochemical Exploration 124, 183-194.

32. **Lawrence C., Harden J., Maher K. (2014):** *„Modeling the influence of organic acids on soil weathering"*. Geochimica et Cosmochimica Acta 139, 487-507.

33. **Li J., Xu R., Tiwari D., Ji G. (2006):** *„Effect of low-molecular-weight organic acids on the distribution of mobilized Al between soil solution and solid phase"*. Applied Geochemistry 21 (10), 1750-1759.

34. **Lottermoser B.G. (2002)**: *„Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia"*. Mineralogical Magazine 66 (4), 475-490.

35. **Manz M. & Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District, Mexico"*. Environmental Pollution 98 (1), 7-13.

36. **Mench M. & Martin E. (1991):** *„Mobilization of cadmium and other metals from two soils by root exudates of Zea mays L., Nicotiana tabacum L. and Nicotiana rustica L"*. *Plant and Soil 132* (2), 187-196**.**

37. **Mench M., Morel J.L., Guckert A., Guillet B. (1988):** *„Metal binding with root exudates of low molecular weight"*. Journal of Soil Science 39 (4), 521-527.

38. **Millet M., Wortham H., Sanusi A., Mirabel P. (1997):** *„Low molecular weight organic acids in fogwater in an urban area: Strasbourg (France)"*. Science of the Total Environment 206 (1), 57-65.

39. **Mostofa K.M., Liu C.Q., Feng X., Yoshioka T., Vione D., Pan X., Wu F. (2013):** *„Complexation of Dissolved Organic Matter with Trace Metal Ions in Natural Waters"*. In: Photobiogeochemistry of Organic Matter, 769-849. Springer Berlin Heidelberg.

40. **Nederlof M.M., Van Riemsdijk W.H., De Haan F.A.M. (1993):** *„Effect of Ph on The Bioavailability of Metals in Soils"*. Integrated Soil and Sediment Research: A Basis for Proper Protection Soil & Environment 1, 215-219.

41. **Oelkers E.H. & Schott J. (1998):** *„Does organic acid adsorption affect alkali-feldspar dissolution rates?"* Chemical Geology 151 (1), 235-245.

42. **Ong H.L., Swanson V.E., Bisqu R.E. (1970):** *„Natural organic acids as agents of chemical weathering"*. US Geological Survey Professional Paper 700, 130-137.

43. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California"*. Applied Geochemistry 16 (14), 1567–1593.

44. **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"*. Applied Geochemistry 19 (7), 1039-1064.

45. **Potysz A., Grybos M., Kierczak J., Guibaud G., Lens P.N.L., van Hullebusch E.D. (2016b):** *„Bacterially-mediated weathering of crystalline and amorphous Cu-slags"*. Applied Geochemistry 94, 92-106.

46. **Potysz A., Kierczak J., Fuchs Y., Grybos M., Guibaud G., Lens P.N.L, van Hullebusch E.D. (2016a):** *„Characterization and pH-dependent leaching behaviour of historical and modern copper slags"*, Journal of Geochemical Exploration 160, 1-15.

47. **Potysz A., van Hullebusch E.D., Kierczak J., Grybos M., Lens P.N.L., Guibaud, G. (2015): „***Copper Metallurgical Slags–Current Knowledge And Fate: A Review"**.** Critical Reviews in Environmental Science and Technology 45 (22), 2424-2488.

48. **Pribyl D.W. (2010):** *„A critical review of the conventional SOC to SOM conversion factor"*. Geoderma 156 (3), 75-83.

49. **Radetzki M. (2009):** *„Seven thousand years in the service of humanity-the history of copper the red metal"*. Resources Policy 34 (4), 176-184.

50. **Rashid M.A. (1971):** *„Role of humic acids of marine origin and their different molecular weight fractions in complexing di-and tri-valent metals"*. Soil Science 111 (5), 298-306.

51. **Reuter J.H. & Perdue E.M. (1977):** *„Importance of heavy metal-organic matter interactions in natural waters"*. Geochimica et Cosmochimica Acta 41 (2), 325-334.

52. **Roy A., Basu S.K., Singh K.P. (2002):** *„Modeling ecosystem development on blast-furnace slag dumps in a tropical region"*. Simulation 78 (9), 531-542.

53. **Schmukat A., Duester L., Ecker D., Heininger P., Ternes T.A. (2013):** *„Determination of the long-term release of metal(loid)s from construction materials using DGTs"*. Journal of Hazardous Materials 260, 725-732.

54. **Schmukat A., Duester, L., Ecker, D., Schmid, H., Heil, C., Heininger, P., Ternes, T.A. (2012):** *„Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength"*. Journal of Hazardous Materials 227, 257-264.

55. **Schott J. & Berner R.A. (1983):** *„X-ray photoelectron studies of the mechanism of iron silicate dissolution during weathering"*. Geochimica et Cosmochimica Acta 47 (12), 2233-2240.

56. **Schulten H.R., & Schnitzer M. (1993):** *„A state of the art structural concept for humic substances"*. Naturwissenschaften 80 (1), 29-30.

57. **Seignez N., Gauthier A., Bulteel D., Damidot D., Potdevin J. L. (2008):** *„Leaching of lead metallurgical slags and pollutant mobility far from equilibrium conditions"*. Applied Geochemistry 23 (12), 3699-3711.

58. **Shi C., Meyer Ch., Behnoodc A. (2008):** *„Utilization of copper slag in cement and concrete".* Resources, Conservation and Recycling 52 (10), 1115–1120.

59. **Siever R. & Woodford N. (1979):** *„Dissolution kinetics and the weathering of mafic minerals"*. Geochimica et Cosmochimica Acta 43 (5), 717-724.

60. **Sobanska S., Ledesert B., Deneele D., Laboudigue A. (2000):** *„Alteration in soils of slag particles resulting from lead smelting".* Earth and Planetary Sciences 331 (4), 271-278.

61. **Spark K.M., Wells, J.D., Johnson, B.B. (1997):** *„The interaction of a humic acid with heavy metals"*. Australian Journal of Soil Research 35 (1), 89-101.

62. **Sposito G. (2008):** *„The Chemistry of Soils",* NY: Oxford University Press, 2$^{nd}$ edition.

63. **Stobrawa K. & Lorenc-Plucińska G. (2008):** *„Thresholds of heavy-metal toxicity in cuttings of European black poplar (Populus nigra L.) determined according to antioxidant status of fine roots and morphometrical disorders"*. Science of The Total Environment 390 (1), 86–96.

64. **Strobel B.W. (2001):** *„Influence of vegetation on low-molecular-weight carboxylic acids in soil solution—a review"*. Geoderma 99 (3), 169-198.

65. **Tipping E. (1993):** *„Modeling the competition between alkaline earth cations and trace metal species for binding by humic substances"*. Environmental science & technology 27 (3), 520-529.

66. **Tipping E., Rey-Castro C., Bryan S.E., & Hamilton-Taylor J. (2002):** *„Al (III) and Fe (III) binding by humic substances in freshwaters, and implications for trace metal speciation"*. Geochimica et Cosmochimica Acta 66 (18), 3211-3224.

67. **van Hees P.A.W., Lundström U.S., Giesler R. (2000):** *„Low molecular weight organic acids and their Al-complexes in soil solution—composition, distribution and seasonal variation in three podzolized soils"*. Geoderma 94 (2), 173-200.

68. **van Hullebusch E.D., Yin N-H., Seignez N., Labanowski J., Gauthier A., Lens P.N.L., Avril C., Sivry Y. (2015):** *„Bio-alteration of metallurgical wastes by Pseudomonas aeruginosa in a semi flow-through reactor"*. Journal of Environmental Management 147, 297-305.

69. **Wang S. & Mulligan C.N. (2009):** „*Enhanced mobilization of arsenic and heavy metals from mine tailings by humic acid*". Chemosphere 74 (2), 274-279.

70. **Welch S.A. & Ullman W.J. (1993):** „*The effect of organic acids on plagioclase dissolution rates and stoichiometry*". Geochimica et Cosmochimica Acta 57 (12), 2725-2736.

71. **Welch S.A., & Ullman W.J. (1996):** „*Feldspar dissolution in acidic and organic solutions: Compositional and pH dependence of dissolution rate*". Geochimica et Cosmochimica Acta 60 (16), 2939-2948.

72. **Wogelius R.A. & Walther J.V. (1992):** „*Olivine dissolution kinetics at near-surface conditions*". Chemical Geology 97 (1), 101-112.

73. **Wu J., West L.J., Stewart D.I. (2002):** „*Effect of humic substances on Cu (II) solubility in kaolin-sand soil*". Journal of Hazardous Materials 94 (3), 223-238.

74. **Yin N., H., Sivry Y., Avril C., Borensztajn S., Labanowski J., Malavergne V., Lens P. N. L., Rossano S., van Hullebusch E. D. (2014):** „*Bioweathering of lead blast furnace (LBF) metallurgical slags by Pseudomonas aeruginosa",* International Biodeterioration & Biodegradation 86 (C), 372-381.

# Preface to Chapter 6

Chapter 5 describes the interactions of slags with soil organic acids and demonstrates that slags susceptibility to weathering depends on their chemical and mineralogical composition, natural pH of slag and organic acids concentrations that jointly determine potential risk that might be encountered in the environment. Nevertheless, it is worth to highlight that the real environmental scenario evolves many other factors that might also play a role in the enhancement or inhibition of the weathering amplitude. The activity of microorganisms and their impact on mobilization of metals from slags as is interesting for consideration. The latter are omnipresent and diverse in the environment. Even though these microorganisms occur at micro scale, their contribution to geochemical cycle of the elements is well known phenomenon. According to information presented in the literature, various minerals such as silicates, glass and sulfides undergo weathering when exposed to action of microorganisms. The extent of alteration varies from one mineral to another and is also specific to deteriorative potential of microorganism acting. As slags are composed of synthetic analogues of minerals, microbially-assisted weathering is likely to happen and is therefore worth of evaluating. The potential interaction of bacteria with slag is presented in flowchart below and more detailed description of bioweathering processes might be found elsewhere (Chapter 2 and introduction section Chapter 6).
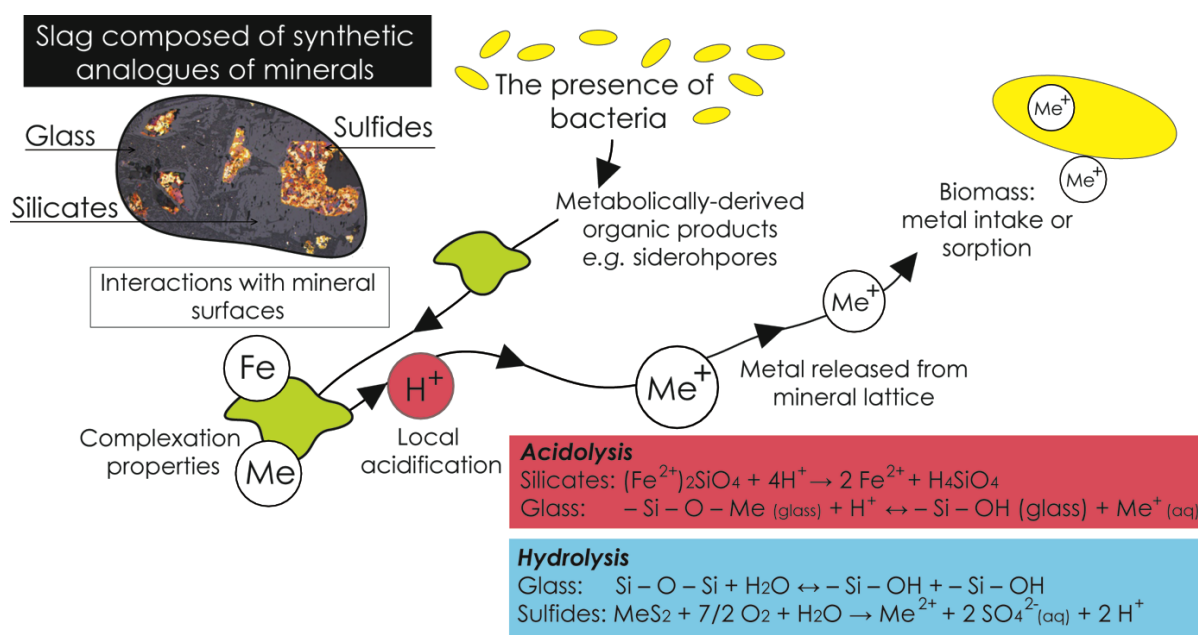


**FIGURE 5.7 Bioweathering mechanisms.**

In these regards, Chapter 6 presents impact of microbial activity on geochemical stability of Cu-slags. The experimental conditions were designed such that the experiments simulate column-like set-up with the solution residence time of 14 days. Bacteria *Pseudomonas aeruginosa* has deliberately been employed due to its common presence in various environmental components that makes this specie ideally suited as weathering agent.

# CHAPTER 6

# BACTERIALLY-MEDIATED WEATHERING OF CRYSTALLINE AND AMORPHOUS Cu-SLAGS

# ABSTRACT

Two types of Cu-slags (CS: crystalline massive slag and GS: granulated amorphous slag) exhibiting a different chemical and mineral phase composition were compared with respect to their susceptibility to bacterial weathering using *Pseudomonas aeruginosa* (n° CIP 105094). Abiotic conditions *e.g.* sterile growth medium and ultrapure water were used for comparison. The experiments were extended up to 112 days with a systematic liquid phase renewal every 14 days. The results revealed significant release of elements in the bacterially mediated weathering experiments. Concentrations of elements (Si, Fe, Cu, Zn and Pb) in the biotic solutions were increased at least by 20% up to 99% compared to abiotic ones. From 3 to 77% of the leached elements were associated to the fraction >0.22 µm. Scanning electron microscopic observations demonstrated greater weathering of mineral phases in biotic experiments than in abiotic ones which is in accordance with the solution chemistry exhibiting higher concentrations of elements leached in biotic set-ups. In the case of CS, glass and sulfides weathering was yet observed in abiotic experiment, whereas partial dissolution of fayalite ($Fe_2SiO_4$) was solely affected by the presence of bacteria. GS having a higher bulk content of metallic elements was found to be more stable than sulfide-bearing CS, while its (GS) glass matrix was found to weather easier under biotic conditions.

**Keywords:** Cu-slags, (bio)weathering, *Pseudomonas aeruginosa*, leaching (Si, Fe, Cu, Zn, Pb).

# 6.1 INTRODUCTION

Copper pyrometallurgical slags constitute important by-products with respect to their volume of production and high residual content of metallic elements depending on the ore origin and characteristic of the industrial process. Due to a lack of sustainable practices in the past, slags disposal has been a common manner, regardless of the weathering and its potential environmental consequences. As a result, there are many industrial areas where slags have been proven to be a source of metallic pollution of the surrounding soils, sediments, and surface waters (*e.g.* Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Piatak et al., 2004; Kierczak et al., 2013; Ettler & Johan, 2014). At present, Cu-slags are often used as secondary raw materials, for example in coastal engineering in north Germany (Schmukat et al., 2012). However, some studies pointed out that such application of Cu-slags could lead to deleterious consequences for the environment (Schmukat et al., 2012). Consequently, slags weathering has gained essential importance for environmental reasons. However, most studies regarding slags weathering have focused on physico-chemical aspects of the process (*e.g.* Sobanska et al., 2000; Parsons et al., 2001; Ettler et al., 2004; Seignez et al., 2006; Kierczak et al., 2009; Tyszka et al., 2014), whereas impact of microbial activity is often neglected and very few publications concerning this issue can be found in the literature (Yin et al., 2014; van Hullebusch et al., 2015).

Bioweathering is a natural process occurring on the mineral and rock surfaces as the result of various metabolic actions of microbial inhabitants (*e.g.* bacteria, fungi) of the environment (Ehrlih, 1998; Brandl and Faramarzi, 2006; Gadd, 2007). Microbial-mediated weathering is known to enhance mineral dissolution through redox reactions, excretion of inorganic and organic acids as well as complexing compounds (White et al., 1995; Brandl and Faramarzi, 2006; Uroz et al., 2009; Gadd, 2010). Due to local changes of solution chemistry (pH and Eh), the mineral surface may be disturbed by the release of cationic constituents from the mineral lattice, consequently facilitating its further tendency to breakdown. Such a process is often initiated by microbial attachment to the solid surface and may be driven by nutrient requirements of microbial consortia. For example, under oxic conditions, many bacteria (e.g. *Rahnella sp.*, *Pseudomonas sp., Bacillus sp.*) produce iron-scavenging compounds, so-called siderophores, as the response to iron starvation conditions (Oulkadi et al., 2014; Ahmed and Holmström, 2014). Then, Fe-bearing mineral phases might be a potential iron source targeted by microorganisms (Konhauser et al., 2011). Furthermore, microbial attachment to the mineral surfaces tends to form a biofilm composed of bacterial cell assemblage surrounded by an extracellular polymeric matrix (Wingender et al., 1999). Biofilm increases the microbial density and/or the concentration of weathering agents and thus enhances weathering of the mineral surface. On the other hand, extracellular polymeric substances (EPS) associated with

biofilm can entrap mobilized elements due to the presence of various binding sites such as: carboxyl, hydroxyl, amino functional groups (Guibaud et al., 2008; Comte et al., 2006; Fein, 2006; Pal & Paul, 2008; Tourney & Ngwenya, 2014; van Hullebusch et al., 2015). Additionally, the microorganisms may assist in immobilization of elements due to sequestering activity (*e.g.* biosorption, bioaccumulation, and biomineralization) and may show great resistance towards metals govern by e.g. efflux transport, sequestration in the cytosol, and chelation of metals outside the cell (Haferburg, 2007; Gadd, 2010).

The weathering conditions encountered in the slag landfill environment are site-specific and might vary considerably depending on local bio-hydro-climatic conditions. Those encompass a broad array of issues such as frequency of rainfall, humidity level, temperature, pH conditions, content and quality of organic matter as well as microbial diversity that collectively determine weathering situation (Chapter 2: Potysz et al., 2015). Since the microorganisms are known to contribute substantially or even escalate the strength of mineral weathering, a number of exhaustive studies have been devoted to the isolation, characterization and potential application of organisms hosted at dumping sites. Male et al. (1997) showed the ability of *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, and Thiobacillus thioparus* to grow on Cu/Ni slag and noted that the slag might serve as source supporting growth of the isolates. Schippers et al. (2002) characterized the indigenous bacterium *Nocardiopsis metallicus sp.* from alkaline slag dump and highlighted the significance of bacteria in metal mobilization. Willscher and Bosecker (2003) isolated heterotrophic microorganisms such as *Arthrobacter oxydans*, *Microbacterium* sp. and *Dietzia natronolimnaea*, *Promicromonospora* sp., *Pseudonocardia autotrophica, Nocardiopsis metallicus* and observed good performance of those isolates in terms of bioleaching activity. Likewise, Cheng et al. (2009) reported the presence of *Bacillus* spp., *Sporosarcina* spp. and *Pseudomonas* spp. associated with Pb/Zn slag dump. Isolates were examined with respect to their ability to extract metals from slag and were found to carry out the process efficiently. Pandey et al. (2010 and 2011) demonstrated the occurrence of As and Pb tolerant bacteria which belong to *Bacillus sp.* and Cd resistant bacteria *Ochrobactrum* sp. At present, the composition of the microflora of dumping sites is not exactly determined. However, the environment of mining and industrial sites provides a unique habitat for microbial life. This environment contains a variety of minerals and involves alteration processes which provide an important chemical gradient impacting the structure and functionality of microbial communities through the dumps. Thus, a variety of microorganisms affiliated to landfill areas and their potential in mobilization of metals in the field should be acknowledged.

*Pseudomonas aeruginosa* is recognized to be an ubiquitous heterotrophic bacteria in soil, water, air and plants (Stanley et al., 2007). Due to its abundance and well-established features, *Pseudomonas aeruginosa* can be considered as environmental representative of bacteria appropriate for studying slag weathering. Numerous studies concerning the extent to which *Pseudomonas sp.* contributes to the weathering were implemented for a wide variety of solid

materials such as metallurgical slags (Yin et al., 2014; van Hullebusch et al., 2015), glass (Aouad et al., 2006; Chen et al., 2014) and municipal solid waste incinerator bottom ash (Aouad et al., 2008). Authors demonstrated that bacteria accelerate the degradation of mineral phases and elements are released in both equilibrated and far from equilibrium conditions (Aouad et al., 2006; Yin et al., 2014; van Hullebusch et al., 2015).

Despite the fact that important progress has been made towards understanding the interactions of bacteria with solid materials, yet relatively little is known about the impact of bacteria on slags weathering, especially concerning the mobilization of metallic elements. In this regards, the aspect of slags bio-weathering has gained relevant interest in recent years.

The present study examined the role of *Pseudomonas aeruginosa* on the weathering of two types of Cu-slags displaying different chemical and structural properties. The following research questions have been addressed: i) whether bacteria enhance bio-weathering of Cu-slags in a long term perspective, ii) whether bacteria can sorb mobilized metallic elements released from slags and iii) which mineral phases undergo weathering under exposure to biotic/abiotic conditions. Experimental set-ups included biotic experiments with *Pseudomonas aeruginosa* as well as abiotic experiments with sterile growth medium and ultrapure water.

## 6.2 MATERIALS AND METHODS

### 6.2.1 Copper slags

Two different types of Cu-slags, crystalline massive slag (CS) and granulated amorphous slag (GS), were selected for this study. Crystalline slag corresponds to historical slag, whereas granulated slag originates from modern-day copper production. Table 6.1 compares their chemical and mineralogical compositions and more detailed information concerning their characteristics is given elsewhere (Chapter 4: Potysz et al., 2016).

**TABLE 6.1 Chemical and mineralogical features of Cu-slags (Potysz et al., 2016).**

| | Crystalline Cu-slag (CS) | Granulated Cu-slag (GS) |
|---|---|---|
| **Bulk chemical composition** | | |
| *Major compounds (wt.%)* | | |
| *Si* | 17.6 | 15.2 |
| *Fe* | 35.5 | 11.5 |
| *Metalic elements (mg/kg)* | | |
| *Cu* | 5657 | 11425 |
| *Zn* | 3962 | 7810 |
| *Pb* | 111 | 21135 |
| **Structure** | | |
| | crystalline | Amorphous |
| ***Mineral phases:*** *(++ major, + minor, (+) traces)* | | |
| • Fayalite ($Fe^{2+}_2SiO_4$) ++ <br> • Glass ++ <br> • Bornite ($Cu_5FeS_4$) + <br> • Chalcopyrite ($CuFeS_2$) (+) <br> • Pyrrhotite ($Fe_{(x-1)}S$) + | • Glass ++ <br> • Metallic Cu-droplets + | |

## 6.2.2 Experimental approach

All incubations were performed according to the same protocol. Crushed and sieved slags (1-2 mm) were placed in perforated polypropylene tubes and then introduced to glassy bottles containing the weathering solution. The holes in polypropylene tubes (0.5±0.1 mm) ensured contact between the weathering solution and the slag. Three different solutions were used in this study: i) growth medium inoculated with the bacteria *Pseudomonas aeruginosa* (biotic incubation - GMB), ii) abiotic growth medium (GM) and iii) abiotic ultrapure water (UPW). Growth medium was prepared by dissolution in ultrapure water (per liter): 4 g of succinic acid ($C_4H_6O_4$), 1 g of ammonium sulphate (($NH_4)_2SO_4$), 0.2 g of disodium hydrogen phosphate ($Na_2HPO_4$) and 6 g of Tris buffer ($C_4H_{11}NO_3$). The initial pH of the growth medium was adjusted to the value of $7.8 \pm 0.1$ using 5 M NaOH. The growth medium was deliberately devoid of iron and trace elements as these compounds were expected to be sustained by the slags (Aouad et al., 2006; Yin et al., 2014). Furthermore, inoculated slag-free GM solution was used for a comparison purpose of bacterial growth.

75 mL of solution and 3 g of slag were used in order to maintain a liquid to solid ratio at 25 (v/w). The experiments were extended up to 112 days with the regular sampling interval of 14 days when slags were replaced by fresh solutions. Experiments were carried out at room temperature (21±1°C) and bottles were continuously agitated on the table shaker at 120 rpm. All experiments were performed in acid (10% $HNO_3$) washed glassy bottles of 250 mL. Prior to experiments, all solutions, slag samples, and glass/polypropylene materials were autoclaved for 20 minutes at 120°C. Slag grains were sterilized separately from the medium. Every

handling was performed under sterile conditions. Experiments were carried out in triplicates except slag-free treatment which was not replicated.

## 6.2.3 Bacterial strain

A gram-negative bacterial strain of bacilli *Pseudomonas aeruginosa* (n° CIP 105094) used in the biotic experiments was available from the Institute Pasteur (Paris, France). Before experiments, bacteria were grown in Luria Bertani medium for 24 h. Afterwards, cells were harvested and cleaned 3 times with sterile 5% NaCl and re-suspended in ultrapure water. Thereafter, cells were introduced to the experimental bottles. No adaptation of bacteria to high metallic element concentrations was done. All biotic experiments began with initial optical density at a wavelength of 600 nm ($OD_{600}$) of 0.008 in order to ensure equal bacterial cell number for all replicates.

## 6.2.4 Sampling protocol

The pH of the weathering solution was measured during sampling immediately after slag removal; the solutions were then divided onto three aliquots. The first aliquot was filtered through 0.22 μm cellulose acetate filters (Minisart) and acidified with 65% $HNO_3$ (2% v/v., Suprapur, Merck) in case of abiotic experiments, while filtered biotic aliquots were subjected to 70% perchloric acid ($HClO_4$) digestion at 80°C for the determination of the dissolved fraction. One biotic aliquot was not filtered but submitted to perchloric acid ($HClO_4$) digestion at 80°C for the determination of total elements released from slag upon incubation experiments. It was assumed that the difference between the total and dissolved fraction represents microbial uptake of elements and/or mineral precipitate formation. The last aliquot was filtered through 0.22 μm acetate cellulose filers (Spartan 13/0.2 RC Whatman) for metabolites determination. In order to confirm sterile conditions were maintained, weathering solutions were plated onto agar plates every sampling and observed with respect to bacterial growth.

## 6.2.5 Analytical methods

### 6.2.5.1 Solution chemistry

The concentrations of major (Si, Fe) and minor (Cu, Zn, Pb) elements in the solutions were analyzed using ICP-MS (inductively coupled plasma mass spectrometry, Agilent 7700x) with [45]Sc and [115]In as internal standards. Detection limits were typically 0.01-0.04 μg/L and 1.69 μg/L for minor and major elements, respectively. Quality control included systematic analysis

of certified reference materials (SLRS-5 standard). Sulfate, phosphate and nitrate concentrations in the solutions were measured colorimetrically using Permachem reagents (HACH). The carbonates content was determined by titration with HCl.

### 6.2.5.2 Physical measurements

Bacterial growth rate was monitored by frequent measurements of optical density ($OD_{600}$) using UV spectrophotometer (CADAS 50S, Dr Lange) at a wavelength of 600 nm. The pH measurements were done using a (GLP 22) pH meter.

### 6.2.5.3 Fluorescence measurements

The fluorescence properties of released microbial metabolites were analyzed using three dimensional excitation-emission spectrofluorophotometry (Shimadzu RF-5301 PC) equipped with a 150-W Xenon lamp. The fluorescence matrixes (3D-EEM) were done over an excitation (Ex) and emission (Em) range of 220-450 nm and 250-550 nm, respectively (Bourven et al., 2012). Measurement settings were fixed at 10 nm, scan wavelength intervals of 1 nm and a speed of 24 nm/s. Measurements were performed in 1 cm quartz optical cells. Prior to measurements, filtered (<0.22 μm) samples were diluted (15 µL/1000 µL) in 50 mM phosphate buffer adjusted to pH of 7.0 (±0.1) in order to diminish fluorescence signal saturation as well as to maintain the fluorescence at the same protonation degree. The data was processed using Panorama fluorescence 3.1 software (LabCognition, Japan).

### 6.2.5.4 Scanning electron microscope (SEM)

At the end of experiments, slags grain were observed with respect to surface changes using Scanning Electron Microscope (QEMSCAN 650F) at 10-20 kV and high vacuum working mode.

### 6.2.5.5 Visual MinteQ modelling

The geochemical simulation was performed using Visual MinteQ modeling software (version 3.1) in order to determine the degree of saturation of the leaching solutions with respect to possible secondary precipitates. The modeling was performed using the chemical composition of the leaching solution for every incubation time.

## 6.3 RESULTS

### 6.3.1 Bacterial growth

A comparison of bacterial growth rates within 14 days demonstrated that bacterial growth was limited in the control slag-free growth medium ($OD_{600}$: 0.03), whereas a significant growth of bacteria was observed in the solution supplemented with slags ($OD_{600}$: up to 0.3) (Figure 6.1). The transfer of slags to fresh growth medium every 14 days enabled a renewal of the bacterial growth cycle and cells revealed a highly comparable growth pattern. After one week of experiment, biofilm formation was observed in biotic experiments with slags (Figure 6.1).
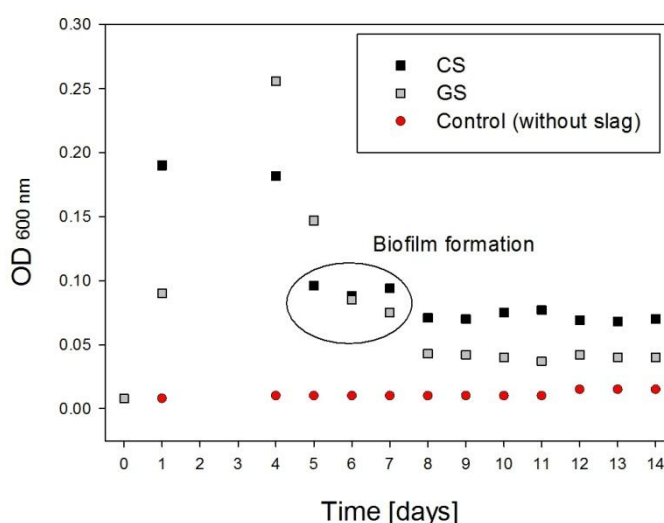


**FIGURE 6.1 Evolution of *Pseudomonas aeruginosa* growth in the experiments supplemented with crystalline slag (CS), granulated slag (GS) and control growth without slag supplementation.**

*OD 600 nm: optical density of solution at a wavelength of 600 nm.*

### 6.3.2 pH evolution

In abiotic UPW experiments, the pH was gradually increasing up from 5.6 to 6.7 (CS) and 7.6 (GS) during 42 days of incubation and then was kept on relatively stable level until the experiment (Figure 6.2 A). Oscillations of pH in the GM experiments were negligible due to the GM buffering capacity and was 7.8 (±0.1). The pH in the biotic experiment with CS increased during 14 days (from 7.8 to 9.2) and was then decreasing gradually to 8.1 (56 days). The pH value in the biotic experiment carried out with GS increased from 7.8 up to 9.2 during 14 days and was maintained on a stable level over the entire experiment duration.

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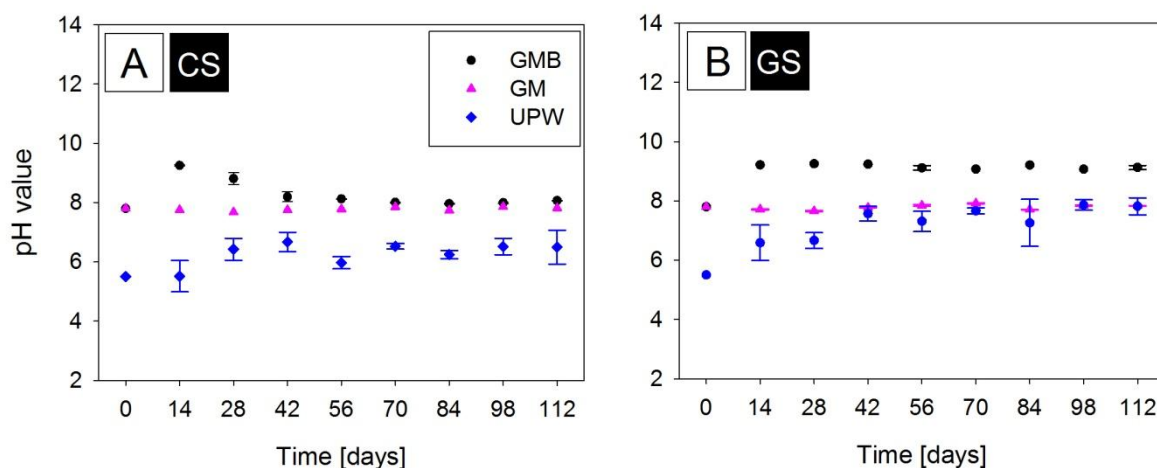
**FIGURE 6.2 Evolution of pH in the experiments carried out with
crystalline - CS (A) and granulated - GS (B) slag.**

*(GMB: growth medium with bacteria, GM: growth medium, UPW: ultrapure water)*

## 6.3.3 Elements release under abiotic and biotic conditions

Release of the major and minor elements resulting from experiments is presented in Figures 6.3 and 6.4 as the cumulative curves expressed in mg of elements released per kg of slag.

The influence of GM on Si release increased gradually throughout the experiment, while a lower release was observed in UPW. A cumulative release of Si in biotic solution presented a steeper trend compared to GM. After 112 days of CS incubation, the amount of Si released was 434.4 and 509.2 mg/kg for biotic experiments (GMB total and GMB <0.22 μm, respectively) and 345.9 mg/kg, 179.9 mg/kg for abiotic experiments (GM and UPW, respectively). Likewise, for GS the cumulative curves showed a gradual increase of the Si content in the solutions and reached 141.8 mg/kg, 304.5 mg/kg, 501.0 and 617.5 mg/kg at the end of the experiment for UPW, GM, GMB <0.22 μm and GMB total, respectively. Mobilization of Fe in abiotic experiments (UPW and GM) was limited and reached 2.1 mg/kg (UPW) and 10.1 mg/kg (GM) after 112 days of experiment with CS. A slightly higher quantity of Fe in GM (21.9 mg/kg) was observed compared to its content in UPW (2.8 mg/kg) after 112 days of experiment with GS. A considerable increase of Fe was observed in the biotic solution to which 237.2 mg/kg (GMB <0.22 μm), 292.6 mg/kg (GMB total) and 382.8 mg/kg (GMB <0.22 μm), 432 mg/kg (GMB total) was released after 112 days for CS and GS, respectively.
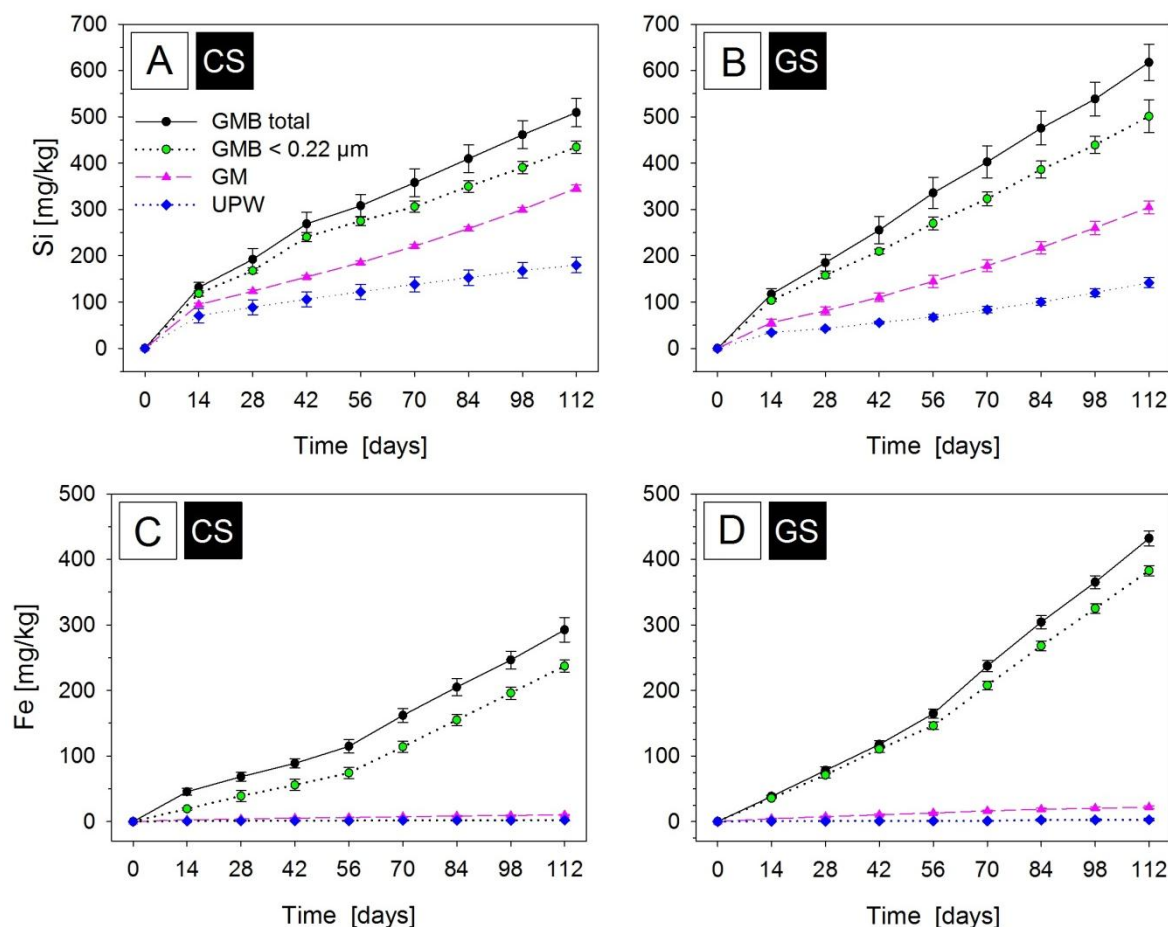
**FIGURE 6.3 Cumulative leaching of Si and Fe from crystalline (CS) and granulated (GS) slags during 112 days of experiments with ultrapure water (UPW), growth medium (GM) and biotic solution (GMB).**

Cu leaching into biotic solutions had relevant importance at the beginning of the experiment when up to 221.8 mg/kg (GMB total) and 85.1 mg/kg (GMB total) is rapidly (14 days) leached out from CS and GS, respectively. Afterwards, a gradual increase of Cu content in the solution was observed and reached 517.2 mg/kg (GMB total) and 141.1 mg/kg (GMB total) at the end of experiments with CS and GS, respectively. In contrast, the cumulative amount of the Cu in abiotic solutions reached 159.4 mg/kg (UPW), 313.9 mg/kg (GM) for CS and 48.9 mg/kg (UPW), 49.2 mg/kg (GM) for GS. The release of Zn into abiotic solutions amounted up to 9.2 mg/kg (UPW) and 7.7 mg/kg (UPW) after 112 days of experiments for CS and GS, respectively. The total content of the Zn biotic solution was significantly higher than in the dissolved fraction and after 112 days it reached 149.3 mg/kg and 121.6 mg/kg for CS and GS, respectively. Low quantities of Pb were leached out from CS and generally do not exceed 1.7 mg/kg in all experiments carried out. The amounts of Pb leached from GS were much higher compared to the quantities released from CS. The cumulative biotic curve increased gradually

reaching 50.6 (GMB <0.22 μm) and 62.3 mg/kg (GMB total) at the end of the experiment with GS.
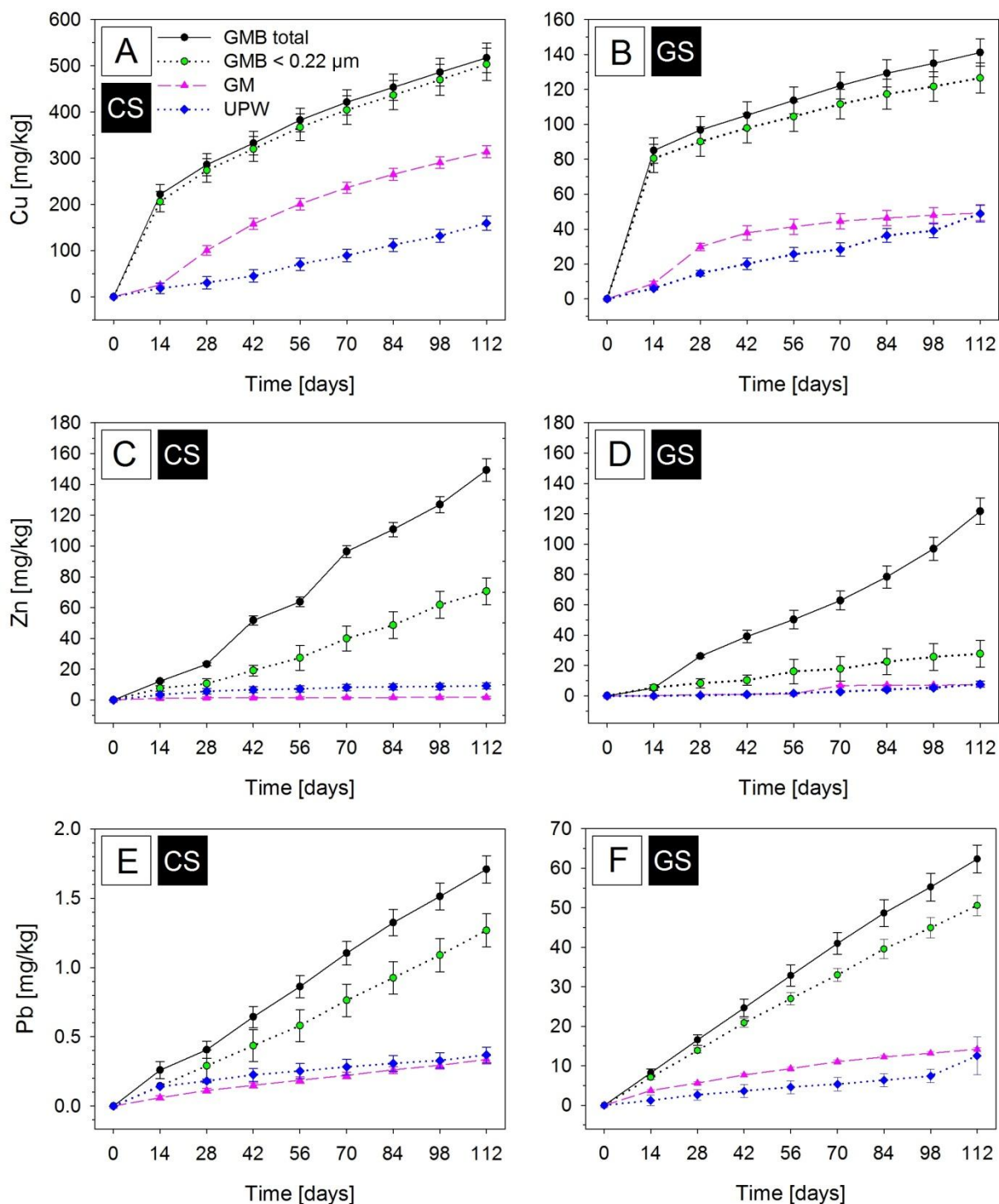


**FIGURE 6.4 Cumulative leaching of metallic elements (Cu, Zn, Pb) from crystalline (CS) and granulated (GS) slags during 112 days of experiments with ultrapure water (UPW), growth medium (GM) and biotic solution (GMB).**

## 6.3.4 Element leaching rates from Cu-slags

The leaching rates observed at the beginning of experiment (14 days) were noticeably higher under biotic conditions compared to abiotic ones for all elements analyzed (Table 6.2). At this early stage (14 days) of the experiment, the highest differences between the amount of element released under biotic and abiotic conditions were observed for Cu. Its leaching rates were 14.7 mg/kg/day (CS) and 5.7 mg/kg/day (GS) for GMB <0.22 μm, while only 1.9 mg/kg/day (CS) and 0.6 mg/kg/day (GS) were released in GM (Table 6.2). The release of Fe was significantly higher under biotic conditions compared to abiotic conditions over the entire time of the experiment. The rates of Fe release (GMB <0.22 μm) were 1.2-3.0 mg/kg/day (CS) and 2.5-4.4 mg/kg/day (GS). The maximum rates achieved under abiotic conditions throughout 112 days for Fe were 0.20 mg/kg/day (GM) and 0.32 mg/kg/day (GM) for CS and GS, respectively. The rate of Si release was higher under biotic conditions than under abiotic ones until 42 days (3.5-8.5 mg/kg/day) and then reached comparable rates (2.5 mg/kg/day) with GM (2.2 mg/kg/day) in case of CS. The difference between the leaching rates for abiotic and biotic conditions was higher up to the end of experiments carried out with GS (Table 6.2). Zn release was more accelerated by bacteria in presence of CS, while lower impact occurred in the experiment with GS. Moreover, the Zn leaching rate achieved at the end of experiment was significantly accelerated if GMB total was taken into account (1.6 mg/kg/day (CS) and 1.8 mg/kg/day (GS)). Pb leaching rates under biotic conditions were higher throughout the experiments with more important biotic acceleration in the experiment with CS. The Pb leaching rates reached 0.01 mg/kg/day (CS) and 0.4 mg/kg/day (GS) at the end of biotic experiment, while leaching rates under abiotic conditions were not faster than 0.003 mg/kg/day (CS) and 0.3 mg/kg/day (GS) (Table 6.2).

**TABLE 6.2 Leaching rates calculated based on concentration of elements in the leachates.**

*(GMB total: growth medium with bacteria digested, GMB: growth medium with bacteria filtered <0.22 μm, GM: growth medium, UPW: ultrapure water)*

***Crystalline slag***

| Time [days] | Si [mg/kg/day] | | | | Fe [mg/kg/day] | | | | Cu [mg/kg/day] | | | | Zn [mg/kg/day] | | | | Pb [mg/kg/day] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW |
| 14 | 9.40 | 8.47 | 6.75 | 5.02 | 3.26 | 1.38 | 0.20 | 0.05 | 15.84 | 14.72 | 1.87 | 1.30 | 0.87 | 0.54 | 0.07 | 0.25 | 0.019 | 0.010 | 0.004 | 0.010 |
| 28 | 4.35 | 3.52 | 2.06 | 1.31 | 1.63 | 1.40 | 0.08 | 0.03 | 4.59 | 4.84 | 5.30 | 0.88 | 0.79 | 0.22 | 0.03 | 0.16 | 0.011 | 0.010 | 0.004 | 0.003 |
| 42 | 5.45 | 5.18 | 2.20 | 1.25 | 1.46 | 1.21 | 0.08 | 0.02 | 3.32 | 3.28 | 4.10 | 1.04 | 2.03 | 0.61 | 0.00 | 0.07 | 0.017 | 0.010 | 0.003 | 0.003 |
| 56 | 2.79 | 2.45 | 2.21 | 1.12 | 1.85 | 1.31 | 0.08 | 0.01 | 3.57 | 3.36 | 3.07 | 1.84 | 0.86 | 0.59 | 0.01 | 0.04 | 0.016 | 0.010 | 0.003 | 0.002 |
| 70 | 3.57 | 2.24 | 2.53 | 1.16 | 3.37 | 2.85 | 0.08 | 0.02 | 2.77 | 2.66 | 2.54 | 1.32 | 2.33 | 0.89 | 0.00 | 0.07 | 0.017 | 0.013 | 0.002 | 0.002 |
| 84 | 3.70 | 3.10 | 2.70 | 1.02 | 3.09 | 2.92 | 0.09 | 0.01 | 2.30 | 2.31 | 2.06 | 1.63 | 1.03 | 0.62 | 0.01 | 0.03 | 0.016 | 0.012 | 0.003 | 0.002 |
| 98 | 3.70 | 2.93 | 2.95 | 1.13 | 2.96 | 2.93 | 0.06 | 0.01 | 2.33 | 2.37 | 1.82 | 1.42 | 1.15 | 0.94 | 0.00 | 0.02 | 0.014 | 0.012 | 0.002 | 0.002 |
| 112 | 3.42 | 3.13 | 3.30 | 0.84 | 3.29 | 2.95 | 0.07 | 0.01 | 2.23 | 2.40 | 1.66 | 1.95 | 1.60 | 0.63 | 0.00 | 0.03 | 0.014 | 0.013 | 0.003 | 0.003 |

***Granulated slag***

| Time [days] | Si [mg/kg/day] | | | | Fe [mg/kg/day] | | | | Cu [mg/kg/day] | | | | Zn [mg/kg/day] | | | | Pb [mg/kg/day] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW | GMB tot. | GMB | GM | UPW |
| 14 | 8.37 | 7.41 | 3.96 | 2.44 | 2.74 | 2.55 | 0.32 | 0.05 | 6.08 | 5.74 | 0.64 | 0.44 | 0.37 | 0.39 | 0.00 | 0.00 | 0.59 | 0.51 | 0.27 | 0.09 |
| 28 | 4.85 | 3.85 | 1.84 | 0.61 | 2.82 | 2.51 | 0.20 | 0.00 | 0.84 | 0.69 | 1.50 | 0.62 | 1.49 | 0.21 | 0.05 | 0.02 | 0.59 | 0.48 | 0.14 | 0.10 |
| 42 | 5.02 | 3.69 | 2.07 | 0.91 | 2.85 | 2.84 | 0.22 | 0.02 | 0.61 | 0.55 | 0.57 | 0.38 | 0.93 | 0.14 | 0.03 | 0.04 | 0.58 | 0.50 | 0.14 | 0.07 |
| 56 | 5.75 | 4.32 | 2.46 | 0.88 | 3.34 | 2.54 | 0.19 | 0.00 | 0.60 | 0.47 | 0.25 | 0.39 | 0.80 | 0.41 | 0.02 | 0.06 | 0.59 | 0.44 | 0.12 | 0.07 |
| 70 | 4.78 | 3.79 | 2.42 | 1.13 | 5.19 | 4.41 | 0.22 | 0.00 | 0.61 | 0.51 | 0.22 | 0.19 | 0.90 | 0.13 | 0.38 | 0.07 | 0.58 | 0.43 | 0.12 | 0.05 |
| 84 | 5.20 | 4.51 | 2.76 | 1.20 | 4.78 | 4.30 | 0.17 | 0.09 | 0.50 | 0.41 | 0.13 | 0.58 | 1.11 | 0.33 | 0.01 | 0.10 | 0.55 | 0.47 | 0.09 | 0.07 |
| 98 | 4.50 | 3.79 | 3.06 | 1.41 | 4.36 | 4.07 | 0.13 | 0.01 | 0.41 | 0.31 | 0.11 | 0.19 | 1.32 | 0.23 | 0.01 | 0.08 | 0.47 | 0.38 | 0.07 | 0.08 |
| 112 | 5.65 | 4.42 | 3.17 | 1.55 | 4.76 | 4.12 | 0.12 | 0.02 | 0.44 | 0.35 | 0.09 | 0.70 | 1.77 | 0.14 | 0.03 | 0.17 | 0.51 | 0.40 | 0.07 | 0.37 |

## 6.3.5 Bacterial related organic products

The fluorescence matrixes for GS and CS incubations in the presence of *Pseudomonas aeruginosa* as well as the abiotic medium control are presented in Figure 6.5. Four specific organic fluorophore peaks were recorded in biotic incubations. According to the literature, the peaks recorded at Ex/Em 220-240/325-350 nm, 270-290/337-350 nm, 270-300/450-475 nm and 370-390/450-475 nm correspond to proteins-like molecules (according to the fluorescence properties of 2 aromatic amino acid; tyrosine, tryptophan), microbial by-product-like, humic-like substances (humic-like and fulvic-like) (Bourven et al., 2012; Bhatia et al., 2013; Bourven et al., 2014) and siderophore-like (pyoverdine) (Dumas et al., 2013; Dartnell et al., 2013), respectively. The maximum intensities of the identified fluorophores are presented in Table 6.3.

**TABLE 6.3 The maximum intensities (average of 3 replicates) of fluorophores identified in biotic filtered solution (<0.22 μm).**

| | Crystalline slag | | Granulated slag | |
|---|---|---|---|---|
| | Maximum intensity recorded | | | |
| *Fluorophores determined* | RDS | | RDS | |
| *14 days* | | | | |
| *Proteins-like* | 315.1 | ±228.2 | 464.1 | ±65.4 |
| *Microbial by-products like* | 196.1 | ±83.0 | 240.4 | ±30.9 |
| *Humic-like substances* | 157.3 | ±70.6 | 203.4 | ±7.20 |
| *Siderophore-like* | 122.6 | ±25.0 | 125.3 | ±2.80 |
| *28 days* | | | | |
| *Proteins-like* | 189.3 | ±83.1 | 368.5 | ±34.2 |
| *Microbial by-products like* | 122.2 | ±65.9 | 206.6 | ±28.6 |
| *Humic-like substances* | 607.3 | ±32.4 | 344.3 | ±56.9 |
| *Siderophore-like* | 366.5 | ±19.8 | 176.7 | ±24.7 |
| *56 days* | | | | |
| *Proteins-like* | 107.9 | ±0.5 | 525.9 | ±31.0 |
| *Microbial by-products like* | 119.7 | ±1.0 | 263.2 | ±18.7 |
| *Humic-like substances* | 127.4 | ±1.6 | 505.7 | ±24.6 |
| *Siderophore-like* | 126.7 | ±11.3 | 234.2 | ±11.4 |
| *72 days* | | | | |
| *Proteins-like* | 87.2 | ±5.3 | 546.8 | ±6.6 |
| *Microbial by-products like* | 264.1 | ±2.6 | 368.5 | ±9.3 |
| *Humic-like substances* | 87.7 | ±5.4 | 582.9 | ±16.5 |
| *Siderophore-like* | 86.4 | ±6.0 | 299.5 | ±5.9 |
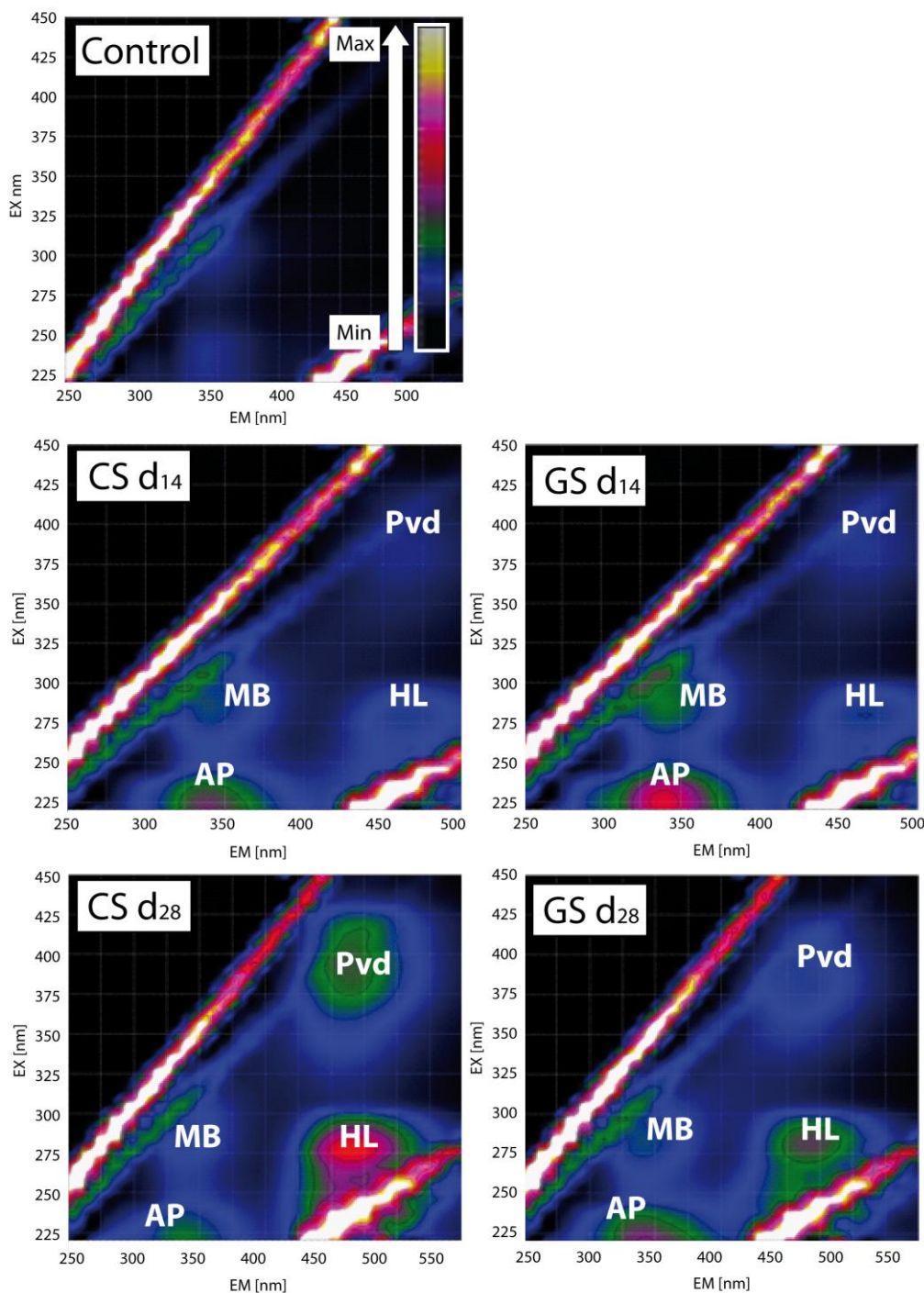
**FIGURE 6.5 Three-dimensional spectra presenting the fluorophores of metabolic products excreted by *Pseudomonas aeruginosa* in the presence of GS and CS after 14 and 28 days of experiment.**

*(Control: growth medium, AP: aromatic proteins, HL: humic-like substances, Pvd: pyoverdine, MB: microbial by-products, $d_{14}$: spectra recorded after 14 days of experiment, $d_{28}$: spectra recorded after 28 days of experiment). Color intensity indicates intensity of peaks.*

## 6.3.6 SEM observations

According to the SEM observations, components of the CS slag such as glass and sulfides (especially bornite: $Cu_5FeS_4$) are partially dissolved even under abiotic conditions (Figure 6.6). A higher degree of alteration was observed on grains placed in GM compared to those treated with UPW. Partial dissolution of sulfides was visible on the edges when slag was exposed to UPW (Figure 6.6 A1), while a larger weathering zone (approximately 10 µm in diameter) resulted from the GM treatment (Figure 6.6 B1). Glass dissolution resulting from the UPW experiment is present as irregular fractures that reach the size up to 42 nm (Figure 6.6 A2), whereas glass corrosion in the form of round-shaped zones approximate in size to 1 µm was observed on the grains immersed in GM (Figure 6.6 B2). An exposure of CS grains to biotic conditions led to more extensive glass and sulfides weathering as shown in Figure 6.6 C1. Glass dissolution features were similar in shape and diameter to those resulting from abiotic GM experiment (Figure 6.6 C3). However, these characteristics are more widespread on the samples immersed in the GMB solution. Furthermore, the breakdown of fayalite ($Fe_2SiO_4$) was solely observed for slag grains that experienced exposure to biotic conditions (GMB). Its decomposition appears as round-shaped altered zones having a diameter approximately up to 10 µm (Figure 6.6 C2).

The GS grains that experienced abiotic weathering conditions showed eroded zones in the form of holes related to removal of Cu-droplets and altered glass (Figure 6.7). Elongated thin glass fractures were observed on the grains resulting from UPW treatment (Figure 6.7 A1), while round-shaped alteration zones similar to those observed on CS grains appeared after GM treatment (Figure 6.7 B1). Glass alteration in biotic solution exhibited highly altered edges of grains (Figure 6.7 C1). Removal of Cu-droplets occurred on the grains treated with all solutions (Figures 6.7 A2-C3), however a higher degree of their depletion was observed on grains which experienced biotic treatment (Figures 6.7 C2 and C3).
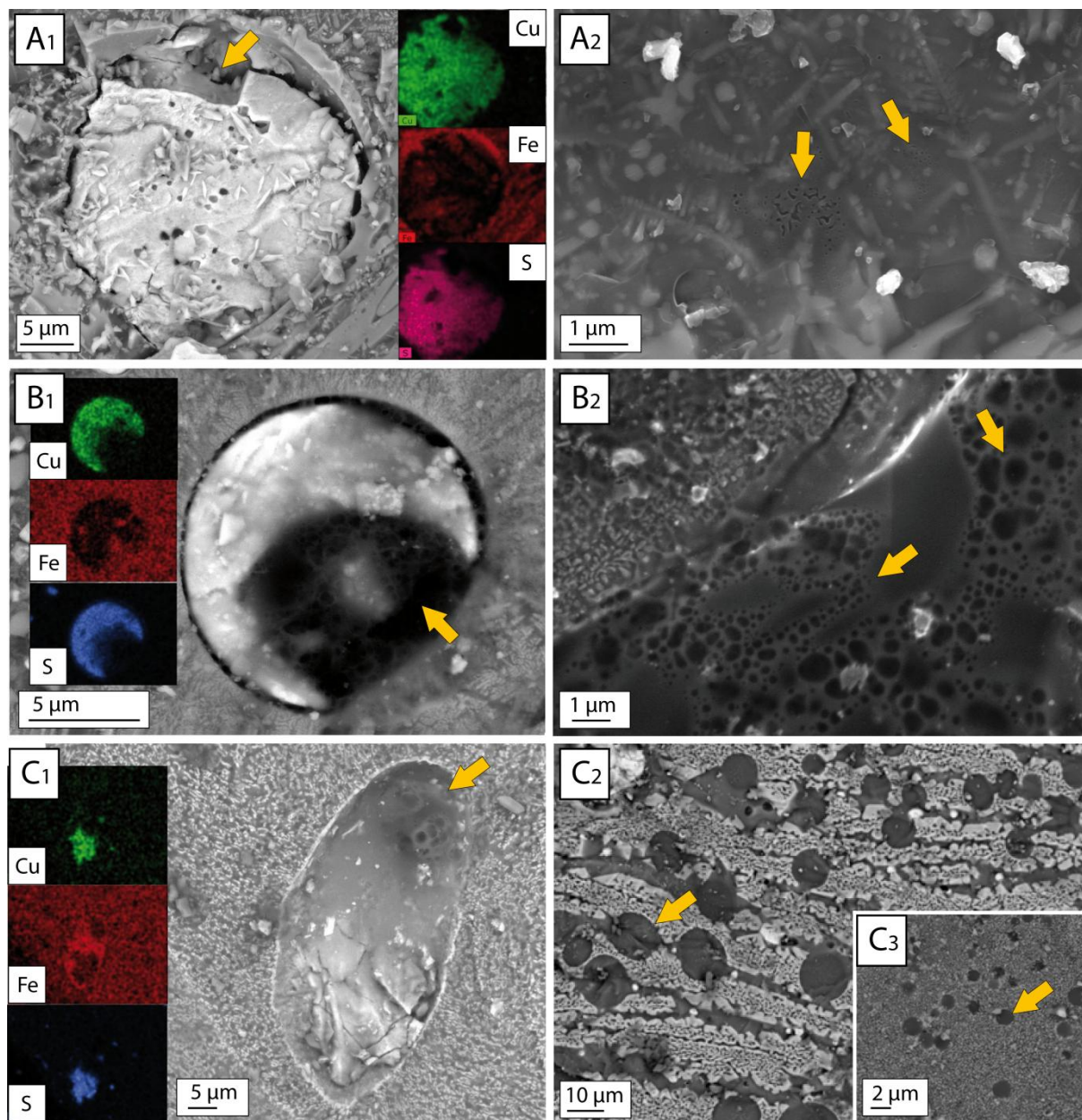
**FIGURE 6.6 SEM images presenting weathering features of crystalline slag after exposure to ultrapure water (a), growth medium (b) and growth medium with *Pseudomonas aeruginosa* (c).**

*A1: Partial weathering of bornite on the edge, A2: Glass fracturing, B1: Extended weathering of bornite, B2: Glass weathering, C1: Dissolution of bornite, C2: Alteration of fayalite, C3: Glass alteration.*
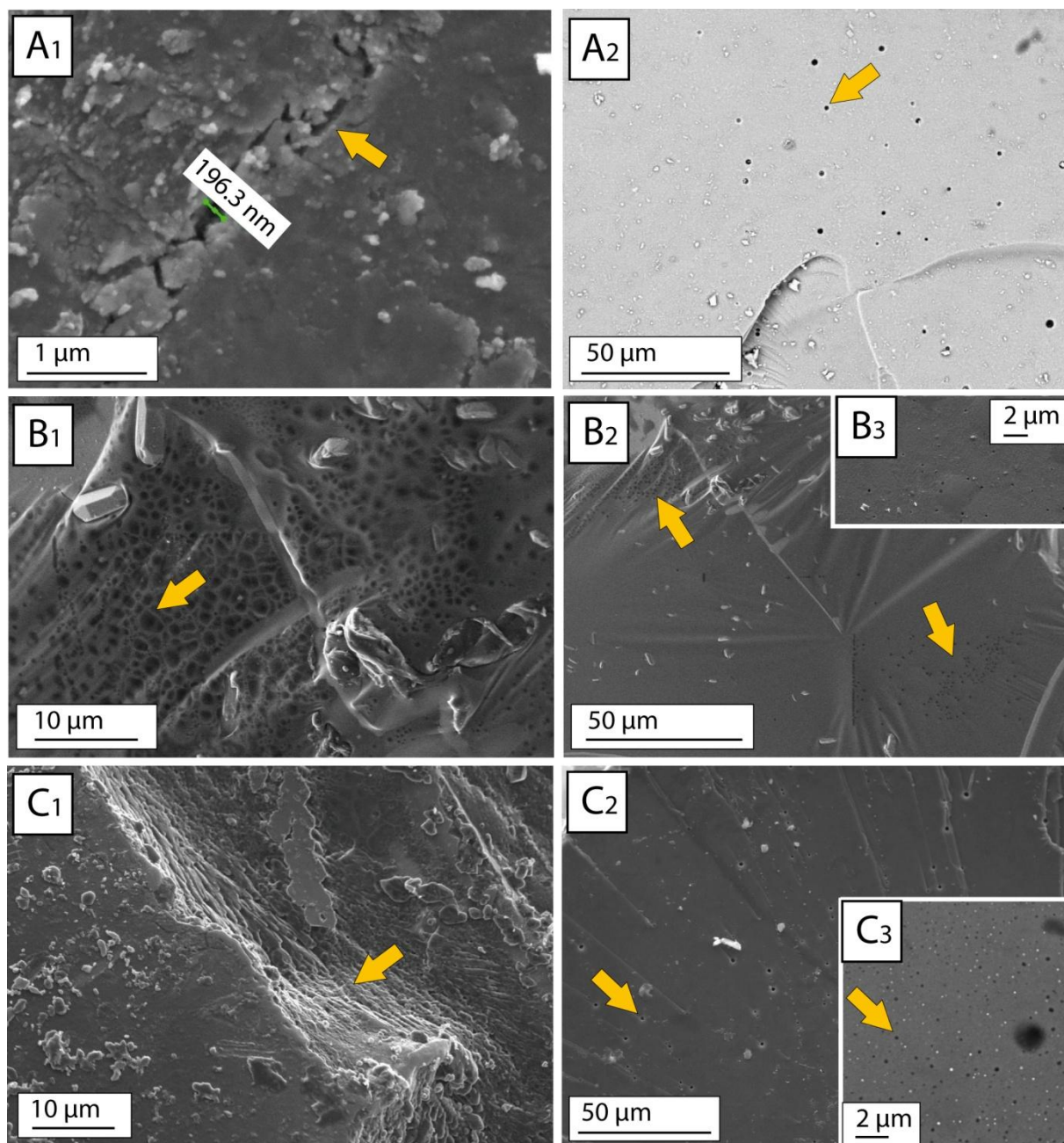
**FIGURE 6.7 SEM images presenting weathering features of granulated slag after exposure to ultrapure water (a), growth medium (b) and growth medium with *Pseudomonas aeruginosa* (c).**

*A1: Glass fracture reaching width up to 200 nm, A2: Cu-droplets removal, B1: round-shaped glass alteration, B2: Cu-droplets removal, C1: glass alteration, C2 and C3: Cu-droplets removal.*

## 6.3.7 Geochemical modeling

Saturation indices (saturated: $-0.5<SI<1$, oversaturated $SI>1$, undersaturated $SI< -0.5$) of selected solubility-controlling phases predicted by Visual MinteQ are presented in Figures 6.8 and 6.9. Special attention was given to phases which could limit the concentrations of metals in the solutions.

### 6.3.7.1 Crystalline slag

At the early stage of biotic experiment (GMB) geochemical modeling predicts a general leachate oversaturation with respect to the number of copper entrapping phases such as brochantite ($Cu_4SO_4(OH)_6$), langite ($Cu_4(SO_4)(OH)_6 \cdot 2H_2O$), antlerite ($Cu_3(SO_4)(OH)_4$), azurite ($Cu_3(CO_3)_2(OH)_2$), $Cu(OH)_2$ and $Cu_3(PO_4)_2:3H_2O$ (Figure 6.8). Cupric sulfates formation may result from the oxidation of sulfides or Cu precipitation with sulfates available from growth medium (1 g/L of ammonium sulfate). In spite of lower saturation indices at the end of biotic experiment (GMB), the solution remained saturated or oversaturated. Furthermore, Zn revealed saturation with respect to smithsonite ($ZnCO_3$) and oversaturation with respect to hydrozincite ($Zn_5(CO_3)_2(OH)_6$), which remained saturated up to the end of the biotic experiment. Precipitation of Pb-phases such as $Pb_3(PO_4)_2$ and $Pb(OH)_2$ was also thermodynamically possible in biotic experiments. Geochemical modelling also predicted formation of cristobalite which was the main Si solubility controlling phase in the biotic solution. Under abiotic conditions (GM) saturation indices of the phases controlling Cu were positive, however, lower compared to indices determined for biotic conditions (GMB). Under abiotic conditions (GM) precipitation of Zn and Pb was not thermodynamically possible as shown by strongly negative values of saturation indices. In case of UPW experiment formation of the secondary phases was not thermodynamically possible. Geochemical modelling predicted cristobalite formation only at the beginning of the UPW experiment. Precipitation of Fe was thermodynamically possible in all experimental setups (Figure 6.8).

### 6.3.7.2 Granulated slag

According to geochemical modelling the biotic solution supplemented with GS was oversaturated with respect to Cu-phases such as antlerite ($Cu_3(SO_4)(OH)_4$), brochantite ($Cu_4SO_4(OH)_6$), azurite ($Cu_3(CO_3)_2(OH)_2$) and $Cu(OH)_2$ (Figure 6.9). Brochantite remained the most significantly saturated at the end of the experiment. Although, GS does not contain sulphides providing sulphate through dissolution, it was available from growth medium. As predicted by thermodynamic modelling, precipitation of Zn-phases, such as $Zn(OH)_2$, hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and zincite (ZnO), and Pb-phases, such as cerrusite ($PbCO_3$) and hydrocerusite ($Pb_3(CO_3)_2(OH)_2$), and $Pb(OH)_2$, was thermodynamically possible under

biotic conditions (GMB). In the GM experiment, geochemical modeling predicted formation of various phases (*e.g.* antlerite, brochantite, langite, azurite, hydrocerrusite, cerrusite) at the beginning of the experiment, while only $Pb(OH)_2$, cerrusite and cristobalite were predicted as possible precipitates at the end of the experiment. In case of UPW experiment, $Pb(OH)_2$ and $Cu(OH)_2$ were strongly saturated. According to Visual MinteQ prediction, Fe precipitation was possible in GMB, GM and UPW experiments (Figure 6.9).
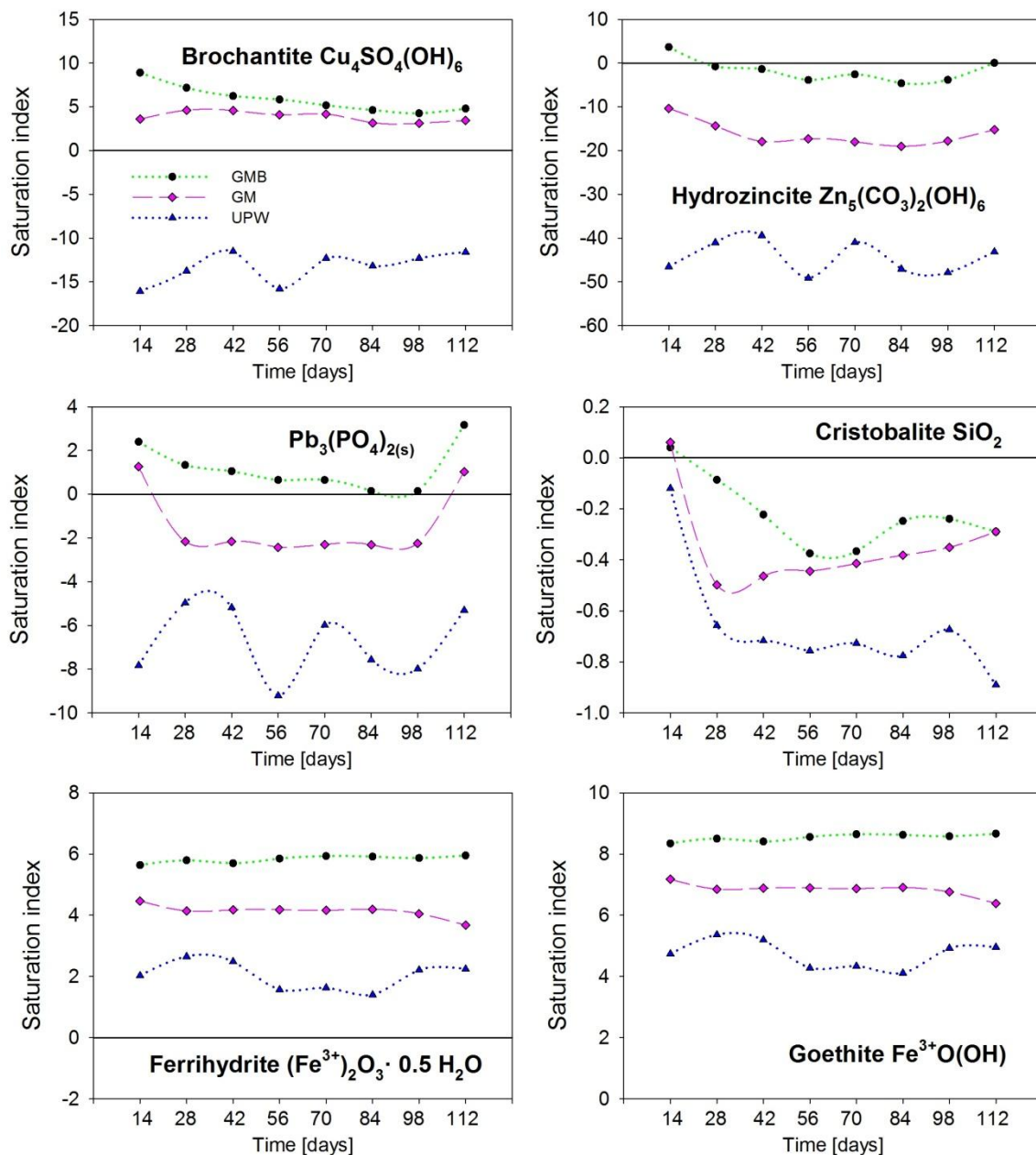


**FIGURE 6.8 Saturation indices of possible secondary precipitates predicted by Visual MINTEQ for experiments with crystalline slag.**
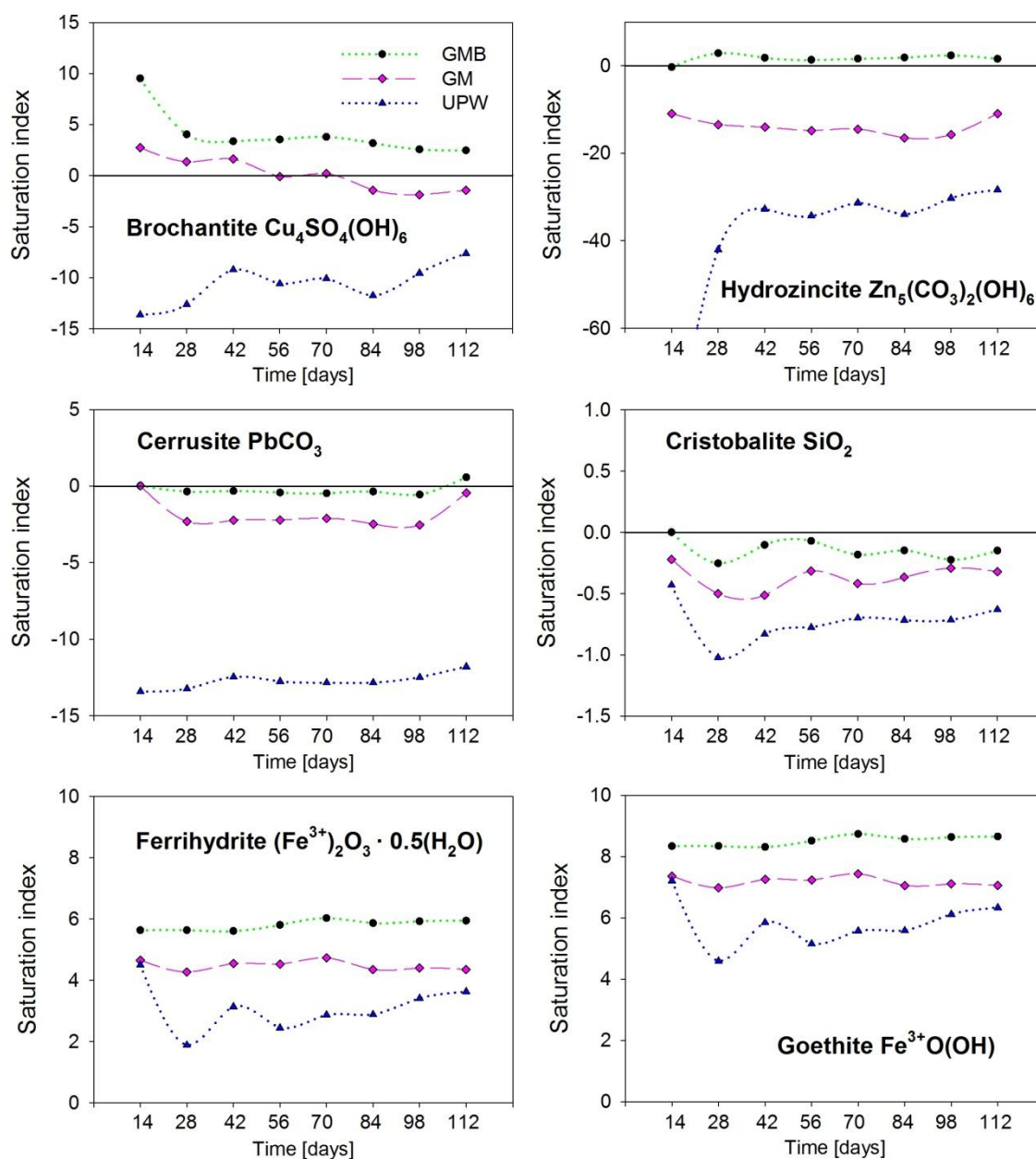
**FIGURE 6.9 Saturation indices of possible secondary precipitates predicted by Visual MINTEQ for experiments with granulated slag.**

## 6.4 DISCUSSION

### 6.4.1 Slags susceptibility to weathering

Results obtained from the experiments indicate that *Pseudomonas aeruginosa* significantly enhanced the release of major and minor elements in solution compared to abiotic experiments (GM and UPW) in a long-term perspective of 112 days (Figures 6.3 and 6.4). Bio-weathering experiments yielded a greater level of metallic elements (Cu, Zn, Pb) leached than major elements (Si and Fe) when relative values are compared (Table 6.4). This may be ascribed to metal-bearing phases (*e.g.* sulfides, Cu-droplets) which display a lower resistance against weathering than other silicate components (fayalite and glass). Concerning metallic elements, it is evident that metal carriers (*e.g.* bornite) of CS are more prone to bio-weathering processes than GS, which is contradictory to the bulk composition of slags (Table 6.1). In total (GMB), as much as 9.1% (Cu), 3.8% (Zn) and 1.5% (Pb) were released from CS, while the relative percentage of contaminants leached did not exceed 1.6% in case of GS (Table 6.4). The total release of major elements analyzed reached less than 0.3% and 0.4% for CS and GS, respectively. Hence, no evident correlation between the bulk composition of slags and the solution chemistry was observed. Therefore, the implication is that the mineralogy of these materials is likely a determining factor.

**TABLE 6.4 Relative values [%] of elements leached for slags exposure to different conditions after 112 days of incubation.**

|  | Si | | Fe | | Cu | | Zn | | Pb | |
|---|---|---|---|---|---|---|---|---|---|---|
|  | **[%]** | **RDS** | **[%]** | **RDS** | **[%]** | **RDS** | **[%]** | **RDS** | **[%]** | **RDS** |
| *Crystalline slag* | | | | | | | | | | |
| GMB | 0.29 | (±0.02) | 0.08 | (±0.01) | 9.1 | (±0.6) | 3.8 | (±0.2) | 1.5 | (±0.1) |
| GMB <0.22 μm | 0.25 | (±0.01) | 0.07 | (±0.01) | 8.9 | (±0.6) | 1.8 | (±0.2) | 1.1 | (±0.1) |
| GM | 0.20 | (<<±0.01) | 0.003 | (<<±0.001) | 5.5 | (±0.2) | 0.04 | (<<±0.01) | 0.30 | (±0.03) |
| UPW | 0.10 | (±0.01) | 0.001 | (<<±0.001) | 2.8 | (±0.3) | 0.20 | (<<±0.01) | 0.3 | (±0.1) |
| *Granulated slag* | | | | | | | | | | |
| GMB | 0.41 | (±0.03) | 0.38 | (±0.02) | 1.20 | (±0.10) | 1.6 | (±0.10) | 0.3 | (±0.02) |
| GMB <0.22 μm | 0.33 | (±0.02) | 0.33 | (±0.01) | 1.10 | (±0.10) | 0.4 | (±0.10) | 0.2 | (±0.01) |
| GM | 0.20 | (±0.01) | 0.02 | (<<±0.01) | 0.40 | (±0.04) | 0.1 | (<<±0.01) | 0.1 | (<<±0.01) |
| UPW | 0.09 | (±0.01) | 0.002 | (<<±0.001) | 0.40 | (±0.04) | 0.1 | (±0.03) | 0.1 | (±0.02) |

*GMB: growth medium with bacteria digested, GMB <0.22 μm: growth medium with bacteria filtered, GM: growth medium, UPW: ultrapure water)*

Bornite is a Cu-bearing sulfide mineral known to undergo dissolution under oxidative conditions (Bartlet, 1992). This phase present in CS was found to weather under abiotic conditions, and to a greater extend under biotic conditions (Figures 6.6 A1-C2). That observation is in accordance with the solution chemistry that showed some amounts of Cu leached out into UPW and even greater amounts release in GM (Figure 6.4). The enhanced biotic effect on CS weathering is reflected in both the solution chemistry and the physical weathering features (Figure 6.6).

The evolution of Si and Fe concentrations in the solutions (Figure 6.3) are indicators of glass and fayalite dissolution. The solution chemistry coupled with SEM results explains experimental weathering events. Si release observed in UPW and higher amounts in GM correlate with glass alteration that occurred to a greater degree on GM grains than those immersed in UPW. A less significant release of Fe than Si reflects the glass composition, which contains Fe in a lower quantity (Chapter 4: Potysz et al., 2016). Both Si and Fe were found in higher concentrations in biotic experiments, however Fe was leached more readily than Si. Under biotic conditions, *Pseudomonas aeruginosa* secreted various soluble organic metabolites including siderophore-like, humic-like substances and aromatic amino-like acids (Figure 6.5 and Table 6.3). According to the literature, the siderophores are strong chelators for iron and other dissolved cations (Kalinowski et al., 2000; Matlakowska et al., 2012; Ahmed and Holmström, 2014). Therefore, enhanced Fe solubility was probably due to the formation of aqueous organic complexes with dissolved Fe and thermodynamic disequilibrium and/or adsorption of organic compounds onto mineral surfaces and weakening of chemical bounds of dissolving mineral structures. Additionally, a study concerning Fe-rich phyllosilicates dissolution by two heterotrophic soil bacteria (*Pseudomonas sp.* and *Bulkolderia sp.*) indicated that abiotic dissolution of minerals proceeds preferentially on the broken bounds or on the charge-deficient sites located on the mineral surface, whereas organic ligand promoted dissolution proceeds without any preferential surface sites (Grybos et al., 2011). A higher Fe release under biotic conditions might be also related to partial decomposition of fayalite which is an Fe-rich phase containing Si in lower quantity (Chapter 4: Potysz et al., 2016). Moreover, increased release of Zn and Pb in biotic experiment with CS also confirms this interpretation as fayalite carries important Zn substitutions and less important Pb impurities (Chapter 4: Potysz et al., 2016). However, supply of those elements in biotic solution is certainly partially influenced by glass dissolution as proven by SEM analysis.

Fayalite, glass and bornite are Fe-bearing phases that could make them prone to bacterial attack for a double reason: firstly they could be recognized as potential metabolic source of Fe (Rogers & Bennett, 2004; Ahmed & Holmsorm, 2015). For example, Rogers & Bennet (2004) demonstrated that silicate glass which contained micronutrients (*e.g.* Fe) was weathered, whereas glass lacking desired elements remained unweathered. Likewise, the study of Ahmed & Holmström (2015) revealed a selectivity of bacteria with respect to

element dissolution from minerals. Elements which are essential for growth of microorganisms (*e.g.* Fe) or those non-toxic are mobilized in higher amounts compared to toxic ones (Ahmed & Holmström, 2015).

The trends observed in the solution chemistry (Figures 6.3 and 6.4) combined with SEM analysis (Figure 6.7) also provide an explanation of the GS weathering pattern. More important Si release into biotic solutions compared to abiotic ones is congruent with SEM observations that demonstrated a greater degree of weathering on grains exposed to biotic conditions. A similar relationship applies to Cu content in solution that refers to Cu-droplets removal and its subsequent dissolution from glass. Furthermore, a higher release of Si and Fe from GS compared to CS implies a greater susceptibility of GS glass to dissolution that may be assigned to its composition. Glass of CS contains a higher Si content than GS (Chapter 4: Potysz et al., 2016), thereby a denser Si network, which may render this glass more resistant to dissolution (Kuo et al., 2008). That would also explain pH variations in biotic solutions (Figure 6.2). Higher pH values in the solution supplemented with GS results from glass hydrolysis (Eq. n°1 and 2) and proton replacement of cations (*e.g.* Mg, Fe, Ca, Na, K) entrapped in Si network (Yin et al., 2014). A gradual drop of the solution pH with CS may occur due to dissolution of sulfides (Eq. n°3) liberating protons and consequently decreasing the pH (Ettler et al., 2003):

$$- Si - O - M_{(glass)} + H^+ \leftrightarrow - Si - OH_{(glass)} + M^+_{(aq)} \qquad \text{Eq. n°1}$$

$$Si - O - Si + H_2O \leftrightarrow - Si - OH + - Si - OH \qquad \text{Eq. n°2}$$

$$MeS_2 + 7/2\ O_2 + H_2O \rightarrow Me^{2+} + 2\ SO_4^{2-}_{(aq)} + 2\ H^+ \qquad \text{Eq. n°3}$$
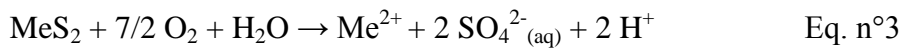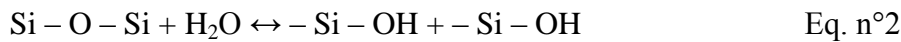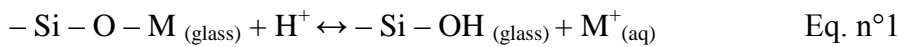
## 6.4.2 Bacterial versus abiotic release of elements

Although biologically-mediated weathering yielded a greater level of elements leached out than those in abiotic experiments, their release could also be observed in abiotic experiments (Figures 6.3 and 6.4). Ultrapure water would be expected to have a larger influence on the process due to its lower pH (Yin et al., 2014; van Hullebusch et al., 2015). However, GM was found to have comparable or larger impact on slags weathering despite its higher pH (Figures 6.3 and 6.4). That may be attributed to the GM composition containing succinic acid which has been shown to increase elements mobilization (Wang & Mulligan, 2013). Wang & Mulligan (2013) demonstrated higher amounts of metals (*e.g.* Cu, Zn, Pb) were mobilized in a succinic acid solution compared to values leached out with distilled water. According to Visual MinteQ modelling up to 0.1% of succinic acid is responsible for Cu complexation, whereas its contribution to complexation of other elements is far below 0.1%. Moreover, susceptibility of the studied slags to weathering is generally higher compared to previously

investigated lead blast furnace (LBF) slags exposed to similar conditions (van Hullebusch et al., 2015).

Due to the mobilization of elements under abiotic conditions, GMB and UPW should also be taken into account when estimating the bacterial impact on slags weathering. The release of elements from slags exposed to biotic conditions (GMB <0.22 μm) was increased by 20-99% (CS) and 39-99% (GS) relative to abiotic experiments (Figures 6.10 A1 and A2). This amplified element release may be assigned to the presence of metabolic by-products excreted by bacteria. Those molecules supply protons that can compete with metals present in mineral phases as well as provide ions assisting in metal complexation (Gadd, 2007).

## 6.4.3  Leaching rates

*Pseudomonas aeruginosa* noticeably accelerated leaching of elements contained in slags especially at the early stages of the experiments (Table 6.2). The importance of this was demonstrated for Fe with significantly higher leaching rates throughout the whole experiment for biotic solutions compared to abiotic solutions. That is in accordance with a previous study on LBF slags bio-weathering, which showed that Fe release was governed by bacteria only (van Hullebusch et al., 2015).

The quantity of Fe released after 56 days was higher for GS as compared to CS (Table 6.2). At the same time fluorescence intensities of microbial by-products (proteins-like, siderophore-like, humic-like substances) rose up for GS (Table 6.3), hence contributed to greater complexation of Fe. On the other hand, a weaker fluorescence signal intensity of microbial by-products observed for CS might be related to metal binding (e.g. Cu) and subsequent fluorescence quenching (Tan et al., 2011; Zhang et al. 2012). It is also possible that released metals had an inhibitory effect on cell proliferation and thus metabolite production. As shown in Table 6.2, higher leaching rates of Cu and Zn were observed for CS.

Even though the Cu release was significantly higher in the early stages (14.7-5.7 mg/kg/day) of biotic experiments, it decreased significantly in the next stages reaching comparable leaching rates under biotic and abiotic conditions after 84 days (Table 6.2). Copper is found to be extractable under both abiotic and biotic conditions; however, the presence of bacteria and related by-products initially accelerates the release of easily leachable Cu appreciably. Over 56 days of CS slag exposure to GM resulted in the release of the same amount of Cu as bacteria do within 14 days. In this context, the influence of bacteria on the GS leaching is even higher since Cu released under biotic conditions within 14 days was 42% higher than the amount determined in GM after 112 days (Figure 6.4). After 112 days of experiment, biotic curves did not reach the equilibrium stage. In contrast, the trends presented by van Hullebusch et al. (2015) appeared to level off after 140 days of LBF slags bio-weathering.

## 6.4.4  Bacterially mediated weathering

Iron is an essential nutrient for bacterial growth due to its importance in enzymatic reactions (Poole & McKay, 2003; Braud et al., 2010). *Pseudomonas aeruginosa* applied to our experiments was intentionally imposed to iron-poor conditions with an assumption that this bacterium will be able to acquire this element from slags. Bacteria were able to obtain Fe contained in both CS and GS slags as bacterial growth rates in the presence of slag were enhanced compared to the growth medium without slags (Figure 6.1). Therefore, our findings clearly showed that slag provides nutrients (*e.g.* Fe, Ca, Mg and microelements) that are present in growth medium in insufficient concentration for bacterial proliferation. This observation is congruent with previous studies demonstrating greater growth rates of bacteria in the solutions supplemented with metallurgical slags or glass (Aouad et al., 2006; Yin et al., 2014). Bacterially mediated iron solubilization could be facilitated by the production of pyoverdine-like compounds as suggested by qualitative analysis (Figure 6.5). This siderophore is known to be produced when iron accessibility is limited, thereby exposing the bacteria to nutrient-stress conditions (Dumas et al., 2013).

Furthermore, results provide evidence that some quantities (3-77%) of released elements could be either taken up by a biofilm and/or associated metabolites or precipitated as proven by differences between the GMB total and GMB <0.22 µm (Figures 6.10 B1 and B2). Microbial ability towards element uptake occurs through biosorption/bioaccumulation or EPS binding (*e.g.* Mullen et al., 1989; Vecchio et al., 1998; Gadd, 2000). Both, bacterial cell walls and extracellular polymers provide binding sites due to the presence of negatively charged functional groups (Fein, 2006; Guibaud et al., 2009; Pal & Paul, 2008; D'Abzac et al., 2013; Tourney & Ngwenya, 2014; van Hullebusch et al., 2015). Total concentrations of elements were increased at least by 3% up to 77% with respect to dissolved concentrations (Figure 6.10).

No significant bacterial uptake of Cu and Pb could be observed, while bacteria exhibited a remarkable contribution toward Zn associated to the fraction >0.22 µm. For example, the high uptake of Zn could refer to the surface charge of bacterial cells that becomes more negative when pH values increase (Chang et al., 1997) and would suggest a greater biomass affinity for this element. This pattern may also be attributed to the pH of the solution. Kazy et al. (1999) demonstrated lower Cu uptake by *Pseudomonas aeruginosa* at pHs of 8-9 compared to the efficiency at slightly lower pHs (6-7). Likewise, Pérez Silva et al. (2009) revealed decreased biosorption of Cu for pH increases from 6.25 up to 7. Moreover, predominant Zn biosorption over Cu at a pH higher than 6.25 has been demonstrated (Pérez Silva et al., 2009). Furthermore, stability constants of siderophore complexes with Cu (Chen et al., 1994; Farkas et al., 1997; Enyedy et al., 2004) and Pb (Hernlem et al., 1996; Farkas et al., 2008) are higher compared to those of Zn (Schijf et al., 2015). That could overcome toxicity effects through Cu and Pb complexation, consequently reducing its uptake by biofilm (Braud et al., 2010). As

shown by Braud et al. (2010), Cu uptake could be diminished by up to 85%, when siderophore was produced. Furthermore, a greater uptake ability of *Pseudomonas aeruginosa* toward Zn respective to Pb has been shown under bio-weathering conditions (van Hullebusch et al., 2015). Moreover, as reported by Stewart et al. (2015) Pb sequestration on Fe and Mn oxides might dominate over EPS sorption resulting in the absence of toxic effect of Pb on microbial communities (Stewart et al., 2015).
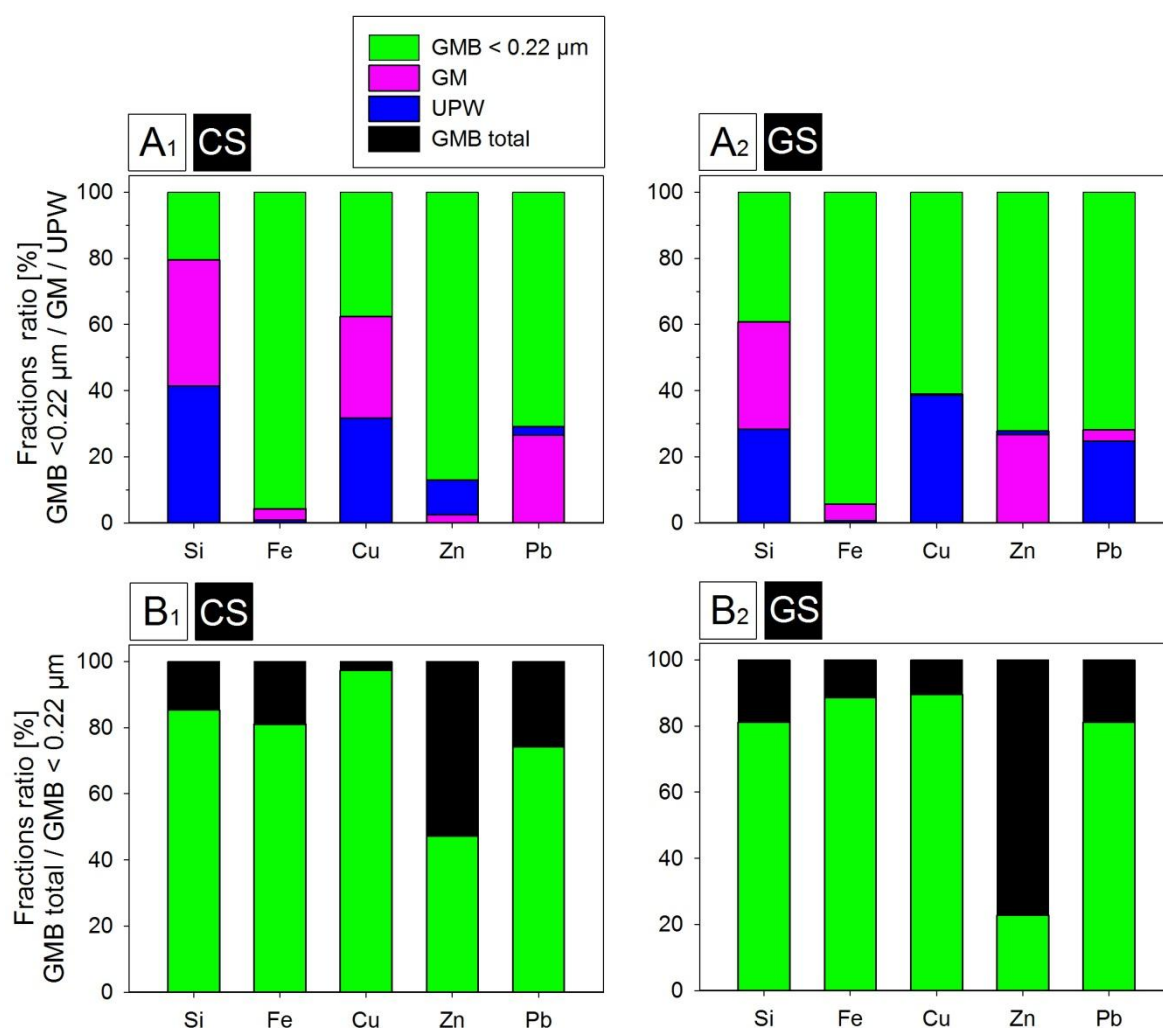


**FIGURE 6.10 Comparison of dissolved fraction ratios [%] and
dissolved biotic fraction versus fraction total.**

*A1 and A2: dissolved abiotic (GM and UPW) fractions are compared with biotic dissolved fraction (GMB <0.22 μm), B1 and B2: dissolved biotic fraction (GMB <0.22 μm) is compared with fraction total (GMB total).*

### 6.4.5  Environmental considerations

The results of the abiotic and biotic slag weathering scenarios are relevant to the conditions encountered on the slag dumping sites. A comparison of the weathering conditions demonstrated that biotic factors may considerably enhance the dissolution of the mineral phases present in slags consequently releasing elements into the environment under aerobic conditions. If the rate of dissolution achieved after 112 days would proceed further, then approximately 7-30 years (CS) and 12-114 years (GS) would be needed for a total release of metallic contaminants into the environment. However, that assumption represents the worst-case scenario because the degradation rate under field conditions would undoubtedly proceed at much lower rates than in laboratory scale. That could be because of the larger grain size of slags, changes in bacterial activity, temperature and/or other environmental parameters as well as precipitation of secondary phases which could entrap elements and reduce the slags surface exposed to weathering (Ettler et al., 2009). This study showed the bacterial contribution to the weathering should not be ignored when slags are disposed.

## 6.5  CONCLUSIONS

The results of the weathering examined on two different types of Cu-metallurgical slags (crystalline massive slag: CS and granulated amorphous slag: GS) demonstrated that the environmental proxy of heterotrophic bacteria (*Pseudomonas aeruginosa)* considerably enhances the release of major (Si and Fe) and metallic (Cu, Zn, Pb) elements relative to effects of abiotic solutions (ultrapure water and growth medium) regardless of the slags chemistry and structure. Bacterial biomass and/or associated metabolites assisted as complexing agents for Zn, Pb and Cu. For this reason not only the dissolved (<0.22 μm) fraction, but also metals bound to biofilm and related metabolites should be taken into account in evaluation of contaminants pathways. Slags grains (CS and GS) immersed in biotic solutions were found to have a greater degree of weathering features than those from abiotic experiments. Additionally, fayalite (CS) weathering zones were solely observed on the grains exposed to biotic conditions. Granulated slag is more susceptible to weathering than crystalline slag as glass, the principal component of GS, was found to weather more readily than glass and fayalite of CS. However, the metal carriers of CS (sulfides *e.g.* bornite) are more susceptible to dissolution than Cu-droplets from GS.

**ACKNOWLEDGEMENTS**

# REFERENCES

1. **Ahmed E. & Holmström S.J.M. (2014):** *„Siderophores in environmental research: roles and applications"*. Microbial biotechnology 7 (3), 196-208.

2. **Ahmed E. & Holmström S.J.M. (2015):** *„Microbe– mineral interactions: The impact of surface attachment on mineral weathering and element selectivity by microorganisms"*. Chemical Geology 403, 13–23.

3. **Aouad G., Crovisier J.L., Geoffroy V.A., Meyer J.M., Stille P. (2006):** *„Microbially mediated glass dissolution and sorption of metals by Pseudomonas aeruginosa cells and biofilm"*. Journal of Hazardous Materials 136 (3), 889-895.

4. **Auoad G., Crovisier J.-L., Damidot D., Stille P., Hutchens E., Mutterer J., Meyer J.-M., Geoffroy V.A. (2008):** *„Interactions between municipal solid waste incinerator bottom ash and bacteria (Pseudomonas aeruginosa) "*. Science of The Total Environment 393 (2), 385–393.

5. **Bartlet R.W. (1992):** *„Solution mining: Leaching and Fluid Recovery of Materials"*. Chapter 6: *„Percolation Leaching Copper Mine Waste (Primary Sulfides)"*. Gordon and Breach Science Publishers 2nd Edition, 159-168.

6. **Bhatia D., Bourven I., Simon S., Bordas F., van Hullebusch E.D, Rossano S, Lens P.N.L., Guibaud G. (2013):** *„Fluorescence detection to determine proteins and humic-like substances fingerprints of exopolymeric substances (EPS) from biological sludges performed by size exclusion chromatography (SEC)"*. Bioresource Technology 131, 159–165.

7. **Bourven I., Costa G., Guibaud G. (2012):** *„Qualitative characterization of the protein fraction of exopolymeric substances (EPS) extracted with EDTA from sludge"*. Bioresource Technology 104, 486–496.

8. **Bourven I., Simon S., Bhatia D., van Hullebusch E.D., Guibaud G. (2014):** *„Effect of various size exclusion chromatography (SEC) columns on the fingerprints of extracellular polymeric substances (EPS) extracted from biological sludge"*. Journal of the Taiwan Institute of Chemical Engineers 49, 148-155.

9. **Brandl H. & Faramarzi M.A. (2006):** *„Microbe-metal interactions for the biotechnological treatment of metal containing solid waste"*. China Particuology 4 (2), 93-97.

10. **Braud A., Geoffroy V., Hoegy F., Mislin G.L.A., Schalk I.J. (2010):** *„Presence of the siderophores pyoverdine and pyochelin in the extracellular medium reduces toxic metal accumulation in Pseudomonas aeruginosa and increases bacterial metal tolerance"*. Environmental Microbiology Reports 2 (3), 419-425.

11. **Chang J-S, Law R., Chang Ch-Ch. (1997):** *„Biosorption of lead, copper and cadmium by biomass of Pseudomonas aeruginosa PU21"*. Water Research 31 (7), 1651–1658.

12. **Chen S., Wu Z., Peng X. (2014):** *„Experimental study on weathering of seafloor volcanic glass by bacteria (Pseudomonas fluorescens) – Implications for the contribution of bacteria to the water–rock reaction at the Mid-Oceanic Ridge setting"*. Journal of Asian Earth Science 90, 15-25.

13. **Chen Y., Jurkevitch E., Bar-Ness E., Hadar Y. (1994):** *„Stability Constants of Pseudobactin Complexes with Transition Metals"*. Soil Science Society of America Journal 58 (2), 390-396.

14. **Cheng Y., Guo Z., Liu X., Yin H., Qiu G., Pan F., Liu, H. (2009):** *„The bioleaching feasibility for Pb/Zn smelting slag and community characteristics of indigenous moderate-thermophilic bacteria"*. Bioresource Technology, 100 (10), 2737-2740.

15. **Comte S., Guibaud G., Baudu M. (2006):** *„Biosorption properties of extracellular polymeric substances (EPS) resulting from activated sludge according to their type: Soluble or bound"*. Process Biochemistry 41 (4), 815-823.

16. **D'Abzac P., Bordas F., Joussein E., van Hullebusch E.D., Lens P.N.L., Guibaud G., (2013):** *„Metal binding properties of extracellular polymeric substances extracted from anaerobic granular sludges"*, Environmental Science and Pollution Research 20 (7), 4509–4519.

17. **Dartnell L.R., Roberts T.A., Moore G. Ward J.M., Muller J.P. (2013):** *„Fluorescence Characterization of Clinically-Important Bacteria"*. PLoS One 8 (9): e75270.

18. **Dumas Z., Ross-Gillespie A., Kümmerli R. (2013):** *„Switching between apparently redundant iron-uptake mechanisms benefits bacteria in changeable environments"*. Proceedings of the Royal Society B: Biological Sciences 282 (1804), 20131055.

19. **Ehrlich H.L. (1998):** *„Geomicrobiology: its significance for geology"*. Earth-Science Reviews 45 (1), 45-60.

20. **Enyedy E.A., Pócsi I., Farkas E. (2004):** *„Complexation of desferricoprogen with trivalent Fe, Al, Ga, In and divalent Fe, Ni, Cu, Zn metal ions: effects of the linking chain structure on the metal binding ability of hydroxamate based siderophores".* Journal of Inorganic Biochemistry 98 (11), 1957–1966.

21. **Ettler V. & Johan Z. (2014):** *„12 years of leaching of contaminants from Pb smelter slags: geochemical/mineralogical controls and slag recycling potential".* Applied Geochemistry 40, 97-103.

22. **Ettler V., Johan Z., Kříbek B., Šebek O., Michaljevič M. (2009):** *„Mineralogy and environmental stability of slags from Tsumeb smelter, Namibia".* Applied Geochemistry 24 (1), 1-15.

23. **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 (7), 567- 577.

24. **Ettler V., Piantone P., Touray J.C. (2003):** *„Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long- term assessment".* Mineralogical Magazine 67 (6), 1269-1283.

25. **Farkas E., Bátka D., Kremper G., Pócsi I. (2008):** *„Structure-based differences between the metal ion selectivity of two siderophores desferrioxamine B (DFB) and desferricoprogen (DFC): why DFC is much better Pb(II) sequestering agent than DFB?".* Journal of Inorganic Biochemistry 102 (8), 1654–1659.

26. **Farkas E., Csóka H., Micera G., Dessi A. (1997):** *„Copper(II), nickel(II), zinc(II), and molybdenum(VI) complexes of desferrioxamine B in aqueous solution".* Journal of Inorganic Biochemistry 65 (4), 281–286.

27. **Fein J.B. (2006):** *„Thermodynamic Modeling of Metal Adsorption onto Bacterial Cell Walls: Current Challenges".* Advances in Agronomy 90**,** 179–202.

28. **Gadd G.M. (2000):** *„Bioremedial potential of microbial mechanisms of metal mobilization and immobilization".* Current Opinion in Biotechnology 11 (3), 271–279.

29. **Gadd G.M. (2007):** *„Geomycology: biogeochemical transformations of rocks, minerals, metals and radionuclides by fungi, bioweathering and bioremediation".* Mycological Research 111 (1), 3-49.

30. **Gadd G.M. (2010):** *„Metals, minerals and microbes: geomicrobiology and bioremediation".* Microbiology 156 (3), 609-643.

31. **Gee C., Ramsey M.H., Maskall J., Thornton I. (1997):** *„Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead".* Journal of Geochemical Exploration 58 (2), 249-257.

32. **Grybos M., Billard P., Desobry-Banon S., Michot L. J., Lenain J.F., Mustin C. (2011):** *„Bio-dissolution of colloidal-size clay minerals entrapped in microporous silica gels".* Journal of colloid and interface science 362 (2), 317-324.

33. **Guibaud G., Bordas F., Saaid A., D'abzac P., van Hullebusch E.D. (2008):** *„Effect of pH on cadmium and lead binding by extracellular polymeric substances (EPS) extracted from environmental bacterial strains".* Colloids and Surfaces B: Biointerfaces 63 (1), 48–54.

34. **Guibaud G., van Hullebusch E.D., Bordas F., d'Abzac P., Joussein E. (2009):** *„Sorption of Cd(II) and Pb(II) by exopolymeric substances (EPS) extracted from activated sludges and pure bacterial strains: Modeling of the metal/ligand ratio effect and role of the mineral fraction".* Bioresource Technology 100 (12), 2959–2968.

35. **Haferburg G. & Kothe E. (2007):** *„Microbes and metals: interactions in the environment".* Journal of Basic Microbiology 47 (6), 453-467.

36. **Hernlem B.J., Vane L.M, Sayles G.D. (1996):** *„Stability constants for complexes of the siderophore desferrioxamine B with selected heavy metal cations".* Inorganica Chimica Acta 244 (2), 179–184.

37. **Kalinowski B.E., Liermann L.J., Givens S., Brantley S.L. (2000):** *„Rates of bacteria-promoted solubilization of Fe from minerals: a review of problems and approaches".* Chemical Geology 169 (3), 357–370.

38. **Kazy S.K., Sar P., Asthana R.K., Singh S.P. (1999):** *„Copper uptake and its compartmentalization in Pseudomonas aeruginosa strains: chemical nature of cellular metal".* World Journal of Microbiology and Biotechnology 15 (5), 599-605.

39. **Kierczak J. Néel C., Puziewicz J., Bril H. (2009):** *„The mineralogy and weathering of slag produced by the smelting of Ni-ores, Szklary, southwestern Poland".* The Canadian Mineralogist 47 (3), 557-572.

40. **Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Neel C., Ettler V., Mihaljevic M. (2013) :** *„Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland)".* Journal of Geochemical Exploration 124, 183-194.

41. **Konhauser K.O., Kappler A., Roden E.E. (2011):** *„Iron in microbial metabolism".* Elements magazine 7 (2), 89-93.

42. **Kuo Y., Wang J., Wang Ch., Tsai Ch. (2008):** *„Effect of water quenching and $SiO_2$ addition during vitrification of fly ash Part 1: On the crystalline characteristics of slags".* Journal of Hazardous Materials 152 (3), 994–1001.

43. **Lottermoser B.G. (2002)**: *„Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia".* Mineralogical Magazine 66 (4), 475-490.

44. **Male D.W., Leduc L.G., Ferroni G.D. (1997):** *„The potential of mining slag as a substrate for microbial growth and the microbiological analysis of slag and slag seepage".* Antonie van Leeuwenhoek 71 (4), 379-386.

45. **Manz M. & Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District, Mexico".* Environmental Pollution 98 (1), 7-13.

46. **Matlakowska R., Skłodowska A., Nejbert K. (2012):** *„Bioweathering of Kupferschiefer black shale (Fore-Sudetic Monocline, SW Poland) by indigenous bacteria: implication for dissolution and precipitation of minerals in deep underground mine".* FEMS Microbiology Ecology 81 (1), 99-110.

47. **Mullen M.D., Wolf D.C., Ferris F.G., Beveridge T.J., Flemming C.A. (1989):** *„Bacterial sorption of heavy metals".* Applied and Environmental Microbiology 55 (12), 3143-3149.

48. **Oulkadi D., Balland-Bolou-Bi C., Michot L.J., Grybos M., Billard P., Mustin C., Banon, S. (2014):** *„Bioweathering of nontronite colloids in hybrid silica gel: implications for iron mobilization".* Journal of applied microbiology, 116 (2), 325-334.

49. **Pal A. & Paul A.K. (2008):** *„Microbial extracellular polymeric substances: central elements in heavy metal bioremediation (Review)".* Indian Journal of Microbiology 48 (1), 49-64.

50. **Pandey S., Saha P., Barai P.K., Maiti T.K. (2010):** *„Characterization of a $Cd^{2+}$ -resistant strain of Ochrobactrum sp. isolated from slag disposal site of an iron and steel factory".* Current Microbiology 61 (2), 106-111.

51. **Pandey S., Saha P., Biswas S., Maiti T.K. (2011):** *„Characterization of two metal resistant Bacillus strains isolated from slag disposal site at Burnpur, India".* Joural of Environmental Biology 32, 773-779.

52. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California".* Applied Geochemistry 16 (14), 1567–1593.

53. **Pérez Silva R.M., Ábalos Rodríguez A., Gómez Montes De Oca J.M., Cantero Moreno D. (2009):** *„Biosorption of chromium, copper, manganese and zinc by Pseudomonas aeruginosa AT18 isolated from a site contaminated with petroleum''.* Bioresource Technology 100 (4), 1533–1538.

54. **Piatak N.M., Seal 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".* Applied Geochemistry 19 (7), 1039-1064.

55. **Poole K. & McKay G.A. (2003):** *„Iron acquisition and its control in Pseudomonas aeruginosa: many roads lead to Rome".* Frontiers in Bioscience 8, 661-686.

56. **Potysz A., Kierczak J., Fuchs Y., Grybos M., Guibaud G., Lens P.N.L, van Hullebusch E.D. (2016):** *„Characterization and pH-dependent leaching behaviour of historical and modern copper slags",* Journal of Geochemical Exploration 160, 1-15.

57. **Potysz A., van Hullebusch E.D., Kierczak J., Grybos M., Lens P.N.L., Guibaud, G. (2015): „***Copper Metallurgical Slags–Current Knowledge And Fate: A Review".* Critical Reviews in Environmental Science and Technology, 45 (22), 2424-2488.

58. **Rogers J.R. & Bennett P.C (2004):** *„Mineral stimulation of subsurface microorganisms: release of limiting nutrients from silicates".* Chemical Geology 203 (1), 91–108.

59. **Schijf J., Christenson E.A., Potter K.J. (2015):** *„Different binding modes of Cu and Pb vs. Cd, Ni, and Zn with the trihydroxamate siderophore desferrioxamine B at seawater ionic strength".* Marine Chemistry 173, 40-51.

60. **Schippers A., Bosecker K., Willscher S., Spröer C., Schumann P., Kroppenstedt R.M. (2002):** *„Nocardiopsis metallicus sp. nov., a metal-leaching actinomycete isolated from an alkaline slag dump".* International Journal of Systematic and Evolutionary Microbiology 52 (6), 2291-2295.

61. **Schmukat A., Duester L., Ecker D., Schmid H., Heil C., Heininger P., Ternes T.A. (2012):** *„Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength".* Journal of Hazardous Materials (227), 257–264.

62. **Seignez N., Bulteel D., Damidot D., Gauthier A., Potdevin J.L. (2006):** *„Weathering of metallurgical slag heaps: multi-experimental approach of the chemical behaviours of lead and zinc".* Waste Management and the Environment III, WIT Transactions on Ecology and the Environment 92, 31-40.

63. **Sobanska S., Ledesert B., Deneele D., Laboudigue A. (2000):** *„Alteration in soils of slag particles resulting from lead smelting".* Earth and Planetary Sciences 331 (4), 271-278.

64. **Stanley J.T., Gunsalus R.P., Lory S., Perry J.J. (2007):** „Microbial Life". Chapter 28: *„Microbial diseases of human".* 677-708. Sunderland, MA: Sinauer Associates.

65. **Stewart T.J., Behra R., Sigg L. (2015):** *„Impact of Chronic Lead Exposure on Metal Distribution and Biological Effects to Periphyton".* Environmental Science and Technology 49 (8), 5044-5051.

66. **Tan S.S., Kim S.J., Kool E.T. (2011):** *„Differentiating between Fluorescence-Quenching Metal Ions with Polyfluorophore Sensors Built on a DNA Backbone".* Journal of. American Chemical. Society. 133 (8), 2664-2671.

67. **Tourney J. & Ngwenya B.T. (2014):** *„The role of bacterial extracellular polymeric substances in geomicrobiology".* Chemical Geology 386, 115–132.

68. **Tyszka R., Kierczak J., Pietranik A., Ettler V., Mihaljevič M. (2014):** *„Extensive weathering of zinc smelting slag in the heap in Upper Silesia (Poland): potential environmental risks posed by mechanical disturbance of slag deposits".* Applied Geochemistry 40, 70-81.

69. **Uroz S., Calvaruso Ch., Turpault M-P., Frey-Klett P. (2009):** *„Mineral weathering by bacteria: ecology, actors and mechanisms".* Trends in Microbiology 17 (8), 378-387.

70. **van Hullebusch E.D., Yin N-H., Seignez N., Labanowski J., Gauthier A., Lens P.N.L., Avril C., Sivry Y. (2015) :** *„Bio-alteration of metallurgical wastes by Pseudomonas aeruginosa in a semi flow-through reactor".* Journal of Environmental Management 147, 297-305.

71. **Vecchio A., Finoli C., Di Simine D., Andreoni V. (1998):** *„Heavy metal biosorption by bacterial cells".* Fresenius Journal of Analytical Chemistry 361 (4), 338-342.

72. **Wang S & Mulligan C.N. (2013):** *„Effects of three low-molecular-weight organic acids (LMWOAs) and pH on the mobilization of arsenic and heavy metals (Cu, Pb, and Zn) from mine tailings".* Environmental Geochemistry and Health 35 (1), 111-118.

73. **White Ch., Wilkinson S.C., Gadd G.M. (1995):** *„The role of Microorganisms in Biosorption of Toxic Metals and Radionuclides".* International Biodeterioration and Biodegradation 35 (1), 17-40.

74. **Willscher S. & Bosecker K. (2003):** *„Studies on the leaching behaviour of heterotrophic microorganisms isolated from an alkaline slag dump".* Hydrometallurgy 71 (1), 257-264.

75. **Wingender J., Neu T.R., Flemming H.C. (1999):** *„Microbial extracellular polymeric substances. Characterization, Structure and Function".* Chapter 1: *„What are bacterial extracellular polymeric substances?"*, Chapter 5: *„EPS and Macro-Environment".* Springerlink

76. **Yin N.-H., Sivry Y., Avril C., Borensztajn S., Labanowski J., Malavergne V., Lens P.N.L., Rossano S., van Hullebusch E.D., (2014):** *„Bioweathering of lead blast furnace (LBF) metallurgical slags by Pseudomonas aeruginosa",* International Biodeterioration & Biodegradation 86(C), 372-381.

77. **Zhang D., Lee D-J., Pan X. (2012):** *„Fluorescent quenching for biofilm extracellular polymeric substances (EPS) bound with Cu(II)".* Journal of the Taiwan Institute of Chemical Engineers 43 (3), 450-454.

# Preface to Chapter 7

Previous chapters (4 - 6) present the research evaluating environmental risk associated with slag disposal. Considered aspects encompass number of variables such as pH conditions, the presence of various organics, impact of microbial activity. Chemical and mineralogical compositions of Cu-slags were considered and the effect of individual factors on slags weathering was compared and discussed. The data gained clearly allowed to conclude that disposal is not favorable approach of slags management and highlights therefore that these wastes should be managed in a more cautious manner or even removed from historical disposal sites.

The problem of industrial waste weathering and metal mobilization has already been recognized (Chapter 2- references therein). Thus, contemporary waste management considers disposal as the last choice of handling the wastes. Therefore, re-use of slags for various purposes such as: cement binders, additives to construction materials, abrasive materials and others has recently been applied instead (Veselská & Majzlan 2015). However, it is worth to point out that any application carries the risk of metal release from slag, thus utilization should be done with right precautions. Another approaches receiving relevant attention in context of slags management are metal leaching and recovery. These lines of management fulfill an objective of sustainable development that aims at re-using the wastes as secondary metal resources instead of wasting these valuable carriers of desired metals (Lee & Pandey, 2012). This goal of waste management is strictly related to the shortage of natural metal resources and steaming uncertainty of metal supply. Metal resources are finite due to their progressive exploration and transition into various goods that end their life as waste. On the other hand, non-destructive usage makes these metals highly recyclable and increasing emphasis has recently been placed to the need of search for recovery technologies relevant to meet metal production need and capacity (Speirs et al., 2015).
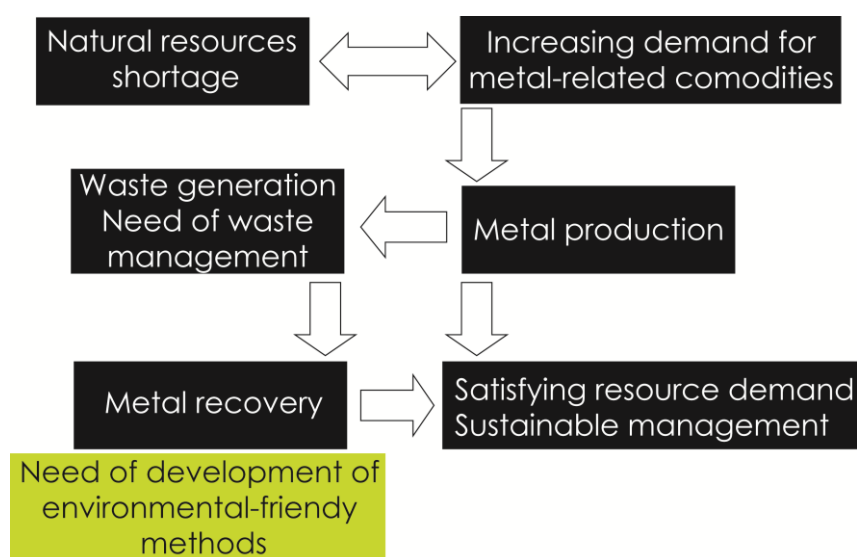


**FIGURE 6.11 A justification for the need of search for "green" methods of metal recovery.**

In these regards, various approaches of metal extraction and recovery are currently being developed. The first step to recover metals from wastes is the critical evaluation of extraction conditions which could allow to re-gain quantity of metal (close to its total content in waste) in a possibly short time. Additionally, operation should be conducted at conditions of low-energy demand in order to ensure economic interest to the process. Currently, microbe-assisted treatment of wastes gains interest due to its environmental-friendly specificity. Number of microbial organisms has been used for assisting bioleaching processes at laboratory scale. These studies are relevant to further expansion of metal bioleaching at larger scale that currently remain undone. According to a literature survey, uniform conditions which could be efficient for any waste do not exist so far as treatment design is specific to waste serving as metal resource. The main metal bioleaching mechanisms evolved include acidolysis and complexation. However, the question of which of these processes plays a superior role when Cu-slags subjected to bioleaching is yet unanswered. In this context, it appears to be worthwhile trying the feasibility of leaching by means of bacteria for studied Cu-slags. Thus, chapter 7 presents the results of a study considering the effect of two types of bacteria on Fe, Cu and Zn bioleaching dynamics and efficiency from Cu-slags. The recovery of these metals is of economical relevance, and additionally the objective is well suited to the goals of contemporary waste management whereby treating wastes as secondary resources will especially be covered.

**Speirs J., McGlade C., Slade R. (2015):** „*Uncertainty in the availability of natural resources: Fossil fuels, critical metals and biomass*". Energy Policy 87, 654-664

**Veselská V., & Majzlan J. (2015):** „*Environmental impact and potential utilization of historical Cu-Fe-Co slags*". Environmental Science and Pollution Research, 1-16.

**Lee J-ch. & Pandey B.D. (2012):** „*Bio-processing of solid wastes and secondary resources for metal extraction-A review*", Waste Management 32 (1), 3-18.

# CHAPTER 7

# COMPARISON OF Cu, Zn and Fe BIOLEACHING FROM Cu-METALLURGICAL SLAGS IN THE PRESENCE OF *PSEUDOMONAS FLUORESCENS* AND *ACIDITHIOBACILLUS THIOOXIDANS*

# ABSTRACT

Metal leaching from metallurgical wastes (slags) by means of environmentally friendly approaches is promising for practical applications. The goal of this study was to compare the feasibility of metal bioleaching from Cu-slags by means of bacteria *Pseudomonas fluorescens* and *Acidithiobacillus thiooxidans*. Two size fractions (< 0.3 mm and 1-2 mm) of two types of Cu-slags (massive crystalline slag and granulated amorphous slag) were used to study metal (Cu, Zn and Fe) bioleaching. The 40-days bioleaching experiments with *P. fluorescens* began at circumneutral pH (7.0), whereas the experiments with *A. thiooxidans* were started under acidic (pH 2.5) conditions. The results demonstrated that *A. thiooxidans* catalyzes metal leaching from both slag types investigated. After 21 days of incubation, optimal leaching was achieved and up to 79 % Cu, 76 % Zn and 45 % Fe could be extracted from crystalline slag under conditions of 1 wt.% pulp density and particle size < 0.3 mm. The optimal efficiency achieved with amorphous slag was 81 % Cu, 79 % Zn and 22 % Fe when 1 % pulp density and 1-2 mm particle size were used. The use of *P. fluorescens* resulted in poor leaching efficiencies as compared to the performance of *A. thiooxidans,* presumably due to the higher pH conditions maintained during the *P. fluorescens* incubations. The maximum metal leaching efficiencies with *P. fluorescens* were achieved at 1 % pulp density and particle size < 0.3 mm and did not exceed 10 % Cu, 4 % Zn, 0.3 % Fe for CS and 4 % Cu, 3 % Zn, 0.7 % Fe for AS. Both slags exhibited a good potential for bioleaching with *A. thiooxidans,* however; further optimization of the processing parameters (e.g. pulp density, particle size and pH) is needed to improve the efficiency.

**Keywords:** Cu-slags, metals (Cu, Zn, Fe,) bioleaching*, Pseudomonas fluorescens, Acidithiobacillus thiooxidans*

# 7.1 INTRODUCTION

Industrial smelting activities have produced huge quantities of by-product slags that still contain significant amounts of residual metals (*e.g.* Cu >1 wt.%) of environmental concern. Currently, these wastes have been used as supplementary materials for civil engineering applications such as cement and concrete additives, road bed filling materials or as hydraulic construction materials (Ettler et al., 2001; Shi et al., 2008; Ettler et al., 2009; Piatak & Seal, 2010; Harish et al., 2011; Chen et al., 2012; Schmukat et al., 2012). In contrast, the use of former pyrometallurgical techniques has led to the disposal of metal-laden slags nearby smelter complexes. Any management practice carries the risk of the release of metallic elements to the environment (Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Piatak et al., 2004; Kierczak et al., 2013; Ettler & Johan, 2014). The presence of metal at excessively high concentration levels in the environment is undesirable, because this may lead to deleterious effects on living organisms and metal accumulation at higher levels of the food chain. Therefore, slag has to be managed in a mode that ensures maximum environmental protection (Schmukat et al., 2012; Schmukat et al., 2013).

The quantities of metals present in copper slags are usually too low and are considered to be economically non-viable for recycling by any traditional recovery process. On the other hand, the slags would be more appropriate for building and construction materials or for any other reuse strategies after their metal content is reduced. Thus, strong emphasis has recently been placed on novel leaching and recovery technologies.

Leaching is a promising treatment and metal recovery route for Cu-slags. An important advantage of this approach is the yield of Cu and other metals whose natural reserves are progressively depleting (Prior et al., 2012). Several approaches for metal leaching from Cu-slags have been reported in the literature (Potysz et al., 2015: references therein). Chemical extraction with various leaching agents such as sulfuric acid, ferric chloride, ammonium chloride, ferric sulfate, ammonium sulfate as well as hydrochloric and nitric acids were found to rapidly and efficiently solubilize metals (up to 99 % of bulk content) from slags. An important disadvantage of chemical processes is the costs involved, mainly associated with chemical reagents and energy demands (Yang et al., 2010). For this reason, the use of microorganisms (bioleaching) for metal extraction has been investigated as an environmentally friendly and economically viable alternative (Banza et al., 2002; Vestola et al., 2010; Erüst et al., 2013; Vainshtein, 2014; Sukla et al., 2015).

The bioleaching process is based on the ability of microbial mediated biochemical reactions to dissolve phases present in slags and solubilize valuable metals (Ehrlich, 1998; Suzuki, 2001; Watling, 2006; Gadd, 2010). The processes involved in bioleaching include acidolysis, complexation and redox transformations. Autotrophic bacteria such as *Acidithiobacillus*

*thiooxidans* and *A. ferroxidans* have been used commonly for bioleaching various materials such as slags, fly ashes and electronic wastes (Krebs et al., 2001; Ishigaki, 2005; Vestola et al., 2010; Brandl, 2001). The effectiveness of those bacteria was mainly attributed to their ability to lower the pH through sulfuric acid production. Acidic conditions are favorable for metal extraction (Suzuki, 2001; Lee and Pandey, 2012) due to proton replacement of metals entrapped in phases. *A. thiooxidans* and *A. ferroxidans* utilize elemental sulfur as an energy source and the bioprocess corresponds to the following acid producing reaction:

$$S + 1.5\ O_2 + H_2O \rightarrow H_2SO_4 \rightarrow SO_4^{2-} + 2\ H^+ \qquad\qquad Eq.\ 1$$
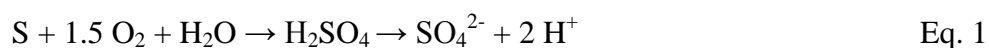
Another important factor that renders acidophilic bacteria efficient is their tolerance to harsh environmental conditions including low pH (*e.g.* pH < 1) and high metal concentrations (Bosecker, 1997; Leduc et al., 1997; Watling, 2006; Erüst et al., 2013).

The ability of heterotrophic bacteria such as *Pseudomonas sp.* to leach the metals has also been reported (Brandl & Faramarzi, 2006; Cheng et al., 2009; Aouad et al., 2006; Aouad et al., 2008; Chen et al., 2014; Yin et al., 2014; van Hullebusch et al., 2015; Potysz et al., 2016a). Circumneutral pH conditions required for the growth of *Pseudomonas sp.* could imply a lower efficiency in terms of metal leaching because of the lower solubility of metals under these conditions. For example, 112-days exposure of Cu-slags to *P. aeruginosa* (pH 7.8) led to the extraction of Cu at levels not exceeding 8.9 % (503 mg/kg) (Potysz et al., 2016a). However, excretion of extracellular organic metabolic compounds, for example siderophores, may be a factor playing a role in the extraction (Bosecker, 1997; Gadd, 2004; Sand & Gehrke, 2006). Microbially-derived metabolites assist the extraction process through proton detachment from the functional groups of the organic compounds creating binding sites with high complexation affinity towards metals. Proton attack of the mineral phase may lead to metal release and its subsequent complexation by the organic molecule.

Although the efficiency of bioleaching is known to be restricted by the tolerance of bacteria towards metals and longer treatment time as compared to chemical leaching, high metal extraction efficiencies can be achieved when process conditions are maintained at optimal levels for high microbial activity (Sukla et al., 1995; Brandl et al., 2001; Vestola et al., 2010). Optimal conditions for bioleaching require a number of parameters to be evaluated because the best leaching approach is specific to the chemical and mineralogical composition of the material subjected to the process. Therefore, the performance of different bacterial strains as leaching agents as well as operating parameters such as pulp density and particle size are important to ascertain the bioleaching performance. In this regard, an exploration of effective bioleaching methods and estimation of underlying benefits should be prioritized.

The objective of this study was to compare the ability of two different bacterial strains to be used as metal leaching agent for Cu-metallurgical slags. *P. fluorescens* (DSM 50091) was employed as the representative of heterotrophic bacteria, known to produce siderophores, whereas *A. thiooxidans* (DSM 9463) was selected as lithoautotroph known for its ability to

produce sulfuric acid from reduced sulfur compounds. Two experimental designs were used for each microorganism. The experimental approaches considered the effect of the particle size (PS) (< 0.3 mm and 1-2 mm) and pulp density (PD) (amount of slag [kg] per volume of solution [L]) (1 and 3 %) on metal (Fe, Cu, Zn) bioleaching efficiencies. The following questions were addressed in this study: i) what is the efficiency of *P. fluorescens* and *A. thiooxidans* in terms of metal leaching from Cu-slags?, ii) what conditions are appropriate for further process development?, and iii) which slag type exhibits greater potential for bioleaching?

# 7.2  MATERIALS AND METHODS

## 7.2.1  Cu slags

Two representative samples of Cu-pyrometallurgical slags were chosen to test the feasibility of a bioleaching process. Granulated amorphous (modern: XXI century) slag (AS) represented glassy material, whereas massive crystalline (historical medieval) slag (CS) was mainly composed of fayalite. Bulk concentrations of metals of interest (Cu, Zn and Fe) and overview of phase composition are presented in Table 7.1. Detailed characterization of slags is given elsewhere (Potysz et al., 2016b).

**TABLE 7.1 Chemical and mineralogical composition of crystalline and amorphous Cu-slag (Potysz et al., 2016a, 2016b).**

| | *Crystalline massive Cu-slag (CS)* | *Granulated amorphous Cu-slag (AS)* |
|---|---|---|
| ***Bulk chemical composition*** | | |
| *Fe (g/kg)* | 355 | 115 |
| *Cu (mg/kg)* | 5657 | 11425 |
| *Zn (mg/kg)* | 3962 | 7810 |
| ***Structure*** | | |
| Crystalline | | Amorphous |
| ***Mineral phases: (++ major, + minor, (+) traces)*** | | |
| • Fayalite $((Fe^{2+})_2SiO_4)$ ++ | | • Glass ++ |
| • Glass ++ | | • Metallic Cu-droplets + |
| • Bornite $(Cu_5FeS_4)$ + | | |
| • Chalcopyrite $(CuFeS_2)$ (+) | | |
| • Pyrrhotite $(Fe_{(x-1)}S)$ + | | |

## 7.2.2  Bacterial strains

### 7.2.2.1  *Acidithiobacillus thiooxidans* DSM 9463

The gram negative bacterial strain of *A. thiooxidans* (DSM 9463) was grown in salt medium composed of 2 g ammonium sulfate $(NH_4)_2SO_4$, 0.25 g of magnesium sulfate $(MgSO_4 \cdot 7H_2O)$, 0.1 g di-potassium hydrogen phosphate $(K_2HPO_4)$, 0.1 g potassium chloride (KCl) and 1% (*wt./v*) of elemental sulfur (S) per 1 L of ultrapure water. pH of the growth medium was adjusted to 2.5 and bacteria was grown two times over one week in order to adjust to pH conditions lower than its optimal (pH= 3.5). 2% (*v/v*) of pre-grown inoculum was introduced to each biotic batch flask.

### 7.2.2.2  *Pseudomonas fluorescens* DSM 50091

The gram negative bacterial strain of *P. fluorescens* (DSM 50091) used as the bioleaching agent was purchased from DSMZ. This bacterium was initially grown in nutrient broth medium (pH 6.9) for 24 h. Afterwards, the cells were harvested and washed 3 times using sterile 5% NaCl. This bacterium was then re-suspended in ultrapure water and 2% (*v/v*) of inoculum was supplemented into respective batch incubations.

## 7.2.3  Bioleaching experiments

Bioleaching experiments were designed to study the effect of particle sizes (1-2 mm and <0.3 mm) and pulp density (1% and 3% (*wt./v*)) on Cu, Zn and Fe extraction efficiencies. The experiments were carried out in acid (10% $HNO_3$) washed Erlenmeyer flasks. All materials were sterilized at 121°C for 20 minutes prior to use. Every experimental step was done under sterile conditions. The reactors were kept closed using cotton plug on an orbital shaker, at 100 rpm, at a controlled temperature of 30°C. Solutions sampled from the batches were filtered using 0.45 μm nitrocellulose filters (Whatman) for determination of element concentrations in the leachates. The pH of the solutions was measured immediately after opening the flasks. Experiments were performed in duplicates. After experiment termination, solid samples were gently rinsed with ultrapure water and kept for drying at room temperature and further scanning electron microscopic observations.

### 7.2.3.1   Bioleaching with *A. thiooxidans*

The bioleaching experiments with *A. thiooxidans* were performed in a mineral salt medium composed of 0.1 g di-potassium hydrogen phosphate ($K_2HPO_4$), 0.25 g magnesium sulfate ($MgSO_4 \cdot 7H_2O$), 2.0 g ammonium sulfate ($(NH_4)_2SO_4$), 0.1 g potassium chloride (KCl) and 2% (*wt./v*) of elemental sulfur per 1 L of ultrapure water. The initial pH value of growth medium was set at 2.5. 2% (vol.) of pre-grown bacterial culture (described above) was inoculated to the batch reactors. Abiotic growth medium supplemented with slag was run as the control. Samples were taken after 1, 2, 3, 6, 9, 14, 21 and 40 days.

### 7.2.3.1.1   Activity test for *A. thiooxidans*

At the end of the biotic experiments, an activity test was done in order to confirm the maintenance of living bacterial cells. An aliquot of 2% (*v/v*) of the leachate from each flask was transferred to fresh medium (pH 2.5) supplemented with 1% (*wt./v*) of elemental sulfur. Flasks were kept for 10 days at 30°C and observed with respect to sulfur oxidation and compared with experimental controls (bacteria not exposed to high metal concentrations). Sulfur oxidation by bacteria could be recognized by changes in solution turbidity and subsequent sulfur settling, whereas in the absence of bacteria, sulfur remained floating on the surface of the medium (Figure S1 Supplementary materials).

### 7.2.3.2   Bioleaching with *P. fluorescens*

The experimental approach included: i) biotic treatment of slags in the presence of *P. fluorescens* bacteria and ii) abiotic treatment with sterile growth medium (GM). The growth medium used in this experiment consists of succinic acid (4 g), ammonium sulfate (1 g), disodium hydrogen phosphate (0.2 g) and Tris buffer (6 g) per 1 L of ultrapure water (Yin et al., 2014). Two percent (*v/v*) of pre-grown bacterial culture (described above) was inoculated to the bioleaching reactors. The initial pH of the medium was adjusted to 7.0 using 5 M NaOH. The experiments were carried out for 40 days, whereas the sampling times were fixed at 3, 7, 14, 21, 30 and 40 days. During each sampling time, 10 mL of supernatant was collected for elemental analysis and the amount of leachate sampled was replaced by the respective volume equivalent of fresh medium. At the end of each experiment, biomass from batch incubations was plated on agar plates (composed of plate counting agar) at aerobic conditions at 30°C and observed by naked eye with respect to bacterial type purity in order to ensure that no cross contamination in the batch experiments occurred.

## 7.2.4 Analytical methods

### 7.2.4.1 Metal measurements

Concentrations of metals (Cu, Zn and Fe) in the leachates were measured using Atomic Absorption Spectrometer (AAS 200 Perkin Elmer). The detection limits were between 0.01 and 0.02 mg/L for all elements analyzed. The calibration was done using standards of known metal concentrations. Quality control included systematic analysis of calibration standards. The procedure was repeated at least once for every 10 samples analyzed. Additionally, repeated analysis of randomly chosen samples was done in order to confirm the values obtained from the previous measurement. The quantities of metals in the solutions were converted to express the values in mg of element released per kilogram of the slag by multiplying the metal concentration in the solution by the liquid to solid ratio (Piatak et al., 2015).

### 7.2.4.2 Scanning electron microscopic (SEM) observations

Slags were examined with respect to alteration features resulting from abiotic and biotic treatments. Dried slag grains were coated with Au and mineralogical analysis was performed under SEM equipped with energy dispersive spectrometer (EDS) (JEOL JSM-601OA) at high vacuum and 15-20 kV working mode.

# 7.3 RESULTS

## 7.3.1 pH change

### 7.3.1.1 *A. thiooxidans* pH profiles

The change of pH observed in the biotic and abiotic experiments with *A. thiooxidans* is presented in Figure 7.1 (A-D). At the initial stages of abiotic experiments with CS, the pH increased from 2.5 up to about 4.3 (for both particle sizes and all pulp densities investigated) and then decreased slightly, reaching near steady state values after 21 days of incubation with pH values between 3.0 and 3.9.

In the case of abiotic leaching with AS, the pH increased to values between 5.7 and 6.0 for the smaller size slag fractions and between 4.9 and 5.0 for the larger sizes slag fractions. For the experiments carried out under biotic conditions, the pH generally dropped more sharply for CS than for AS except for 1-2 mm slag size with a pulp density of 1 %. The pH, as low as 0.5-

0.7 (PD 1-3 %) and 0.6-1.1 (PD 1-3 %) was observed after 40 days under biotic conditions with CS for the particles 1-2 mm and < 0.3 mm, respectively. In the case of AS, a pH lowering (until 0.8) was reached only for the particle size 1-2 mm at 1 % pulp density, whereas the pH did not become lower than 3.2 when slag at a 3 % pulp density was used. The use of smaller particle sizes (< 0.3 mm) of AS resulted in a progressive pH decrease, but its value did not decrease beyond 3.2 (PD 1 %).

### 7.3.1.2 *P. fluorescens* pH profiles

The pH profiles in abiotic and biotic batch experiments with *P. fluorescens* are displayed in Figure 7.1 E and F. The pH in the abiotic batches was stable due to the buffering capacity of the solution (*i.e.,* addition of 6 g/L of Tris). However, despite the presence of Tris buffer in biotic medium, a pH increase was observed (Yin et al., 2014). The pH profiles from biotic experiments were comparable for both slag types tested. At the early stage of the biotic experiments performed with particle sizes 1-2 mm, the pH increased to 8.0 (PD 1 %) and 8.8 (PD 3 %) in the case of CS and 7.8 (PD 1 %) and 8.3 (PD 3 %) for AS. At the end of the experiments (40 days), the values increased up to 9.5-9.7 and 9.8 for CS and AS, respectively. An increase in the pH values during batch incubations with finer particles was less pronounced and after 40 days of batch incubations, the pH values were 7.3-7.4 and 7.5-7.6 for CS and AS, respectively (Figure 7.1 E and F).
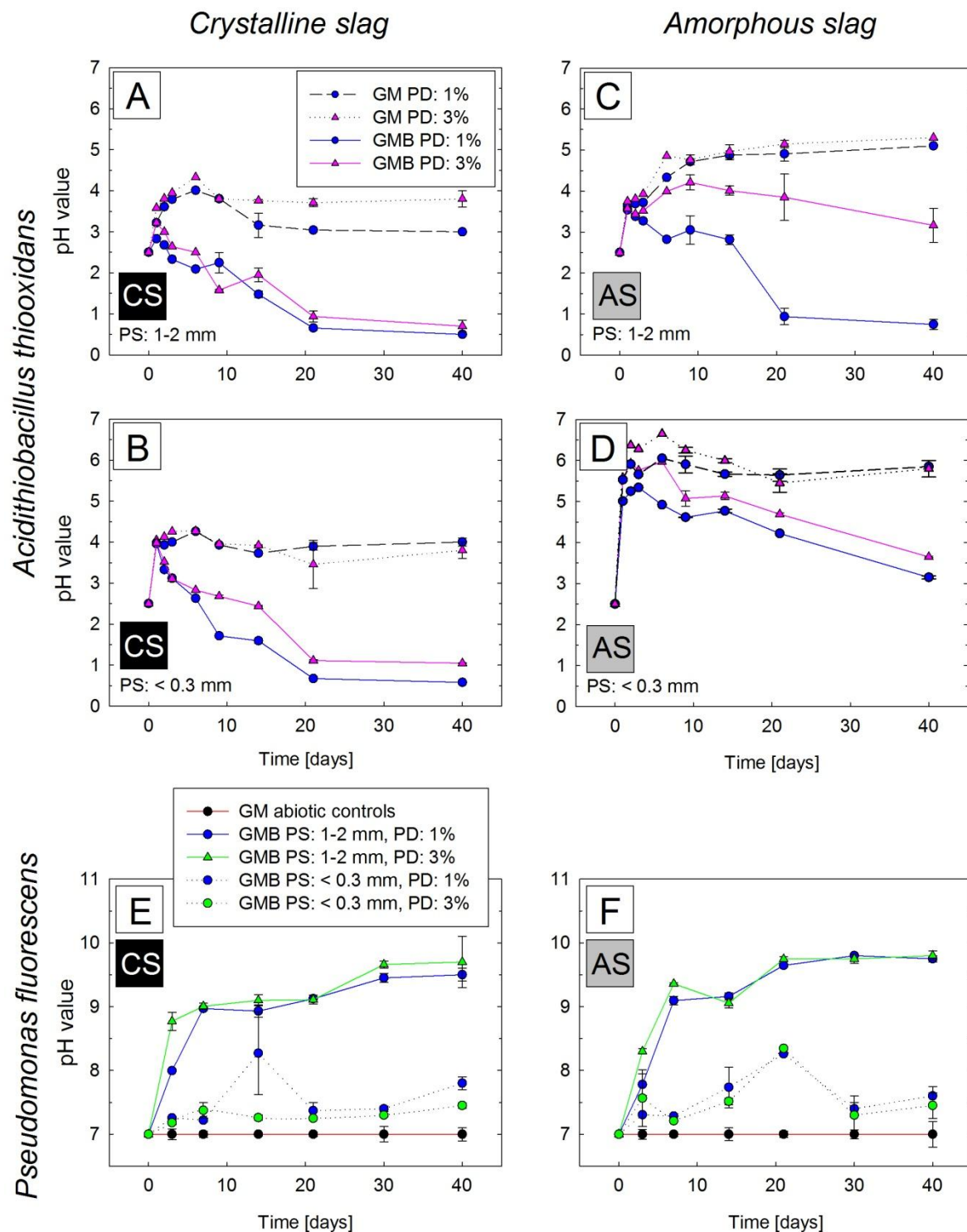
**FIGURE 7.1 Evolution of pH throughout the experiment with *A. thiooxidans* (A-D) and *P. fluorescens* (E-F).**

*(CS: crystalline slag, AS: amorphous slag, GM: growth medium, GMB: growth medium with bacteria, PS: particle size, PD: pulp density)*

## 7.3.2  Solubilization of metals (Cu, Zn, Fe) during bioleaching

### 7.3.2.1    Effect of *A. thiooxidans* on metal solubilization

The element release from Cu-slags subjected to abiotic and biotic incubations is presented in Figures 7.2 – 7.5 and these profiles were expressed in mg of element released per kg of slag. The use of *A. thiooxidans* as the leaching agent yielded high metal extraction efficiencies. Under biotic conditions with CS, the release of metals steeply increased within 21 days of incubation, for all the conditions tested. Afterwards, the Cu and Zn bioleaching followed a near steady state. In contrast, the release of Fe did not reach steady state even after 40 days of incubation. Under biotic conditions, the use of smaller particle sizes (< 0.3 mm) of CS led to better bioleaching, reaching a maximum of 4694 mg/kg (Cu) and 3465 mg/kg (Zn) after 40 days of incubation at 1 % pulp density. At the same time, up to 2595 mg/kg (Cu) and 2415 mg/kg (Zn) were released from the particle size 1-2 mm at 1 % pulp density. The slag particle size did not have any significant effect on Fe release as similar quantities were released after 40 days of incubation, reaching up to 254-217 g/kg (PD 1-3 %) and 257-197 g/kg (PD 1-3 %) for the particle sizes < 0.3 mm and 1-2 mm, respectively. A comparison of metal values leached after 40 days of abiotic and biotic experiments indicated that *A. thiooxidans* improved the extraction efficiency by a factor 3.0 (Cu), 8.3 (Zn) and 9.5 (Fe) (Figure 7.2).

Different trends of elements leaching were observed when AS was subjected to the bioleaching. Slag with a particle size 1-2 mm exposed to bioleaching conditions released 10,000 mg/kg (Cu), 5500 mg/kg (Zn) and 69.0 g/kg (Fe) at a 1 % pulp density at the end of the experiment. A much lower extraction efficiency was achieved when the pulp density of 1-2 mm particles was increased from 1 to 3 % and the amount of metals extracted reached maximum values of 2038 mg/kg (Cu), 975 mg/kg (Zn) and 3 g/kg (Fe). A reduction of the particle size of AS to < 0.3 mm showed a steep increase of the metal release throughout the experiment, especially after 21 days. Higher values of extracted metals from slag particles < 0.3 mm were observed at lower pulp density (1 %) as compared to 3 % and reached up to 5400 mg/kg (Cu) and 3375 mg/kg (Zn). The extraction yields under biotic incubations were improved by factors of 8.7 (Cu), 6.8 (Zn) and 42.4 (Fe), respectively, as compared to incubations with growth medium without bacteria (Figure 7.3).

**FIGURE 7.2 The release of metals from crystalline slag in the experiment with**
*A. thiooxidans.*

*(GM: growth medium, GMB: growth medium with bacteria, PS: particle size, PD: pulp density)*

**FIGURE 7.3 The release of metals from amorphous slag in the experiment with**
*A. thiooxidans***.**

*(GM: growth medium, GMB: growth medium with bacteria, PS: particle size, PD: pulp density)*

### 7.3.2.2  Contribution of *P. fluorescens* to metal solubilization

During the initial stages of the bioleaching experiments, the values of extracted metals were generally low (Figure 7.4). During the initial stages of the experiments (3 days), *P. fluorescens* improved metal extraction from CS by factors up to 3.4 (Cu), 1.2 (Zn) and 1.3 (Fe) (Figure 7.4) compared to experiments performed in the presence of growth media alone. Likewise, leaching under biotic conditions with AS was improved by factors of 1.6 (Cu) and 4.0 (Fe) compared to abiotic leaching, whereas Zn release was initially higher under abiotic conditions (Figure 7.5). Significant differences between biotic and abiotic experiments occurred after 30 days when the amount of metals leached out under biotic conditions was up to 26.7 times (Fe) and 60.0 times (Fe) higher as compared to abiotic leaching for CS and GS, respectively. After 40 days of incubation, the amount of metals released was 585 mg/kg (Cu), 166 mg/kg (Zn) and 936 mg/kg (Fe) for the biotic incubation with CS (Figure 7.4). At the same time, the amount of metals leached out in the biotic incubation with AS reached 474 mg/kg (Cu), 200 mg/kg (Zn) and 790 mg/kg (Fe) (Figure 7.5). The values of extracted metals under abiotic conditions did not exceed 177 mg/kg (Cu), 3 mg/kg (Zn), 8 mg/kg (Fe) for CS (Figure 7.4) and 99 mg/kg (Cu), 2 mg/kg (Zn), 15 mg/kg (Fe) for AS (Figure 7.5).
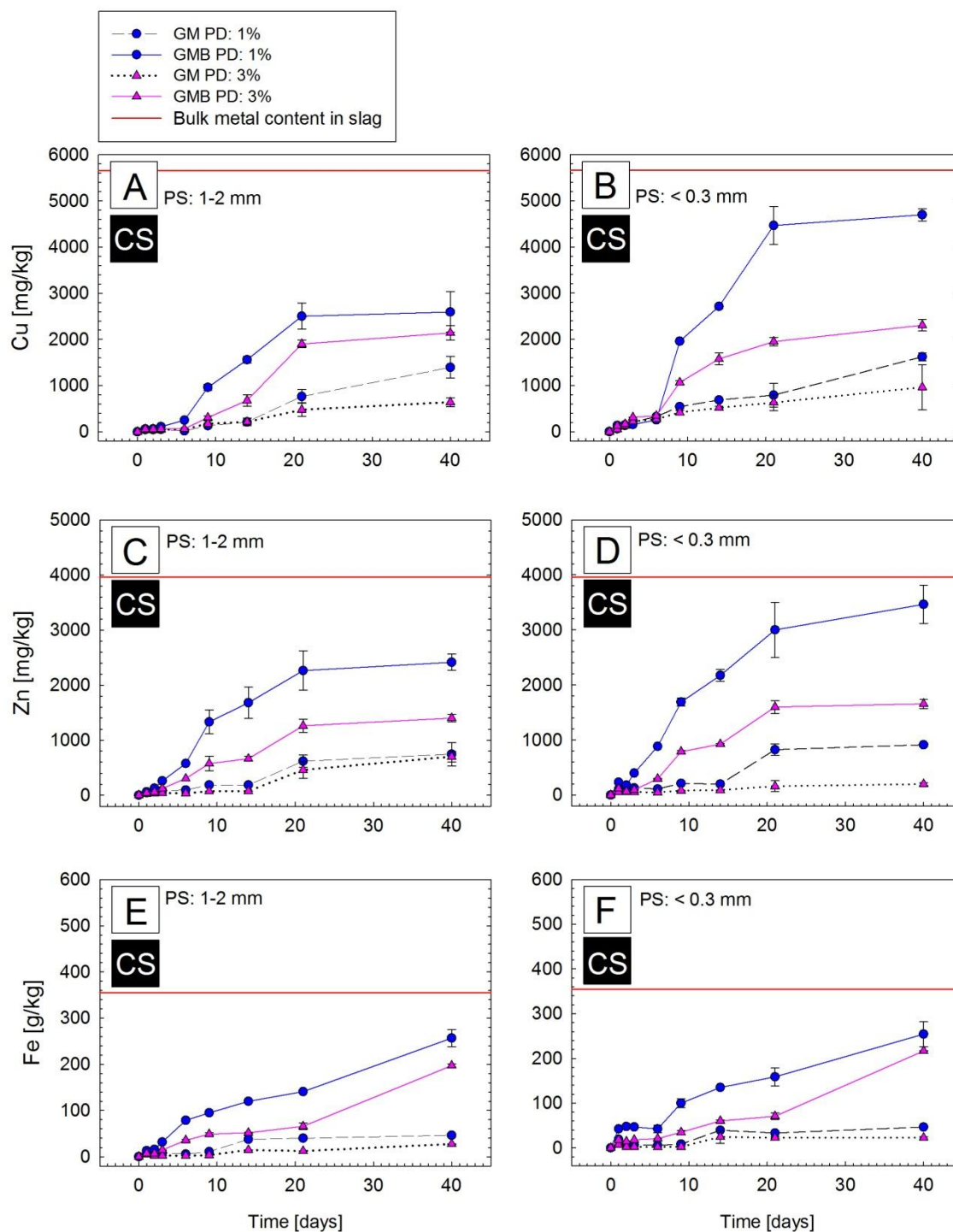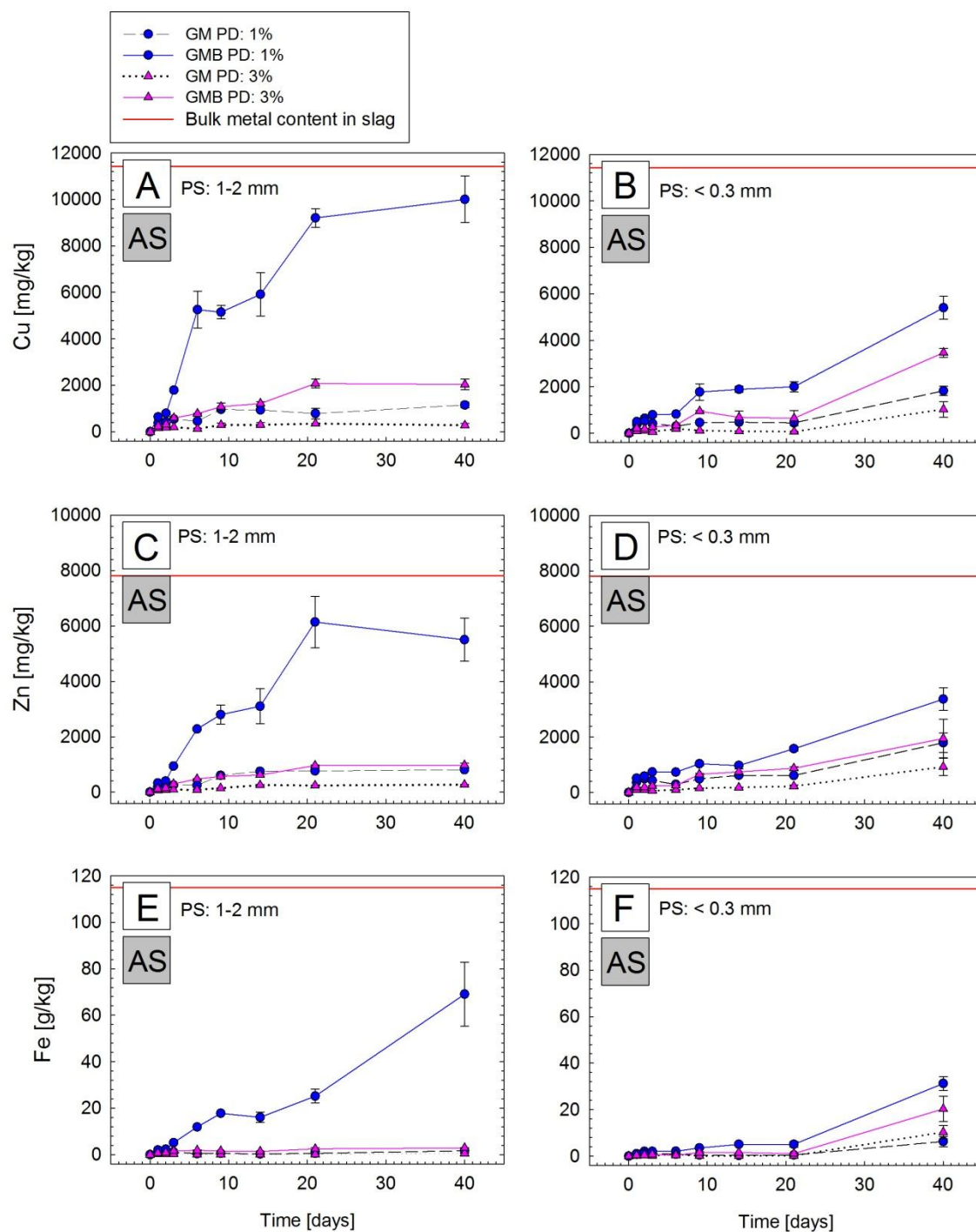
**FIGURE 7.4 The release of metals from crystalline slag in the experiment with**
**P. fluorescens.**

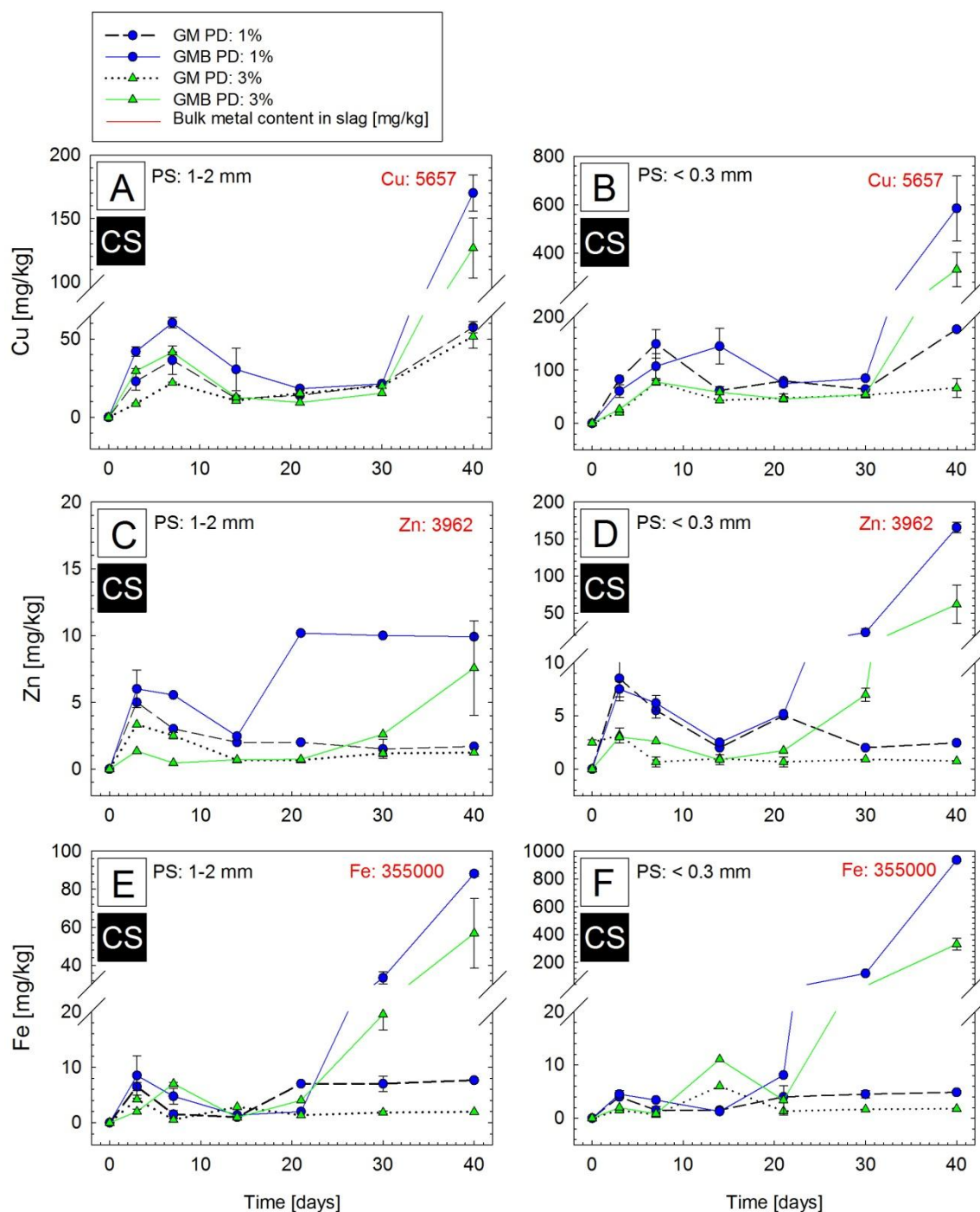*(GM: growth medium, GMB: growth medium with bacteria, PS: particle size, PD: pulp density)*

**FIGURE 7.5 The release of metals from amorphous slag in the experiment with**
*P. fluorescens***.**

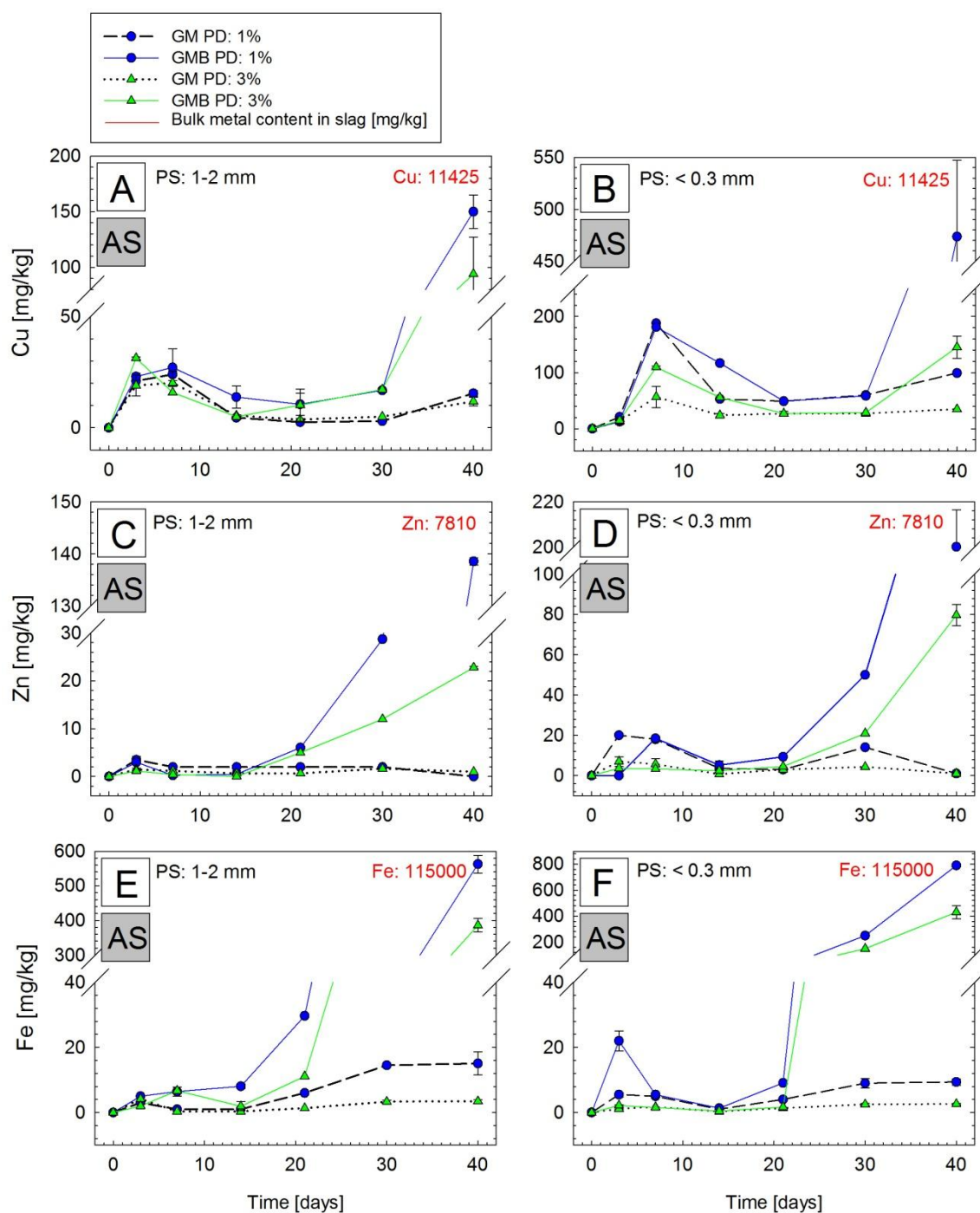*(GM: growth medium, GMB: growth medium with bacteria, PS: particle size, PD: pulp density)*

## 7.3.3 SEM observations

Scanning electron microscopic observations were carried out on the slag grains resulting from biotic and abiotic incubations. Representative alteration features were selected based on numerous observations. Comparison of slags dissolution under exposure to different experimental conditions is shown in Figures 7.6 - 7.8.

### 7.3.3.1 Slags alteration under exposure to *A. thiooxidans*

*Crystalline slag*

Crystalline slags resulting from abiotic and biotic incubation were found to have distinct dissolution features (Figure 7.6). Grains exposed to abiotic leaching displayed the presence of etched zones on glass, fayalite and sulfides (Figures 7.6 A1 and A2). Similar signs of dissolution were observed in the case of biotic incubation; however, the erosion zones appeared to have deeper perforation when compared to features of grains from abiotic experiments (Figures 7.6 B1, B2 and B3). The dissolution of phases present in CS under biotic conditions is also shown in Figures 7.6 C1 and 6 C2.

*Amorphous slag*

Amorphous slags exposed to abiotic solutions were found to be strongly perforated (Figures 7.7 A1 and A2). An important removal of Cu-droplets from glass was noted (Figure 7 A2). Dissolution features of grains resulting from biotic incubation at 3 % pulp density exhibited similar features to those resulting from abiotic incubations (Figures 7 B1 and B2), whereas grains resulting from the biotic incubation at 1 % pulp density displayed strong alteration (Figure 7.7 C1 and C2). The changes on AS (PS: 1-2, PD: 1 %) were visible even at macroscale (Figure S2 Supplementary materials). The color with biotic treatment changed from brownish to white and the material became friable. In contrast, the original material is vitreous and angular (Potysz et al., 2016b). According to SEM observations, nearly complete removal of metallic contaminants was achieved because only the remaining impurities entrapped within the newly formed crystals could be ascertained (Figure 7.7 C1). Long-term (40 days) exposure of AS to a strongly biological acidic solution resulted in the conversion of the material to calcium sulfate with impurities of Si, Cu, Pb and Fe according to energy dispersive spectroscopy (EDS).
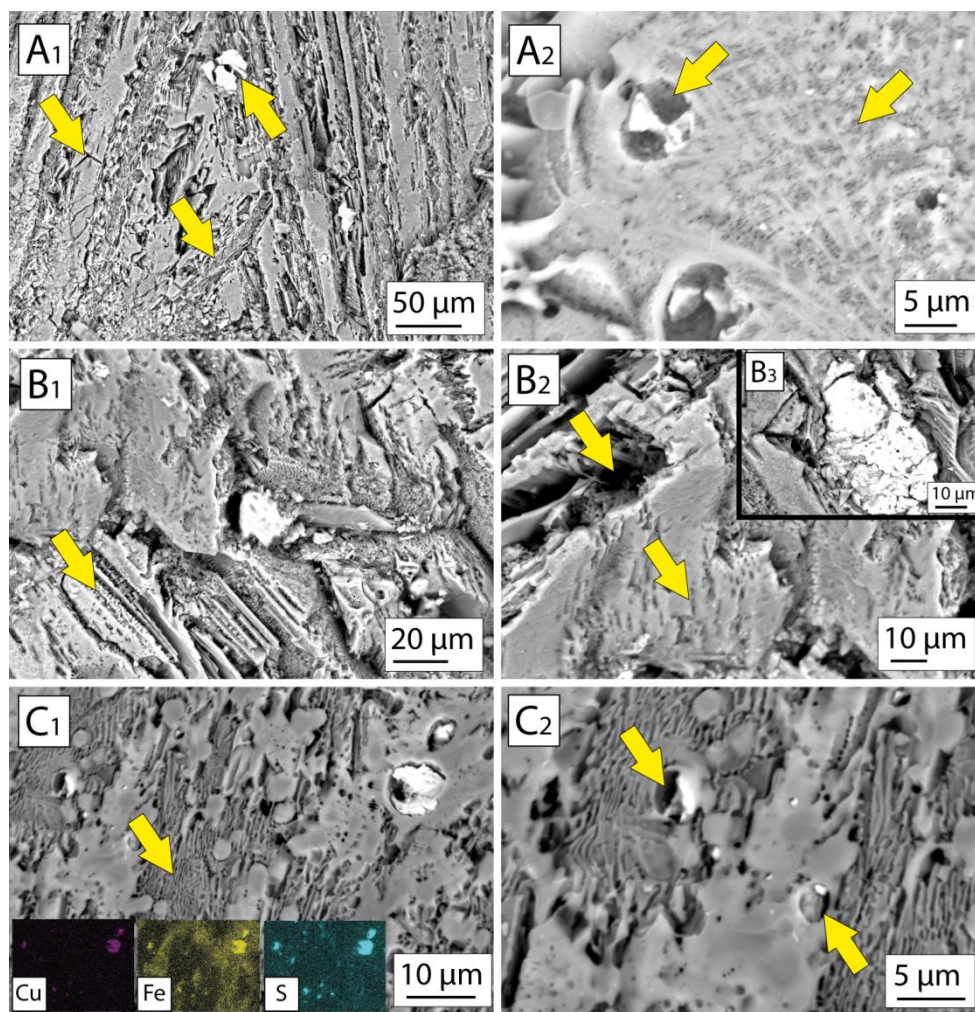
**FIGURE 7.6 SEM images of CS grains after abiotic (A) and biotic leaching (B-C) with *A. thiooxidans.***

*Arrows indicate: A1 and A2: glass and sulfides dissolution (GM), B1 and B2: fayalite dissolution, B3: partial dissolution of sulfides (GMB), C1: fayalite and glass dissolution, C2: Sulfide dissolution (GMB).*
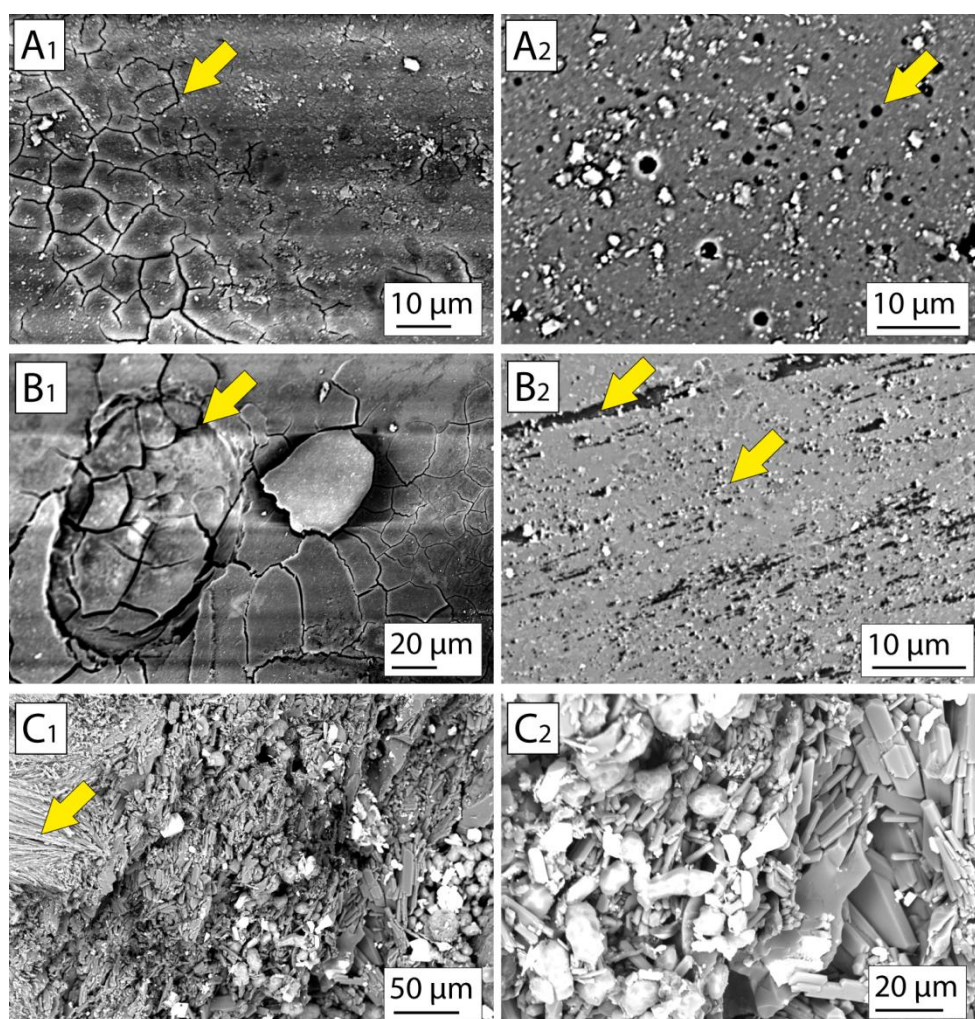
**FIGURE 7.7 SEM images of AS grains after abiotic (A1 and A2) and
biotic leaching (B1-C2) with *A. thiooxidans*.**

*Arrows indicate: A1: glass fracturing, A2: Cu-droplets removal, B1: glass fractionation,
B2: glass dissolution and Cu-droplets removal (GMB PD: 3%), C1 and C2: Amorphous slag
fractures (GMB PD: 1%).*

### 7.3.3.2 Slags alteration under exposure to *P. fluorescens*

Alteration features observed on slag grains from the incubations with *P. fluorescens* were less
pronounced (Figure 7.8) compared to those resulting from the incubations with *A.
thiooxidans*. The CS grains resulting from abiotic experiments were barely altered as shown
in Figure 7.8 A. The breakdown of sulfides was commonly found (Figure 7.8 B), whereas
round-shaped alteration zones on fayalite were observed occasionally (Figure 7.8 C).
Likewise, AS was less altered with *P. fluorescens* as compared to acidic experiments with *A.
thiooxidans* (Figure 7.7). Removal of Cu-droplets from glass was found frequently (Figure 7.8

D), only with a lower degree of liberation as compared to AS exposed to acidic leaching by *A. thiooxidans* (Figures 7.7 and 7.8).
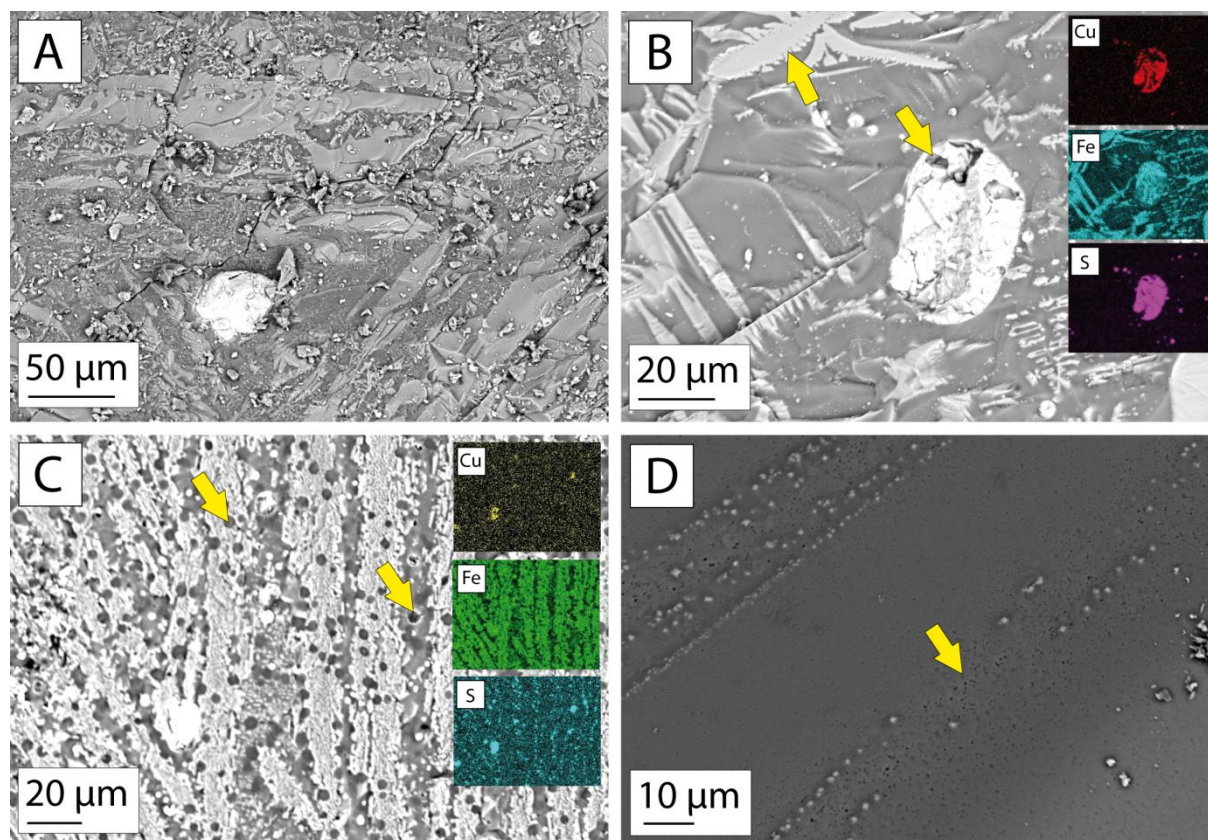


**FIGURE 7.8 SEM images of slag grains resulting from the leaching with**
**P. fluorescens.**

*Arrows indicate: A: grain resulting from abiotic treatment (GM), B: biotic treatment (GMB) of CS, dissolution of Cu sulfide, C: biotic treatment of CS, fayalite and glass alteration, D: biotic treatment (GMB) of GS, Cu-droplets liberation.*

## 7.4. DISCUSSION

### 7.4.1 Effect of particle size and pulp density on metal extraction from Cu-slags by *A. thiooxidans*

Crystalline (CS) and amorphous (AS) slags subjected to bioleaching leach several metals efficiently in the presence of *A. thiooxidans*. The most efficient conditions tested for CS were 1 % pulp density and < 0.3 mm particle size. After 21 days, 79 % of Cu and 76 % of Zn were extracted, whereas an extended bioleaching time up to 40 days maximized the leaching

efficiencies up to 83 % (Cu) and 88 % (Zn) (Figure 7.9). These results are in a good agreement with the observed change in pH, which showed an initial increase and important decrease from 1.6 to 0.7 (days 14-21), reaching near steady trend afterwards (days 21-40) (Figure 7.1). Despite the fact that the same pH decrease occurred in the experiments with a larger particle size (1-2 mm), the bioleaching efficiencies did not reach more than 46 % (Cu) and 61 % (Zn) after 40 days for this slightly larger particle size (Figure 7.9).
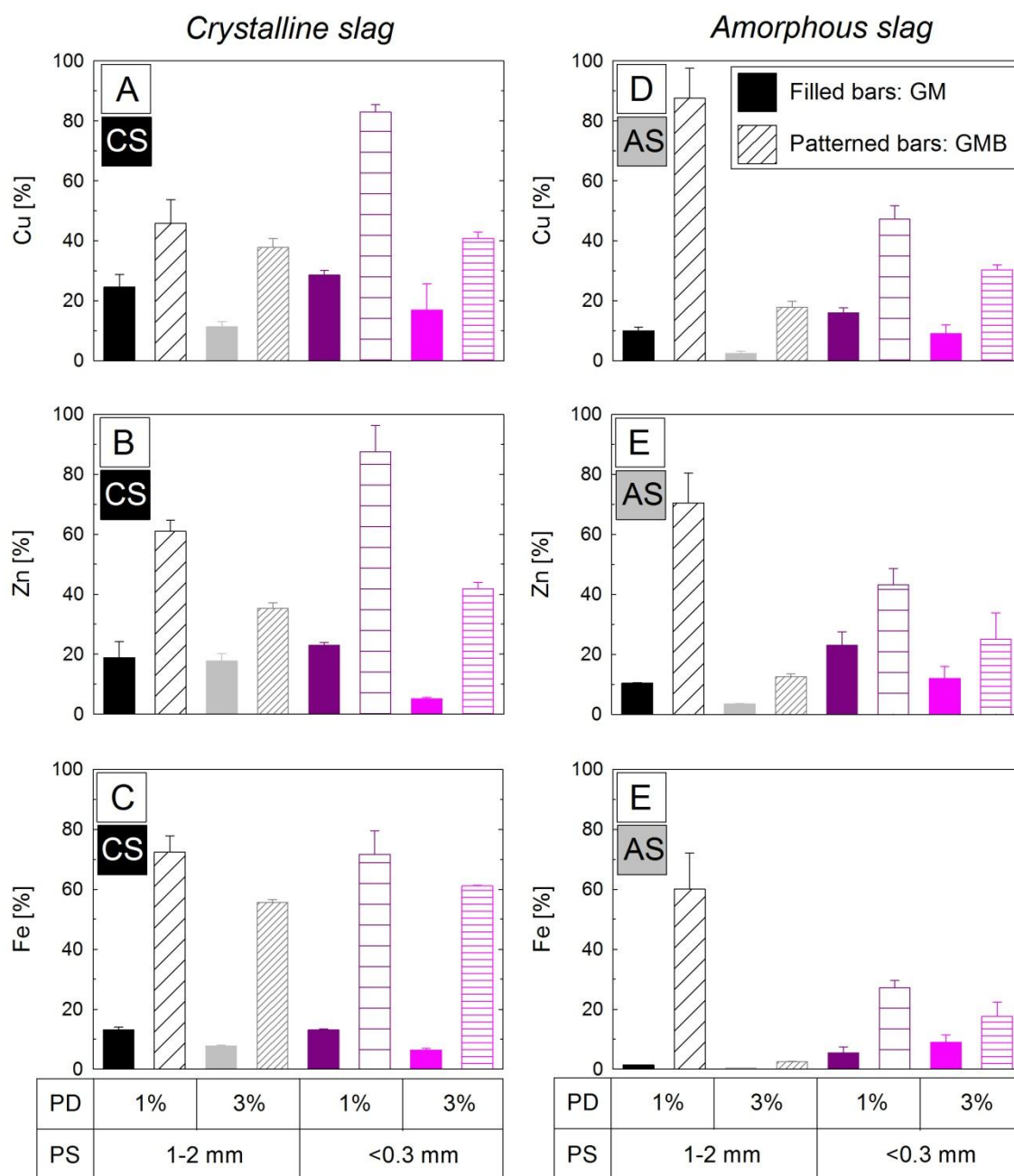


**FIGURE 7.9 Extraction yields achieved in the experiments with *A. thiooxidans.***

(Filled bars: *GM: growth medium*, Pattern bars: *GMB: growth medium with bacteria*, *PS: particle size, PD: pulp density*)

An initial pH increase may be due to $H^+$ replacing $Fe^{2+}$ during fayalite dissolution (Eq. 2) (Kleiv & Thornhill, 2006). Furthermore, hydrogen ion replacement with glass constituents may have the same effect (Eq. 3). The continued decrease of solution pH may either be due to: i) microbial $S^0$ oxidation and consequent formation of sulfuric acid (Eq. 1) either ii) the dissolution of sulfides (Eq. 4). The formation of sulfuric acid hindered the neutralization input provided by the silicates. The dissolution features on fayalite, glass and sulfides were confirmed by SEM observations (Figure 7.6).

$(Fe^{2+})_2SiO_4 + 4H^+ \rightarrow 2\,Fe^{2+} + H_4SiO_4$ 　　　　　　 Eq. 2

$- Si - O - M\,_{(glass)} + H^+ \leftrightarrow - Si - OH\,_{(glass)} + M^+_{(aq)}$ 　　　 Eq. 3

$MeS_2 + 7/2\,O_2 + H_2O \rightarrow Me^{2+} + 2\,SO_4^{2-}{}_{(aq)} + 2\,H^+$ 　　　 Eq. 4
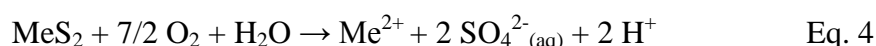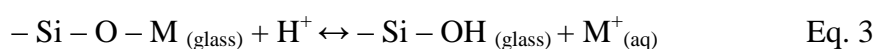
The particle sizes of CS in the experiments with *A. thiooxidans* did not have any significant effect on the Fe extraction efficiencies as the quantities released were comparable and after 40 days the extraction efficiencies were 72 % (1 % PD) and 56 % (3 % PD) for 1-2 mm size material and 72 % (1 % PD) and 61 % (3 % PD) for < 0.3 mm size material (Figure 7.9). The trends observed for these metals might be attributed to the mineralogical composition of CS. As Cu is mainly associated with Cu-bearing sulfides (Potysz et al., 2016b), the reduction of the particle size undoubtedly favored the exposure of these phases to the bioleaching solution, whereas larger particle sizes and subsequent encapsulation of the main Cu-carriers reduced Cu leaching (Carranza et al., 2009). The slag particle size may have little effect on Fe leaching because the omnipresent Fe-bearing phases (*i.e.*, fayalite and glass) have unrestricted exposure to the bioleaching solution. A similar observation was made by Liu et al. (2011) who reported lack of the effect of the particle size on Fe release from pyrite leached with *A. thiooxidans*. In contrast, particle size had an effect on Zn leachability, even though it is mainly present as an impurity of fayalite and glass. Zinc impurities reveal an irregular compositional distribution gradient along fayalite and glass according to microprobe data (Potysz et al., 2016b). Additionally, Zn occurs as wurtzite ((Zn,Fe)S) micro-inclusions distributed within bornite (Kierczak et al., 2013). Furthermore, some impurities of Zn are also incorporated in chalcopyrite and pyrrhotite (Potysz et al., 2016b). Hence, the reduction of the particle size renders accessibility of these minor sulfide components and Zn-enriched zones of fayalite and glass better and results in a higher liberation of Zn from smaller (< 0.3 mm) slag particles.

The results of this study, metal extraction from AS was accomplished using larger size slag (1-2 mm) and 1 % pulp density. Optimal conditions for AS were found to be at 1 % pulp density. The metal leaching yield accomplished after 21 days was: 81 % (Cu) and 79 % (Zn) (Figure 7.9). When bioleaching was extended up to 40 days, a somewhat higher extraction

efficiency (87.5 %) was achieved for Cu and almost the same (70 %) for Zn. The extraction yield gained for smaller-sized slags of AS did not exceed 48 % for Cu and Zn. As the leaching trends obtained for particle sizes < 0.3 mm did not reach steady state, further extension of the processing time could improve the removal of metals from slag. Similarly to CS, Fe solubilization presented a steep increase throughout all experiments with smaller (< 0.3 mm) and larger (1-2 mm) particles at 1 % pulp density, mainly due to its liberation from the glass matrix.

In the case of AS, a smaller particle size, which would be expected to give a greater extraction efficiency, showed an adverse effect on Cu and Zn leaching. The reason for this behaviour might be the pH trend which dropped to lower pH for particle sizes 1-2 mm (pH 0.8) as compared to smaller particle sizes < 0.3 mm (pH 3.2). A possible explanation is that the neutralizing potential of the larger-sized slag was lower than in batches with smaller-sized fractions (Male et al., 1997). Moreover, higher pulp density has a greater neutralizing potential (Chen et al., 2001). Nevertheless, the 1-2 mm particles at a 3 % pulp density revealed a lower efficiency than those of < 0.3 mm despite the initially lower pH values. The final higher pH achieved in the batch incubations with AS of < 0.3 mm particle size would imply that both the neutralizing potential of the material and a higher solid content (3 %) had an effect on the bioleaching efficiency. Those parameters thus inhibited the bioleaching performance or at least extended the time required by *A. thiooxidans* for sulfuric acid production (Chen et al., 2001).

The better performance of *A. thiooxidans* in the experiments carried out with CS suggests that sulfides present in its structure served as an additional sulfur source for bacteria (Eq. 5 - 7). This is supported by the observation that AS lacking this element did not support bacterial growth. As demonstrated by Bevilaqua et al. (2002), *A. thiooxidans* cannot perform the leaching process efficiently when it is devoid of sulfur source, hence sulfides could be an additional complementary energy source in CS bioleaching. Male et al. (1997) also emphasized that the slag itself may serve as an energy substrate for microbial growth. These authors demonstrated that medium lacking an electron donor, but supplemented with slag, allowed bacterial cultures of *Acidithiobacillus sp*. to proliferate (Male et al., 1997).

$$MS + H_2SO_4 + 0.5\,O_2 \rightarrow MSO_4 + S + H_2O \qquad \text{Eq. 5}$$

Extraction allows the removal of metals that renders slags less toxic. Moreover, such an approach could partially satisfy market demand on metals which would be otherwise lost in the slags. Smaller particle sizes of the AS led to a rapid increase of solution pH and this problem should be addressed in the optimization of the process. This could be achieved by starting the bioleaching process at a much lower pH (< 2.5) and allowing the material to neutralize to a pre-set pH until the slag neutralizing capacity is exhausted and the desired value of 3.5 to 4.0 (optimal conditions for *A. thiooxidans*) is achieved. Bacteria could be

introduced to the reactor as soon as these conditions are met during operation. From a process intensification viewpoint, optimizing parameters such as sulfur addition, inoculum volume and pulp density could certainly improve the efficiency of CS bioleaching. Moreover, reduced particle size (far below 0.3 mm) could also be a favorable factor in the case of CS.

Mixing the bacterial culture (*A. thiooxidans*) together with Fe-oxidizing acidophiles such as *A. ferrooxidans* is not recommended for the improvement of bioleaching. According to literature reports, mixed cultures of bacteria do not show better performance as compared to pure cultures if the process conditions are not properly adjusted (Donati et al., 1995). As evidenced by Santelli et al. (2001), Fe oxidizing bacteria may suppress the dissolution of Fe-silicates such as fayalite. The suppression can presumably be due to the supersaturation of Fe with respect to secondary phases, subsequently forming a passivation layer and inhibiting the surface area of the minerals exposed to the leaching solution as well as re-adsorption of the released metals.

## 7.4.2 Extraction efficiencies of Cu-slags bioleaching with *Pseudomonas fluorescens*

The increase of pH observed in the experiments with *P. fluorescens* was greater when larger particle sizes were used, whereas the use of smaller particle sizes resulted in very little pH increase. Firstly, the increase of pH might be related to the dissolution of phases present in the slags (Eqs. 2 and 3). However, higher dissolution rates of slags of smaller particle sizes (Figures 7.4 and 7.5) would be expected to have a higher contribution to neutralizing reactions, thus, a larger pH increase. The reason for the lower pH increase in the case of smaller particles sizes may be the larger excretion of organic metabolites having an acidifying effect that hinders the neutralizing reaction of silicates. Moreover, higher dissolution rates of sulfides (Eq. 4) for smaller particles compared to larger particles could be a reason for the lower pH value in the case of CS ($< 0.3$ mm).

*P. fluorescens* was found to have a poorer performance in terms of metal extraction from slags. Because the efficiencies reached after 40 days of incubation did not go beyond 10.3 % (Cu), 4.2 % (Zn) and 0.3 % (Fe) for CS (Figure 7.10), an application of these bacteria for the leaching process does not appear to be beneficial in terms of metal recovery. Similarly, the extraction efficiencies achieved for AS did not exceed 4.2 % (Cu), 2.6 % (Zn) and 0.7 % (Fe) even when the particle sizes were $< 0.3$ mm. On the other hand, the contribution of this bacterium to the weathering process may be relevant from an environmental point of view since their presence may increase the doses of metals released at industrial waste dumping sites. If *P. fluorescens* is considered to be used as a leaching agent for slags, further important improvements of the process are necessary in order to fully exploit the advantages of this

bacterium. Our data show that reduced particle sizes of both slag types resulted in higher concentrations of metals in the leachates as compared to particle sizes 1-2 mm.

To improve the performance of *P. fluorescens*, an adjustment to a lower pH value could be undertaken since the survival of these bacteria at lower pH conditions (*e.g.* pH - 5.0) has been reported in the literature (Soesanto et al., 2011). Another improvement of the performance of this species could be leaching solution renewal which supplies nutrients and removes toxic metals from the liquid phase at the same time. The frequency of liquid solution renewal could be set based on the metal concentration in the solution. However, such an approach would tremendously increase the volume of the process solution, hence treatment cost as well. Therefore, among the two tested bacteria, *P. fluorescens* is not appropriate for economically viable bioleaching, whereas the acid producing *A. ferroxidans* exhibited a superior performance in terms of metal extraction efficiencies when the same treatment duration considered.
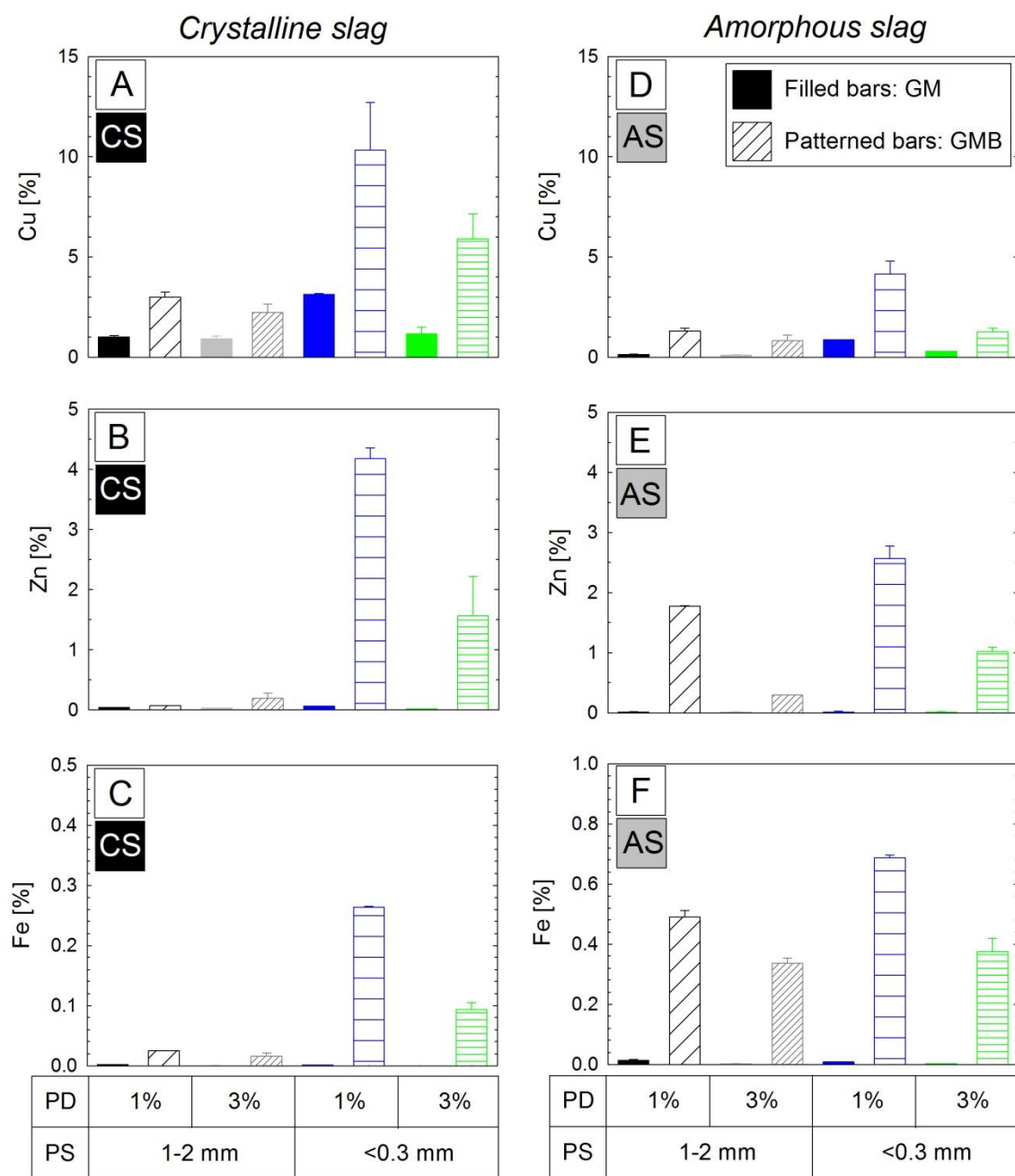
**FIGURE 7.10 Extraction yields achieved in the experiments with *P. fluorescens.***

(Filled bars: *GM: growth medium,* Pattern bars*: GMB: growth medium with bacteria, PS: particle size, PD: pulp density)*

## 7.5  CONCLUSIONS

Implementation of bioleaching as treatment method is promising for the future management of metallurgical slags. *A. thiooxidans* was found to be a good leaching agent assisting in the release of metals from both amorphous (AS) and crystalline (CS) slags. The catalysis was mainly associated with lowering solution pH that could not be ascertained under abiotic conditions regardless of the same initial pH. The most efficient conditions for CS were: 1 % pulp density, fraction size < 0.3 mm and 21 days operating time. As much as 78.9 % of Cu and 75.7 % of Zn could be extracted from CS. At the same time, up to 80.5 % of Cu and 78.6 % of Zn were extracted from AS at a 1 % pulp density and 1-2 mm fraction size. Process parameters such as pulp density, inoculum density (cell number), particle size, and pH can be optimized further to facilitate the extraction process. The contribution of *P. fluorescens* to metal extraction (e.g. 10 % of Cu) was rather marginal as compared to *A. thiooxidans*. For this reason, *P. fluorescens* does not appear to be a suitable biocatalyst for metal recovery from slags.

# REFERENCES

1. **Aouad G., Crovisier J.L., Geoffroy V.A., Meyer J.M., Stille P. (2006):** „*Microbially mediated glass dissolution and sorption of metals by Pseudomonas aeruginosa cells and biofilm*". Journal of Hazardous Materials 136 (3), 889-895.

2. **Aouad G., Crovisier J.-L., Damidot D., Stille P., Hutchens E., Mutterer J., Meyer J.-M., Geoffroy V.A. (2008):** „*Interactions between municipal solid waste incinerator bottom ash and bacteria (Pseudomonas aeruginosa)* ". Science of The Total Environment 393 (2), 385–393.

3. **Banza A.N., Gock E., Kongolo K. (2002):** „*Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction*". Hydrometallurgy 67 (1-3), 63-69.

4. **Bevilaqua D., Leite A.L.L.C., Garcia O., Tuovinen O.H. (2002):** „*Oxidation of chalcopyrite by Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans in shake flasks*". Process Biochemistry 38 (4), 587-592.

5. **Bosecker K. (1997):** „*Bioleaching: metal solubilization by microorganisms*". FEMS Microbiology reviews 20 (3-4), 591-604.

6. **Brandl H. & Faramarzi M.A. (2006):** „*Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste*". China Particuology, 4 (02), 93-97.

7. **Brandl H., Bosshard R., Wegmann M. (2001):** „*Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi*". Hydrometallurgy 59 (2-3), 319–326.

8. **Carranza F., Romero R., Mazuelos A., Iglesias N, Forcat O. (2009):** „*Biorecovery of copper from converter slags: Slags characterization and exploratory ferric leaching tests*". Hydrometallurgy 97 (1), 39-45.

9. **Chen M., Han Z., Wang L.: (2012):** „*Recovery of valuable metals from copper slags by hydrometallurgy*". Advanced Material Research 402. 35-40.

10. **Chen S., Wu Z., Peng X. (2014):** „*Experimental study on weathering of seafloor volcanic glass by bacteria (Pseudomonas fluorescens) – Implications for the contribution of bacteria to the water–rock reaction at the Mid-Oceanic Ridge setting*". Journal of Asian Earth Science 90, 15-25.

11. **Chen S.Y. & Lin, J.G. (2001):** „*Bioleaching of heavy metals from sediment: significance of pH*". Chemosphere 44 (5), 1093-1102.

12. **Cheng Y., Guo Z., Liu X., Yin H., Qiu G., Pan F., Liu H. (2009):** „*The bioleaching feasibility for Pb/Zn smelting slag and community characteristics of indigenous moderate-thermophilic bacteria*". Bioresource Technology 100 (10), 2737-2740.

13. **Donati E., Curutchet G., Pogliani C., Tedesco P. (1996):** „*Bioleaching of covellite using pure and mixed cultures of Thiobacillus ferrooxidans and Thiobacillus thiooxidans*". Process Biochemistry, 31 (2), 129-134.

14. **Ehrlich H.L. (1998):** „*Geomicrobiology: its significance for geology*". Earth-Science Reviews 45 (1), 45-60.

15. **Erüst C., Akcil A., Gahan C.S, Tuncuk A., Deveci H. (2013):** „*Biohydrometallurgy of secondary metal resources: a potential alternative approach for metal recovery*". Journal of Chemical Technology and Biotechnology 88 (12), 2115-2132.

16. **Ettler V. & Johan Z. (2014):** „*12 years of leaching of contaminants from Pb smelter slags: geochemical/mineralogical controls and slag recycling potential*". Applied Geochemistry 40, 97-103.

17. **Ettler V., Johan Z., Křibek B., Šebek O., Michaljevič M. (2009):** „*Mineralogy and environmental stability of slags from Tsumeb smelter. Namibia*". Applied Geochemistry 24, 1-15.

18. **Ettler V., Legendre O., Bodénan F., Touray J.C. (2001):** „*Primary phases and natural weathering of old lead-zinc pyrometallurgical slag from Pribram. Czech Republic*". Canadian Mineralogist 39, 873-888.

19. **Ettler V., Piantone P., Touray J.C. (2003):** „*Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long- term assessment*". Mineralogical Magazine 67 (6), 1269-1283.

20. **Gadd G.M. (2004).** Microbial influence on metal mobility and application for bioremediation. Geoderma 122 (2), 109-119.

21. **Gadd G.M. (2010):** „*Metals, minerals and microbes: geomicrobiology and bioremediation*". Microbiology 156, 609-643.

22. **Gee C., Ramsey M.H., Maskall J., Thornton I. (1997):** *„Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead".* Journal of Geochemical Exploration 58 (2), 249-257.

23. **Harish V., Sreepada R.A., Suryavanshi U., Shanmuganthan P., Sumathy A. (2011):** *„Assessing the effect of leachate of copper slag from the ISASMELT process on cell growth and proximate components in microalgae Chlorella vulgaris (Beijerinck)".* Toxicological and Environmental Chemistry 93 (7), 1399-1412.

24. **Ishigaki T., Nakanishi A., Tateda M., Ike M., Fujita M. (2005):** *„Bioleaching of metal from municipal waste incineration fly ash using a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria".* Chemosphere 60 (8), 1087-1094.

25. **Kierczak J., Potysz A., Pietranik A., Tyszka R., Modelska M., Néel C., Ettler V., Mihaljevič M. (2013):** *„Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland).* Journal of Geochemical Exploration 124, 183-194.

26. **Kleiv R.A. & Thornhill M. (2006):** *„Mechanical activation of olivine".* Minerals Engineering 19 (4), 340-347.

27. **Krebs W., Bachofen R., Brandl H. (2001):** *„Growth stimulation of sulfur oxidizing bacteria for optimization of metal leaching efficiency of fly ash from municipal solid waste incineration".* Hydrometallurgy 59 (2), 283-290.

28. **Leduc L. G., Ferroni G.D., Trevors J. T. (1997):** *„Resistance to heavy metals in different strains of Thiobacillus ferrooxidans".* World Journal of Microbiology and Biotechnology 13 (4), 453-455.

29. **Lee J-ch. & Pandey B.D. (2012):** *„Bio-processing of solid wastes and secondary resources for metal extraction-A review",* Waste Management 32 (1), 3-18.

30. **Liu Y.G., Zhou M., Zeng G. M., Wang X., Li X., Fan T., Xu W.H. (2008):** *„Bioleaching of heavy metals from mine tailings by indigenous sulfur-oxidizing bacteria: effects of substrate concentration".* Bioresource Technology 99 (10), 4124-4129.

31. **Lottermoser B.G. (2002):** *„Mobilization of heavy metals from historical smelting slag dumps. North Queensland. Australia".* Mineralogical Magazine 66 (4), 475-490.

32. **Male D.W., Leduc L.G., Ferroni G.D. (1997):** *„The potential of mining slag as a substrate for microbial growth and the microbiological analysis of slag and slag seepage".* Antonie van Leeuwenhoek 71 (4), 379-386.

33. **Manz M. & Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District. Mexico".* Environmental Pollution 98 (1), 7-13.

34. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California".* Applied Geochemistry 16 (14), 1567–1593.

35. **Piatak N, M., Parsons M. B., Seal R. R. (2015):** *„Characteristics and Environmental Aspects of Slags: A review".* Applied Geochemistry 57, 236-266.

36. **Piatak N.M. & Seal II R.R. (2010):** *„Mineralogy and the release of elements from slag from the Hegeler Zinc smelter. Illinois (USA)".* Applied Geochemistry 25, 302-320.

37. **Piatak N.M., Seal 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".* Applied Geochemistry 19, 1039-1064.

38. **Potysz A., Grybos M., Kierczak J., Guibaud G., Lens P.N.L. van Hullebusch E.D. (2016a):** *„Bacterially-mediated weathering of crystalline and amorphous Cu-slags".* Applied Geochemistry 64, 92-106.

39. **Potysz A., Kierczak J., Fuchs Y., Grybos M., Guibaud G., Lens P.N.L, van Hullebusch E.D. (2016b):** *„Characterization and pH-dependent leaching behaviour of historical and modern copper slags",* Journal of Geochemical Exploration 160, 1-15.

40. **Potysz A., van Hullebusch E.D., Kierczak J., Grybos M., Lens P.N.L, Guibaud G. (2015): „***Copper Metallurgical Slags–Current Knowledge And Fate: A Review"***.** Critical Reviews in Environmental Science and Technology 45 (22), 2424-2488.

41. **Prior T., Giurco D., Mudd G., Mason L., Behrisch J. (2012):** *„Resource depletion, peak minerals and the implications for sustainable resource management".* Global Environmental Change 22 (3), 577-587.

42. **Sand W. & Gehrke T. (2006):** *„Extracellular polymeric substances mediate bioleaching/biocorrosion via interfacial processes involving iron (III) ions and acidophilic bacteria".* Research in Microbiology 157 (1), 49-56.

43. **Santelli C.M., Welch S.A., Westrich H.R., Banfield J.F. (2001):** „*The effect of Fe-oxidizing bacteria on Fe-silicate mineral dissolution*". Chemical Geology 180 (1), 99-115.

44. **Schippers A. & Sand W. (1999):** „*Bacterial leaching of metal sulfides proceeds by two indirect mechanisms via thiosulfate or via polysulfides and sulfur*". Applied and Environmental Microbiology 65(1), 319-321.

45. **Schmukat A., Duester L., Ecker D., Heininger P., Ternes T.A. (2013):** „*Determination of the long-term release of metal(loid)s from construction materials using DGTs*". Journal of Hazardous Materials 260, 725-732.

46. **Schmukat A., Duester L., Ecker D., Schmid H., Heil C., Heininger P., Ternes T.A. (2012):** „*Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength*". Journal of Hazardous Materials 227, 257-264.

47. **Shi C., Meyer C., Behnood A. (2008):** „*Utilization of copper slag in cement and concrete*"**.** Resources, Conservation and Recycling 52 (10), 1115-1120.

48. **Sobanska S., Ledésert B., Deneele D., Laboudigue A. (2000):** „*Alteration in soils of slag particles resulting from lead smelting*". Earth and Planetary Sciences 331 (4), 271-278.

49. **Soesanto L., Mugiastuti E., Rahayuniati R.F. (2011):** „*Morphological and Physiological features of Pseudomonas fluorescens P60*". In 4th International Seminar of Indonesian Society for Microbiology, 22-24.

50. **Sukla L.B., Esther J., Panda S., Pradhan N. (2015):** „*Biomineral Processing: A Valid Eco-Friendly Alternative for Metal Extraction*". Research and Reviews: Journal of Microbiology and Biotechnology 3(4), 1-10.

51. **Sukla L.B., Kar R.N., Panchanadikar V. (1995):** „*Bioleaching of copper converter slags using Aspergillus niger isolated from lateritic nickel ore*". International Journal of Environmental Studies 47 (2), 81-86.

52. **Suzuki I. (2001):** „*Microbial leaching of metals from sulfide minerals*". Biotechnology Advances 19, 119-132.

53. **Vainshtein M. (2014):** „*Bioleaching of Metals as Eco-friendly Technology*". In Current Environmental Issues and Challenges (pp. 197-205). Springer Link, Netherlands.

54. **van Hullebusch E.D., Yin N-H., Seignez N., Labanowski J., Gauthier A., Lens P.N.L., Avril C., Sivry Y. (2015):** „*Bio-alteration of metallurgical wastes by Pseudomonas aeruginosa in a semi flow-through reactor*". Journal of Environmental Management 147, 297-305.

55. **Vestola E.A., Kuusenaho M.K, Narhi H.M., Tuovinen O.H., Puhakka J.A., Plumb J.J., Kaksonen A.H. (2010):** „*Acid bioleaching of solid waste materials from copper, steel and recycling industries*". Hydrometallurgy 103 (1), 74-79.

56. **Watling H.R. (2006):** „*The bioleaching of sulphide minerals with emphasis on copper sulphides*". Hydrometallurgy 84 (1), 81-108.

57. **Yang Z., Rui-lin M., Wang-dong N. Hui W. (2010):** „*Selective leaching of base metals from copper smelter slag*". Hydrometallurgy 103 (1), 25-29.

58. **Yin N.-H., Sivry Y., Avril C., Borensztajn S., Labanowski J., Malavergne V., Lens P.N.L., Rossano S., van Hullebusch E.D. (2014):** „*Bioweathering of lead blast furnace (LBF) metallurgical slags by Pseudomonas aeruginosa*", International Biodeterioration & Biodegradation 86 (C), 372-381.

# CHAPTER 8

# GENERAL DISCUSSION AND PERSPECTIVES

**Copper metallurgical slags:**
**From the risk associated with former disposal sites**
**to opportunities and limitations**
**arising from metal recovery**

# ABSTRACT

Metallurgical slags are inevitable part of copper smelting production. Former industry used to dispose these wastes at dumping sites without appropriate environmental supervision. The lack of appropriate monitoring and preventive actions led to mobilization of metals (e.g. Cu, Zn, Pb) from weathered slags. As the consequence, the presence of metal excess is a case of numerous historical dumping districts. Due to increasing emphasis paid to sustainable and environmental-friendly waste management, an evaluation of ways other than disposal needs to be carried out. Bio/leaching approaches to metal extraction are promising treatment route for Cu-slags. Well-adjusted conditions require however critical analysis of operating parameters in order to achieve efficient extraction and design properly working reactor configurations. Metal-laden leachates obtained at bio/leaching stage have to be further treated in order to gain metal of interest and to obtain the product of high purity. To do so, well suited separation method needs to be selected. This perspective chapter considers environmental issues associated with former disposal sites and discusses aspects needed for consideration of environmental risk associated with the weathering of these wastes. Further, this perspective chapter provides an overview of bio/leaching approaches and discusses opportunities and limitations that these processes have. The studies needed for further improvement of these methodologies are presented as perspectives of the research.

**Keywords:** metal, metallurgical slag, disposal site, environment, bio/leaching

# 8.1 General discussion and perspectives

Copper is currently routinely used as an essential component of variety of electronic and other goods indispensable for the functioning of modern society (Themelis, 1994; Hong et al., 1996; Radetzki, 2009). Demand for metal-related commodities is ever-increasing year by year, thus copper production capacity needs to be accomplished. For this reason, pyrometallurgical production that accounts for approximately 90% among other processing approaches is not expected to decrease in the coming years (Kuenen et al., 2013). Accordingly, wastes generation and associated emissions are self-evident for the years ahead. Therefore, an estimation of incoming environmental pollution, consideration of the way mitigating the problem and related concern should be prioritized (Dimitrijević et al., 2009). An important progress has been made towards reducing the contamination input as well as implementing the technological systems minimizing environmental impact which this sector has (Gordon, 2002). In spite of introducing those technological improvements, the environmental aspect remains an open debate (Bridge, 2000). The generation of slags is inevitable part of pyrometallurgical processing. These by-products are the most significant wastes in terms of production volume as per ton of copper approximately double volume equivalent of slag is produced (Gorai et al., 2003). Former industry used to dispose slags at the poorly protected dumping sites without any environmental supervision from disposal event on. The lack of appropriate monitoring and preventive actions led to mobilization of metals from weathered slags. As the consequence, the presence of metals at excessive concentration levels is a case of numerous historical dumping districts. Therefore, sustainable waste management currently remains an outstanding problem and appropriate management methods that could prevent or at least mitigate environmental damages associated with disposal and/or reuse receive relevant attention. Future implementation of preventive methodologies should be regarded as priority branch of sustainable slag management and number of possible studies could be addressed.

At any point along slag life-cycle, evaluation steps have to be passed through. Those encompass chemical and mineralogical characterization as well as determination of slag leachability that jointly determine slag properties and thus management method to be selected. A good leachability of metals suggest that slags might be subjected to further metal leaching/recovery treatment, whereas poor metal leachability renders slags more suitable for civil engineering applications. Figure 8.1 illustrates general route of "slag life" and emphasizes key points to be taken into consideration prior to implementing final management strategy.

Currently, waste management desires to reuse metal-laden wastes in a possibly efficient way. Slags are characterized by high residual metal content incorporated in wastes at the smelting production stage. The presence of metals makes slags highly recyclable and strong emphasis

has recently been placed to the need of search for leaching and recovery technologies. Such approach fulfills the objective of sustainable waste management through treating slags as secondary resources instead of wasting these valuable carriers of copper and other metals. Moreover, the goal of metal recovery is strictly related to the shortage of natural resources and steaming uncertainty of metal supply. Since metals are transited into various goods and end up their life as useless waste, the development of recovery technologies has gained even broader perspective of application, not only for slags, but for the other metal-bearing wastes as well.

An overview given in following sections concerns two issues associated to Cu-slags that include: disposal and reuse. The sections focused on slags disposal, consider environmental issues associated with weathering processes undergoing at dumping sites and highlight the future directions of research. Further, this chapter provides an overview of the opportunities and limitations arising from bio/leaching and recovery strategies.
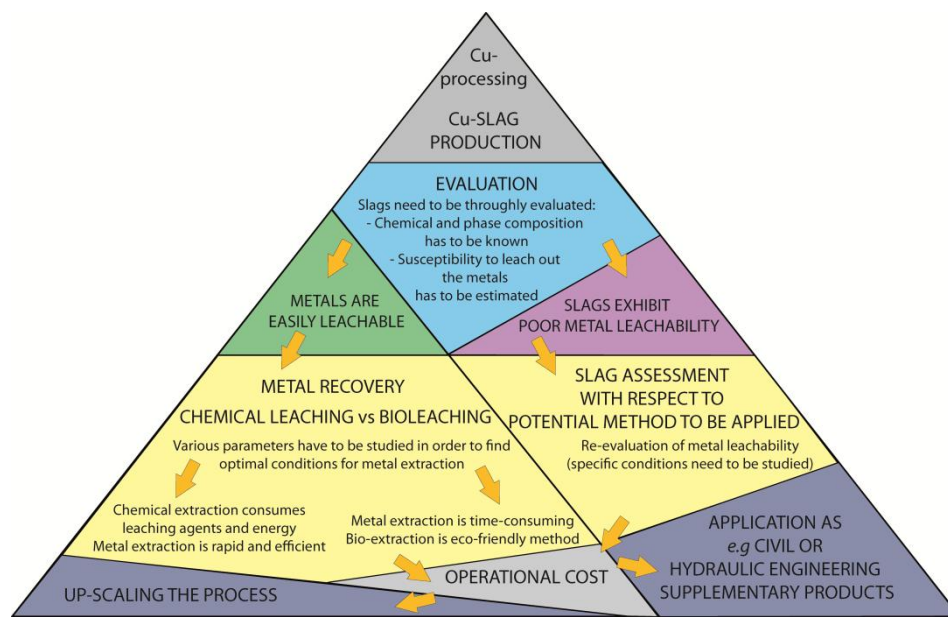


**FIGURE 8.1 Life-cycle of metallurgical slag including the ultimate stages to be undertaken prior implementing the final management strategy.**

## 8.2 Research overview and relevance

This PhD work aimed at evaluating the environmental stability of slags issued by copper smelting activities. Cu-slags resulting from different periods of industrial activities and various pyrometallurgical processes were chosen for comparative studies (Figure 8.2). Experimental part of this work assembles the results concerning characterization of four types of Cu slags *(historical slag, shaft furnace slag, granulated* slag and *lead slag)* and comparison of their: i) chemical and mineral phase compositions (Chapter 4) ii) leaching susceptibility under exposure to different pH-stat conditions (Chapter 4), iii) weathering enhancement by organic acids commonly found in soil environment and (Chapter 5) iv) bacterially mediated weathering (Chapter 6). In these studies related to environmental aspects (Chapters 4-6) special attention was given to the release of metallic contaminants such as Cu, Zn and Pb. Another important point of this work was to consider the future application of studied slags for metal recovery by implementing biological extraction method (Chapter 7). Different scenarios evaluated in this work aimed at fulfilling the research objectives specified in Chapter 1. An overview of the results obtained and conclusions drawn are presented and discussed. The outlook of the perspectives arising from this work as well as aspects related to contaminated sites are presented.
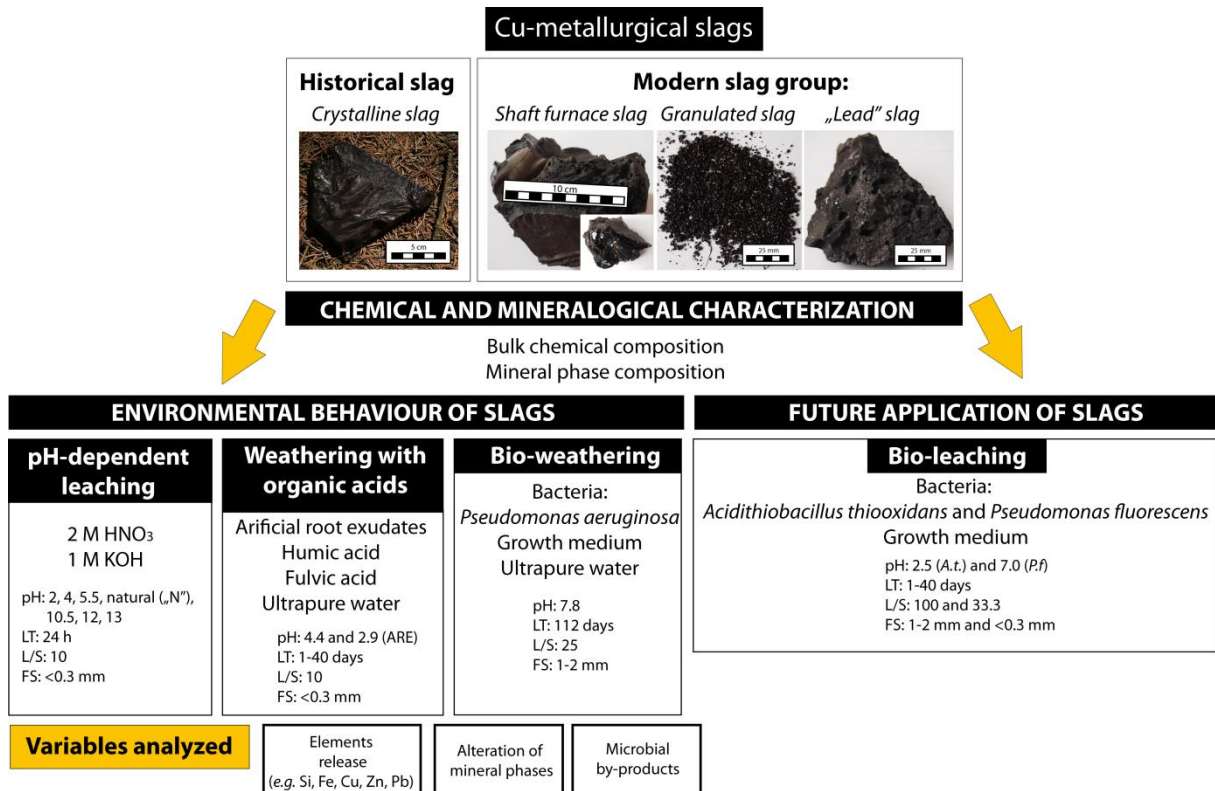


**FIGURE 8.2 Overview of the experimental work carried out in the frame of PhD activity.**

## 8.2.1  A key role of phase and chemical composition in mobility of metallic elements harboured in slags

The importance of chemical and mineralogical characterization of metallurgical slags lies in prediction of environmental risk that these wastes can pose. Furthermore, mineral phases hosting metallic contaminants are necessary to be recognized since susceptibility of the individual phases to weathering varies and consequently might exhibit different level of contribution to environmental hazard through the release of metals. Likewise, the knowledge about the mineral phases being main metal carriers is relevant for development of efficient bio/leaching conditions that desire to be adjusted such that metal carries might be solubilized. For this reason, bulk elemental composition, the distribution of the elements as well as volumetric proportion of the phases has to be known.

In these regards, the first stage of research work focused on characterization of Cu-metallurgical slags generated in historical times (*Historical crystalline slag*) as well as those resulting from modern-day production, collected from various stages of pyrometallurgical process. The latter included: *Shaft furnace slag*, *Granulated slag* and *Lead slag.*.
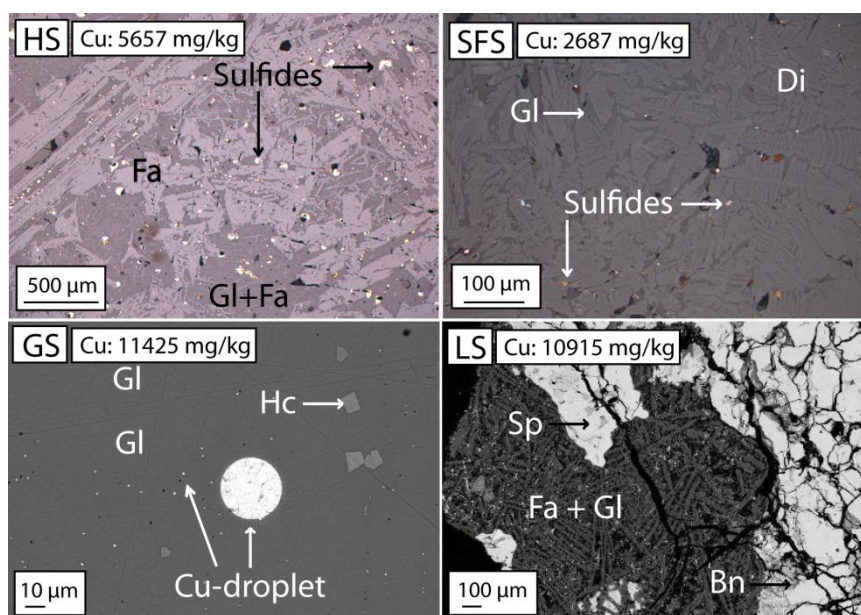


**FIGURE 8.3 Summary of chemical and phase composition of individual slags.**

*(CS: crystalline slag, GS: granulated slag, Fa: fayalite, Gl: glass,
Di: diopside, Hc: hercynite, Sp: sphalerite, Bn: bornite)*

The result of this part of the PhD work demonstrated that chemical and phase composition varies from one slag type to another (Figure 8.3). Due to these different characteristics, slags were evaluated with respect to metal release susceptibility. The pH dependent leaching experiments were carried out under the range of acidic and alkaline conditions for 24 hours. The results of leaching tests clearly confirmed that metal release from Cu-slags mainly

depends on mineral phases accommodating contaminants of concern and their volumetric proportions in the individual slags. In other words, experimental data demonstrated that bulk chemical composition of such wastes does not always show relationship with leaching behavior. Acidic conditions were found to have the highest impact on all the slags since the amounts of metal leached out reached the highest values (Figure 8.4). That indicates that low-pH dumping scenario of slags is of great environmental concern. On the other hand, future perspective of slag chemical treatment arises from good metal extractability. Potential economic benefit steaming from such an approach could be gained if the conditions are optimized. Therefore, some further studies are required in order to improve the leaching efficiency (discussed in section 8.5.3).
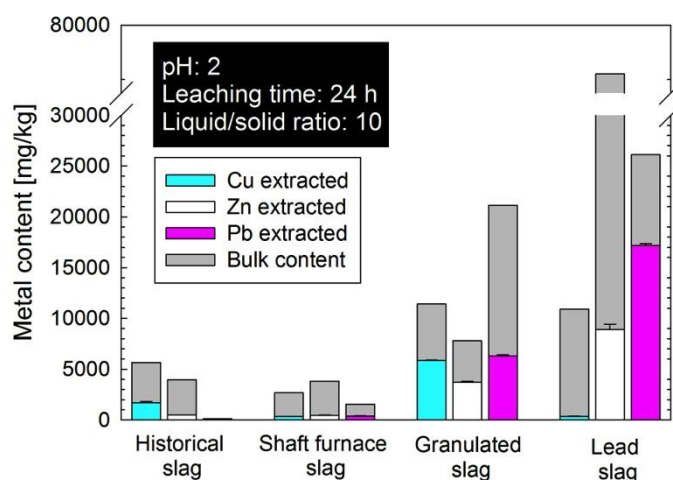


**FIGURE 8.4 Concentrations of metals extracted from slags exposed at pH 2 (24 h).**

## 8.3 Dumping case and issued contamination

The relevance of the studies concerning weathering scenarios is justified by the existence of the number of dumping sites where no physical barriers against metal passage were introduced at the waste discarding stage (see e.g. Kierczak et al., 2013). This scenario is especially valid for historical industrial areas as former waste management approach did not consider carefully the environmental consequences that slag can bring when weathered (Figure 8.5). The weathering process and resulting environmental consequences have been already brought into public knowledge by number of authors (Gee et al., 1997; Manz & Castro, 1997; Sobanska et al., 2000; Parsons et al., 2001; Lottermoser, 2002; Ettler et al., 2003; Piatak et al., 2004; Kierczak et al., 2013; Ettler & Johan, 2014). The outstanding contradiction between the sustainable development and environmental pollution encourages action related to this aspect to be undertaken. At the present time, disposal of slags is not put

into practice for environmental reasons. More specifically, those include concerns about mobilization of metals, landscape obstruction and space consumption (Gonzalez et al., 2005). Nevertheless, the existence of formerly created dumping sites is still a case of numerous places across the world (*e.g.* Poland, Chile, USA). Thus, an implementation of monitoring and remediation actions for these areas is of critical need.

Field monitoring combines many individual aspects that should be taken into consideration when degree of environmental hazard is attempted to be determined. First stage of environmental risk assessment has to consider potential input of metals that weathered slags can serve into surrounding environment. Local effluent of leachate charged in metallic elements can migrate downward and sideward soil profile following other environmental components such as ground/surface waters and sediments which promote metals dispersal. Further retention by biota and flora makes metals more accessible for higher links of food chain leading to possible intake by humans. Furthermore, it has to be pointed out that the result of metal retention in local environment may lead to the dispersal of contaminant to much further distances. Thus, seasonal variations of weathering conditions and geological settings of the areas should be taken into account in environmental monitoring. Casper et al. (2004) demonstrated As, Cd and Cu pollution of soils, sediments and aquatic systems in the Churnet River Valley (United Kingdom). Authors pointed out that degree of contamination that in some cases may appear not to be high, could be misleading. For instants, in a dynamic systems such as rivers, contaminated sediments are mixed with those less polluted and consequently may hide the real contamination effect (Casper et al., 2004). Similar observation applies to the study of Kierczak et al. (2013) who observed lower content of metals in stream water sampled under the high-flow conditions compared to those determined for the low-flow period. These differences were attributed to rainwater and/or snowmelt dilution effect. Furthermore, Çubukçu & Tüysüz (2007) evidenced higher metals contamination of soil after harvesting event if compared to vegetation periods when metals uptake by plants dominated over soil deposition. Dispersal of pollution is also highly driven by prevailing wind direction that should be taken into account for monitoring the metal migration (Ettler, 2016).
.
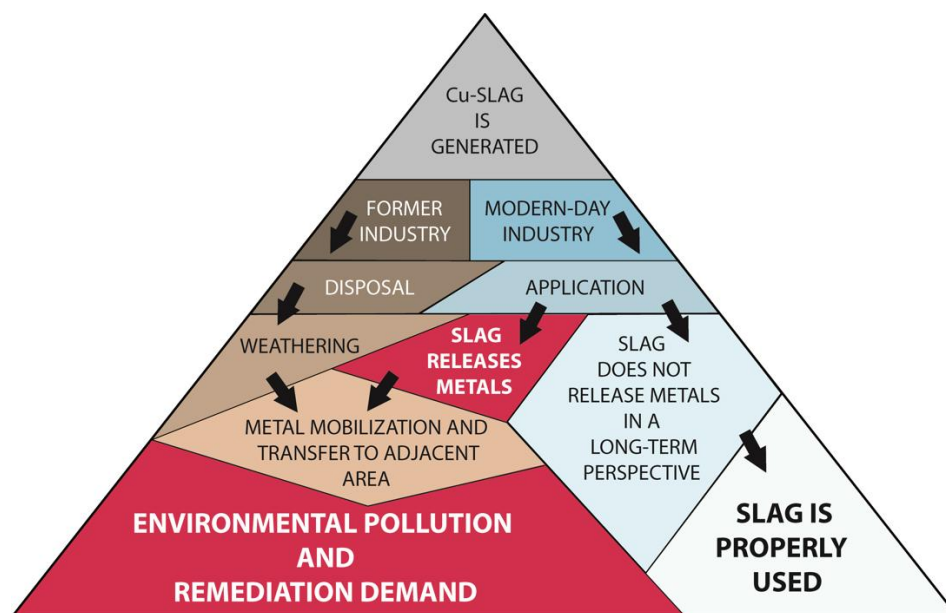
**FIGURE 8.5 Industrial approaches regarding slag management applied formerly and nowadays and consequences faced.**

## 8.3.1 Soil-weathering case

Since disposed slags have remained with direct contact with surface ground or in some cases are even buried or covered by soil layer (Figure 8.6), the organic acids being natural soil component as well as root exudates are of obvious presence in such places, hence might have an impact on slags stability. In these regards, Cu-slags were evaluated with respect to metal release under exposure to: humic and fulvic acids as well as artificial root exudates.
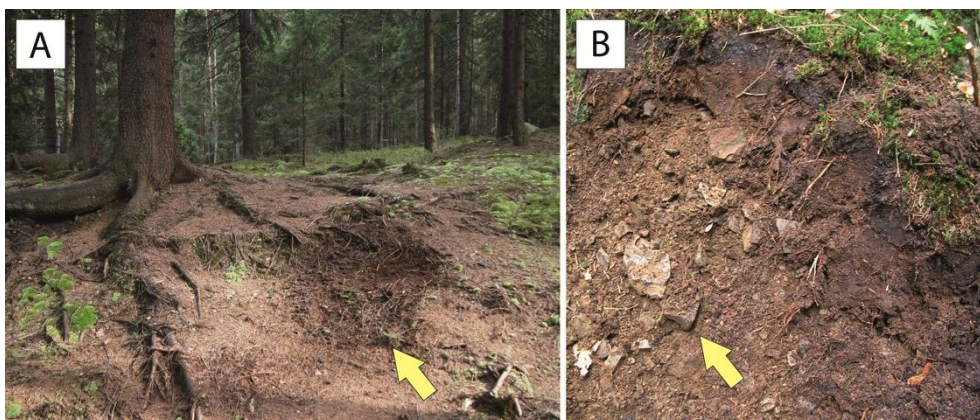


**FIGURE 8.6 Slags buried in soil.**

An important outcome of this study indicates that artificial root exudates (ARE) contribute significantly to mobilization of metals from all types of studied slags. Humic and fulvic acids were found to have lower contribution to metal release compared to ARE. Nevertheless, when

comparing the quantities of metals leached by organic solutions with those released using ultrapure water, HA/FA exhibit the importance even in a short-term perspective (Figure 8.7). Contribution of organic matter to slag weathering has also importance for selecting appropriate remediation strategies. In these regards, following fundamental perspectives arise from the aspect of pyrometallurgical slags dumping. First, the disposal sites lacking physical impermeable barriers preventing migration of metallic contaminants require urgent implementation of such a lining blockage if another action such as collection of wastes from disposal site is not feasible. Moreover, an evaluation of remediation methods which could repress or more preferably exclude already existing metal contaminations of dumping sites is of critical demand.

The vegetation cover which is believed to be a remediation method might not always be a good solution (Houben et al., 2013; Bunzl et al., 2001). The screening study concerning mobilization of metals from slags by various organic acids revealed that potential counterbalance between two specific variables i.e. i) mobilization of metals from slags by root exudates and/or other organic acids as well as ii) accumulation dynamic and capacity of plants should be wisely estimated (Chapter 5). Therefore, a deep study concerning real rhizosphere scenario including presence of plants occurring at dumping sites and related exudates would be interesting to carry out. For example, adding the slag to plant pot could be done in order to demonstrate how the rhizosphere affects the weathering rates. Moreover, the interaction of solid samples with real soil could deliver profound knowledge about the fate of metals released from slags.
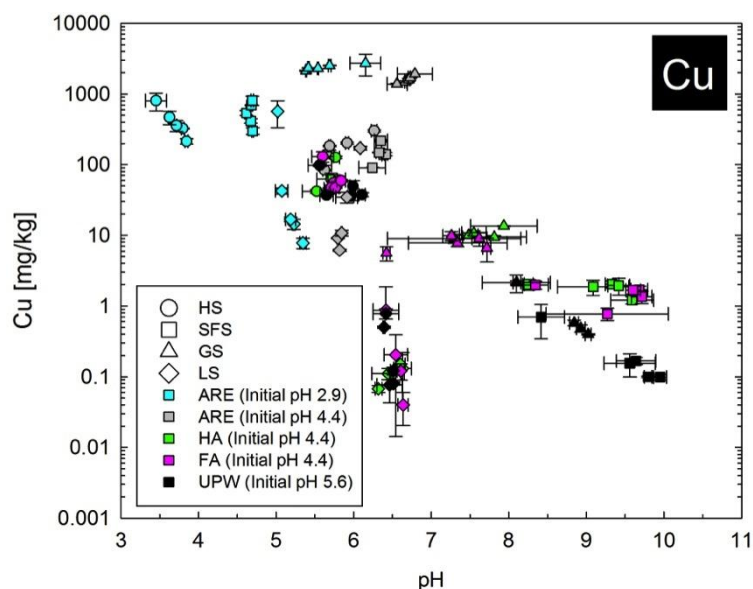


**FIGURE 8.7 Summary of the data obtained from the experiments simulating soil weathering scenario.**

*(HS: historical slag, SFS: shaft furnace slag, GS: granulated slag, LS: lead slag).*

## 8.3.2 Phytomining (in situ removal, plant-based recovery)

Remediation technologies are progressively developing as the response to current level of the environmental pollution that became an alarming issue. Broad array of methodologies are being implemented as remediation treatment of contaminated sites (Virkutyte et al., 2002; Yao et al., 2012) and this aspect should also be perceived as an important issue related to slag disposal.

Phytoextraction has developed as an idea for treatment of sites where the levels of valuable metals are too high to resident in the environment. The existence of hyper accumulating plants has been initially found to be useful as the assistance in the remediation technology (Rascio & Navari-Izzo, 2011). Acidification of rhizosphere, is the way hyperaccumulating plants increase bioavailability of metals. Cu uptake capacity of hyperaccumulators is estimated at the level of 1 mg/g (Verbruggen et al., 2009; Rascio & Navari-Izzo, 2011). On the other hand, naturally growing plants on contaminated areas will be considered as hyperaccumulators if they exhibit tolerance 100-1000 greater as compared to plants growing at uncontaminated sites (Rascio & Navari-Izzo, 2011). As shown, by previous study (Chapter 5) mobilization of metals by root exudates was significant, hence taking an advantage of plant and applying the phyto-treatment method, especially for polluted areas is a perspective for slag industrial sites when combined with the hyperaccumulators. According to literature survey various plants exhibit different degrees of tolerance towards metals which makes them good candidates for metal bio-recovery applications as well. A brief overview of Cu up-take capacity plants growing on contaminated sites is presented in Table 8.1.

The conventional phytoremediation approach is initially intended to reduce the contamination level of industrial areas. Nevertheless, it has developed into somewhat more practical and even economically benefited purposes. That approach is named "phytomining" and aims at extracting of precious metals such as Ag etc. and subsequent harvesting the plants (crop). Gathered crop need to be subjected to further treatment (combustion) that aims at recovery the previously up-taken metals (Van Der Ent et al., 2015). Plant ash after combustion could be kept as the metal reserve until the moment when economic benefit would be brought (Sheoran et al., 2009). Phytomining receives great deal of attention especially for valuables such as silver, nevertheless might be a perspective for Cu recovery too. Such an approach could be introduced at the industrial areas where slag and associated emissions have contributed to local pollution from the discarding event onwards. Such a strategy coupled to simultaneous profit can be put into practice and bring double advantage of reducing pollution and recovering Cu and other metals as well.

**TABLE 8.1 Cu uptake capacity of plants (aboveground biomass) growing on different contaminated sites around the world (A review).**

| Plant | Site location | Cu accumulation Capacity | Reference |
|---|---|---|---|
| *Minuartia verna* | Könnern GERMANY | 1074 mg/kg | *Ernst (1974)* |
| *Stachys coccinnea* | Zacatecas MEXICO | 112 mg/kg | *González & González-Chávez (2006)* |
| *Acalypha cupricola Crepidorhopalon Perennis Vigna dolomitica Vernonia petersii* | Upper-Katanga REPUBLIC OF CONGO | >1000 mg/kg or ~1000 mg/kg | *Faucon et al. (2007)* |
| *Convolvulus arvensis* | Laboratory conditions | 560 mg/kg | *Gardea-Torresdey et al. (2004)* |
| *Polypogon fugax* | Sarcheshmeh IRAN | 4012 mg/kg | *Ghaderian et al. (2012)* |
| *Acorus calamus Typha angustifolia Eleocharis valleculosa Phalaris arundinacea Leersia hexandra* | *Hubei, Guangdong and Hunan Provinces* CHINA | <100 mg/kg ~100 mg/kg- >160 mg/kg | *Deng et al. (2004)* |
| *Lavandula dentata* | South MAROCCO | 125 mg/kg | *Boularbah et al. (2006)* |
| *Tamarix sp.* | Cartagena–La Unión mining district SPAIN | ~11 mg/kg | *Conesa et al. (2003)* |
| *Eriophorum angustifolium* | Boliden mine site SWEDEN | 22.6 mg/kg | *Stoltz & Greger (2002)* |
| *Silene cucubalus* | Salzburg AUSTRIA | 722 mg/kg | *Wenzel & Jockwer (1999)* |
| *Arundinella yunnanensis* | Lanping lead–zinc mine area, CHINA | 61.7 mg/kg | *Yanqun (2004)* |
| *Paspalum notatum Gentiana pennelliana Rubus fruticosus Solidago altissima* | FLORIDA | 352 mg/kg 200 mg/kg 265 mg/kg 241 mg/kg | *Yoon et al. (2006)* |

## 8.3.3 Bio-weathering

Microorganisms are recognized to be a factor playing an important role in the rock weathering processes (Gadd, 2010). Since mineral phases of slag are the synthetic equivalents of naturally formed minerals, the bio-weathering is likely to occur at dumping sites. Microbial proximity of slags might therefore impact their stability and related metal mobility. It has already been shown that the presence of bacteria plays a role in slag alteration (Yin et al., 2014a; van Hullebusch et al., 2015; Potysz et al., 2016a). However, there are still many questions that remain to be answered. The effect of different bacteria/fungi species and their effect in multi species combination is needed to see how bioweathering proceeds in a more complex environment.

The study concerning slag bio-weathering was undertaken in order to compare behaviour of two wastes exhibiting different chemical and textural properties in the presence of bacteria (Chapter 6). The key research objectives addressed in this work referred to mineral phases that can be altered by bacteria as well as mobility of metals in such set-up. Besides, metal mobilization, metal up-take capacity of bacterial biomass has also been taken into consideration..

The results of this part of the dissertation provide notable information about contribution of bacteria to slag weathering and related metal release. An exposure of slags to bacteria resulted in mobilization of up to 9.1 wt. % of Cu from crystalline slag, while the amount of metals leached out from granulated slag did not exceed 1.6 wt. %. Chemical composition of the leachates coupled with mineralogical studies demonstrated that metal accommodating phases such as sulfides are more susceptible to dissolution than intermetallic phases of GS. However, when comparing general behavior of these two slags, it is evident that granulated amorphous slag is more susceptible to weathering than crystalline slag. That is because glass being the principal component of GS weathers easier than major phases of CS (fayalite and glass). Furthermore, an interesting outcome of this study is the presence of alteration zones on fayalite whose dissolution was exclusively driven by the presence of bacteria. Fundamental findings from this work are presented in Figure 8.8.

The perspectives arising from this part of the thesis include following aspects:

1) Contribution of different bacteria species or its evaluation in multi-species combination

2) Size exclusion chromatography could be applied for extracellular molecules separation and elements binding when coupled with ICP-MS (on-going).

3) Transmission electron microscopy (TEM) could be useful for determination of secondary phases predicted by Visual MinteQ model.
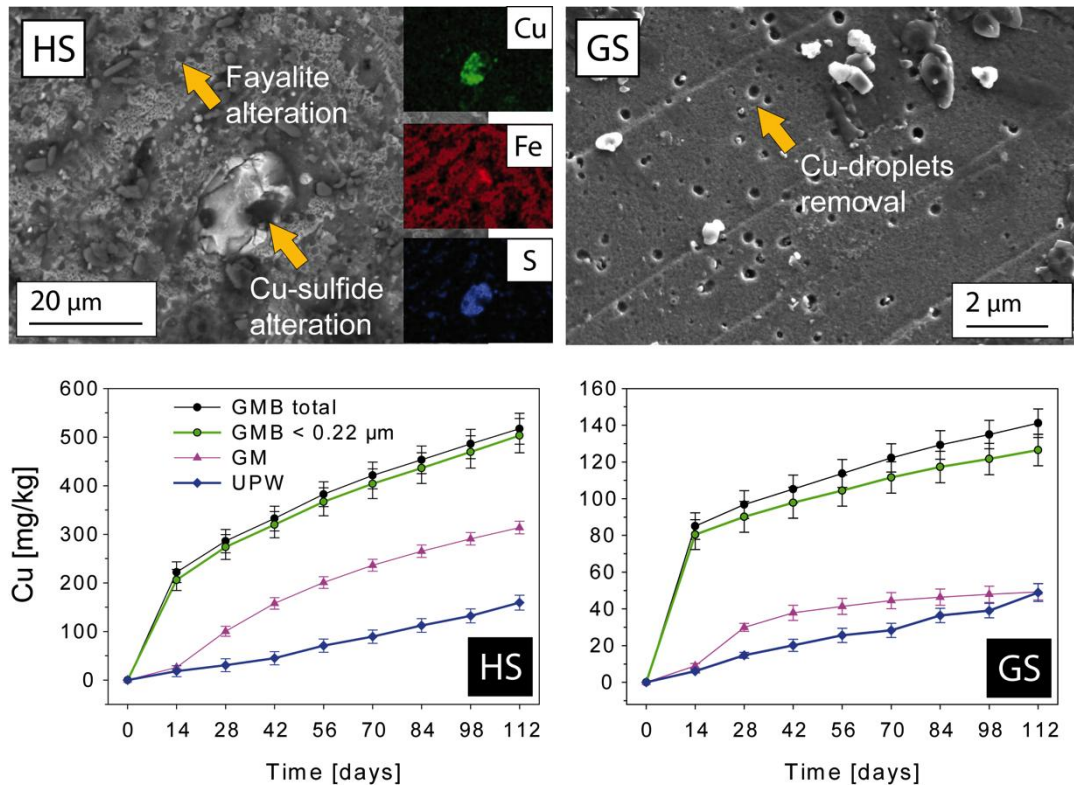
**FIGURE 8.8 Results of the study considering bio-weathering scenario.**

## 8.4 Metal leaching and recovery

Slags are valuable carriers of metals whose extraction appears to be reasonable treatment way in order gain metals that would otherwise be lost in these wastes. This method relies on treating the waste with an extracting solution. The latter may be a traditional chemical agent (chemical leaching) or solution containing microorganisms assisting as the extracting agents (bioleaching). The choice of method and conditions depends on slag properties, mainly metal leachability govern by solid phase being its carrier.

### 8.4.1 Bio-leaching (microbial-based recovery)

Bioleaching is an environmentally friendly approach to metal extraction in which microorganisms play a fundamental role (Ehrlich, 1998; Suzuki, 2001; Watling, 2006; Gadd, 2010). The enhancement of the process through application of microorganisms is also a strong economic driver. Contribution of microorganisms is linked to several processes including: acidolysis, complexolysis and redox reactions (Gadd, 2010). Acidolysis is a mechanism in which proton replacement of metal in mineral phase plays a key role. Acid production occurs when perhaps acidophilic organisms utilize elemental sulfur that results in production of

sulfuric acid and subsequent lowering the pH. Likewise, this mechanism has also a partial role when microbially-derived metabolites assist in the process. These organic compounds may lead to local acidification of leachate and metal removal from the solid phase. However, the complexation mechanisms plays even more prominent role when organic molecule is present. Proton detachment from organic molecule creates binding sites of high affinity to different metals. Complexation phenomenon leads then to transfer of metal from insoluble form incorporated in slag into soluble organic complexes present in aqueous leachate. However, the mechanisms of primary importance depend on microbial organisms employed to assist as leaching catalyst. A prime example of organic complex affecting stability of poorly soluble silicates is siderophore compound. Buss et al. (2007) demonstrated enhanced dissolution of silicates when exposed to siderophores. Likewise, Torres et al. (2014) demonstrated that Fe-binding siderophores can accelerate dissolution of olivine compared to abiotic rates. Breaking silica network of silicate minerals may be attributed to selective microbial iron acquisition when nutrient availability from other sources is otherwise limited (Rogers & Bennett, 2004). An important evolvement has been made towards understanding the interactions of microbial organisms with minerals. It is known that the extend of degradation varies from one mineral to another and is also specific to deteriorative potential of microorganism acting. Moreover, minerals can serve as energy source for microorganisms or play a vital role in nutrient acquisition. Demonstrated so far potential of bioleaching unfurls opportunities of slags treatment and is therefore worth of evaluating.

The objective of the part of dissertation focusing on dynamic and efficiency of metal leaching with the assistance of bacteria (Chapter 7) is to ensure future management of slags in environmentally friendly manner. Moreover, such an approach is of strong importance for satisfying metal demand of modern day society.

Since bioleaching process depends upon number of factors, preliminary study of bio-leaching process embraced consideration of two crucial parameters including particle size and pulp density on metal leaching. Two different bacterial strains were implemented as the leaching agents in order to make a comparison between acidic and circumneutral bioleaching. *Acidithiobacillus thiooxidans* and *Pseudomonas fluorescens* were found to have different strength of contribution to metal extraction, whereby *A. thiooxidans* demonstrated much higher efficacy as compared to *P. fluorescens*. The results clearly indicated that implementation of bacteria to metal leaching plays a catalyzing role and is promising for potential recovery of valuable elements remaining in slags (Figure 8.9). An interesting outcome of this study is that reduced particle size of the slag which is expected to increase their contact with leaching solution is not always appropriate. Granulated (amorphous) slag was found to exhibit higher leachability when larger particle size was used. That was attributed to neutralization capacity of the smaller fraction of slag which likely created unfavorable conditions for bacteria and hindered its performance. The reduction of fraction

size had nevertheless a good implication for crystalline (historical) slag. The explanation for this phenomenon is that the main mineral phases hosting Cu are Cu-sulfides. Although present in low volumetric proportions compared to silicates, they carry major part of Cu. An encapsulation of these sulfides between the crystals of fayalite and within glassy matrix makes necessary to reduce particle size, hence increase the sulfides exposure leaching solution.

The results obtained in this part of the thesis point out the possibility of application of the bioleaching process for slags. That approach would allow to remove metals from the slags and consequently enable their use for a variety of applications afterwards. *A. thiooxidans* was found to efficiently catalyze metal extraction. The gainful outcome of the extraction highlights perspectives arising from the process.
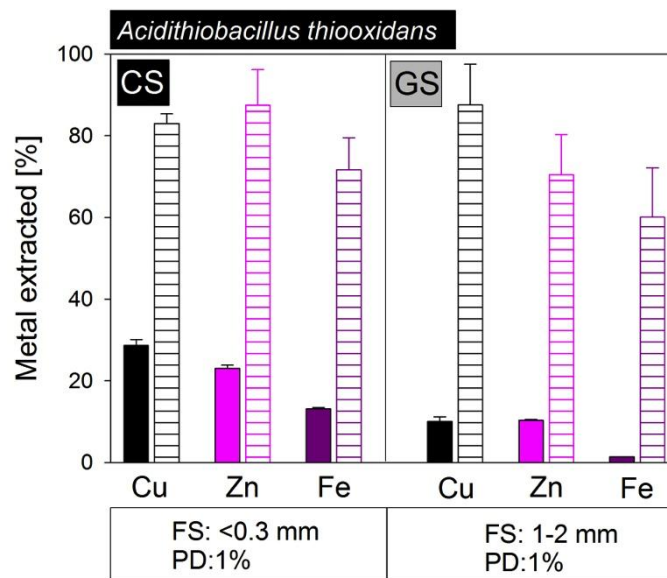


**FIGURE 8.9 Crucial results of the bioleaching experiments carried out with A: CS and B: GS.**

*(CS: crystalline slag, GS: granulated slag, FS: fraction size, PD: pulp density, filled bars: abiotic experiment-growth medium, pattern bars: biotic experiment with A. thiooxidans)*

According to data collected as well as the information derived from the literature demonstrating successful results, the implementation of bioleaching process for Cu-slags can be done. Nevertheless, main difficulties that can be encountered during bioleaching, include following aspects related to the process: i) the release of toxic compounds from slag might have an inhibitory effect on microbial growth, ii) formation of secondary phases (*e.g.* jarosite) on the material creating inhibiting layer towards leaching solution, iii) leachate composition which can be a problem to overcome on metal recovery stage. Furthermore, formation of a silica gel under acidic conditions is a well recognized processing difficulty (Anand et al., 1983; Banza et al., 2002; Deng & Ling, 2007; Yang et al., 2010). Besides the entrapment of

metals leached, the silica gel might also form a protective (passivation) layer on slag grains preventing their dissolution. For this reason, tracking the Si release dynamics is a critical step to be undertaken in future research.

### 8.4.1.1 Optimization of bioleaching conditions

Since optimal leaching approach is specific to chemical and mineralogical composition of the material subjected to the process, there are numbers of factors working in parallel which remain to be evaluated and optimized for bioleaching of metals from Cu-slags. The following targeted parameters are worthwhile trying: particle size, liquid to solid ratio (pulp density), type of microorganism, growth medium composition (nutrient supply) and temperature.

#### 8.4.1.1.1 Particle size

Particle size aims to enlarge the surface area of the waste slag exposed to leaching agent. Generally, it is assumed that lower particle size gives better extraction efficiency, however it has to be noted that crushing and pulverizing the material consumes energy, while the process would require decreasing the number of energy demanding operations. For this reason, from the economical viewpoint the need of particle size reduction has to be minimized. On the other hand, it is very important parameter of bio/leaching. The importance of low particle size is especially important when volumetrically minor, but principal metal carriers sulfide minerals are expected to leach copper. In other words, Cu that is mainly associated with Cu-bearing sulfides (*e.g.* bornite, chalcopyrite), therefore the reduction of the particle size undoubtedly favors the exposure of these mineral phases to be attacked by bio/leaching solution. In contrast, larger slag grain size and subsequent encapsulation of main Cu-carriers ensures greater prevention and reduces Cu leaching (Carranza et al., 2009; Chapter 7). Slag particle size might have little effect on Fe leaching because the omnipresent Fe-bearing phases (i.e., fayalite and glass) have unrestricted exposure to the bio/leaching solution. The excess of Fe content in the leachate is therefore hard to avoid. Thus, the purification methods which could allow to separate copper from other metals present in excess is of great relevance. Despite an exposure of Cu-bearing phases is expected to enhance the process efficacy, higher neutralizing capacity of the small particle size of slag has to be considered. As recently shown, the reduction of particle size of amorphous glassy slag had an adverse effect on leaching efficiency due to neutralizing capacity and subsequent increase of pH creating unfavorable conditions for acidophilic bacteria (Chapter 7). Therefore, it might be concluded that reduction of particle size has a greater importance only for slags whose Cu-carries are mostly sulfides rather than other metallic phases such as metallic copper droplets. Mineral composition of slag has thus to be known in order to design optimal conditions for microorganism applied as bioleaching agent.

### 8.4.1.1.2  Liquid to solid ratio (pulp density)

Liquid to solid ratio (pulp density) is an important variable of bio/leaching process. Lower pulp density ensures higher quantity of chemical/biotic agent per mass of slag and allows therefore better and quicker extraction. However, it is necessary to highlight that this parameter notably determines applicability of the bioleaching at the industrial scale. For example, the use of 2% pulp density instead of 1% allows to reduce the quantity of bioleaching solution by 2 times and decreases the operation cost by default (Niu et al., 2014). Due to high metal content in the leachate, the tolerance of microorganism to elevated metal concentrations should also be taken into consideration. On the other hand, it has already been shown that adjustment of microorganisms to stringent conditions can be done. The existence of microorganisms that developed their tolerance under environmental conditions has been reported too. Therefore, implementation of adjustment step or isolation of indigenous microorganism is a way to enhance the process success.

### 8.4.1.1.3  Microorganisms

Different microorganisms need to be tested and wisely chosen for bioleaching development. An isolation of microbial organisms from dumping sites is a way to omit the toxicity effect since microorganisms present in the environment are often resistant to elevated metal concentrations. Number of studies has been undertaken to investigate the diversity of microorganisms affiliated to slag dumping sites as well as impacts of these microorganisms on metal mobilization. The microorganisms isolated encompass broad array of species including *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, and Thiobacillus thioparus* (Male et al., 1997), *Nocardiopsis metallicus sp.* (Schippers et al., 2002), *Arthrobacter oxydans*, *Microbacterium* sp. and *Dietzia natronolimnaea*, *Promicromonospora* sp., *Pseudonocardia autotrophica, Nocardiopsis metallicus* (Willscher and Bosecker, 2003), *Bacillus* spp., *Sporosarcina* spp. and *Pseudomonas* spp. (Cheng et al., 2009) and *Ochrobactrum* sp. Pandey et al. (2010 and 2011). The occurrence of various types of organisms at the dumping sites and their ability to mobilize metals can therefore be simply used for development of bioleaching.

Another possibility is to adjust selected bacteria to higher metal concentrations in order to improve the efficiency. To do so, pre-grow of bacteria with gradual addition of metal into solution has to be carried out until survivor of organism is maintained at optimal level for microbial proliferation and activity. An improvement of bioleaching can also be done through applying mixed cultures of microorganisms. For example, incubations with sulfur and iron oxidizing acidophiles the metal extraction can be enhanced. On the other hand, iron oxidation may lead to formation of secondary precipitates such as *e.g.* jarosite and subsequent

passivation effect. However, such an approach has to be tested because maybe leaching enhancement prevails over counteracting passivation layer.

Implementation of moderate thermophilic or thermophilic microorganisms is also interesting to study. Since those microbes are known to survive at higher temperatures, an activation factor could improve the extraction. The limitation of this approach is the optimum temperature that has to be selected based on temperature requirement of microorganism to be applied.

### 8.4.1.1.4 Growth medium composition (nutrient supply)

Growth medium compositions (nutrient supply) need to be tested depending on type of microorganism and bioleaching mechanism utilized. *Acidithiobacillus sp.* bacteria consume elemental sulfur for their growth resulting in sulfuric acid production. High acid content is desired, so high bacterial activity and rapid sulfur conversion are needed for initiation of leaching reaction. Therefore, higher sulfur supplementation could be undertaken for improving the performance of these bacteria. However, as pointed out by Liu et al. (2008), supplementation of sulfur has an effect on process efficiency in the range of 0.5-2%, whereas, a further increase of sulfur content in the reactors did not have appreciable effect on the efficiency. That indicates that even narrow range of nutrient supplementation may bring different level of process efficiency.

Nutrient supply is also important when desired microbial by-product is expected to be excreted by microorganism. For example, siderophores are known for their complexing affinity towards Fe and other metals. Hence, the presence of these molecules is crucial for improving metal solubility. For example, it has been shown that the production of siderophore by *Pseudomonas sp.* was affected by the nature organic carbon source provided in solution and clear difference between various supplies has been shown, whereby succinate medium was found to promote siderophores production (Rachid & Ahmed, 2005).

### 8.4.1.1.5 Additional treatments

Formation of the diffusion barrier (passivation layer) is a known process difficulty encountered in numerous bio/leaching studies (Pan et al., 2012; Dong et al., 2013). Additional treatment is thus required in order to overcome passivation layer retarding solid phase dissolution. Its formation is due to several possible reasons: i) the presence of silica gel, ii) formation of iron precipitates, iii) elemental sulfur supplemented in the solution and its deposition onto solid, iv) intermediate compounds resulting from solid phase dissolution, all of them contributing to slowing down the dissolution process.

An application of ultrasound has been reported as method enhancing the process efficacy due to increased biomass and subsequent organic acids (leaching agents) production (Swamy et

al., 2005). Likewise, Anjum et al. (2010) demonstrated that ultrasonic treatment contributed to enhanced bioleaching with *Aspergilus niger* pointing out the same reason for process improvement. Hence, application of ultrasound could be tried after optimization of other parameters. A key advantage of this approach is lack of waste generation steaming from ultrasound itself, however energy consumption should be considered while analyzing the operation cost.

Based on literature survey an assumption about the strong future perspective regarding bioleaching can be done. Since a high gain of metal can be credited to bioleaching under laboratory conditions, its development on larger scale outlines the treatment relevance. However, number of studies still needs to be performed in order to decrease the drawback of bioleaching to the minimum and to further develop well suited reactor configurations.

## 8.4.2  Heap leaching

A practical application of bioleaching process goes backwards to 1950, when "Kennecot Cu extraction" has begun (Panda et al., 2015). So far only secondary sulfide ores have been used for real-scale heap leaching application (Ruan et al., 2013), whereas low grade sulfides or concentrates are being practiced on a demonstration scale at the present time (Panda et al., 2015). The reason for that is activation energy required for chalcopyrite dissolution. Those difficulties could also be of major problem for Cu-slags heap leaching. Moreover, most of sulfides present in slag are associated with silicate minerals. The presence of silicate could contribute to acid buffering reaction during processing as well as increase the viscosity (liquid flow) of bioleaching solution consequently making this difficult for further Cu purification (Dopson et al., 2008). Currently, much effort is being devoted to overcome the technological difficulties and optimize the processing of chalcopyrite. Hence an assumption about the perspective of employing heap bioleaching for slags treatment can be done. For this reason, preliminary evaluations of bioleaching approaches at the laboratory scale are important for establishing slag amenability to bioleaching as well as for deeper understanding the optimum conditions along with limitations of the process. The development of the reactors with stringent control of working parameters is therefore desirable. Further challenge to be faced in technology development would be maintenance of appropriate operating mode throughout the heap. Moreover, the process could be of importance only if overall economy is favorable. Heap bioleaching implementation undoubtedly requires significant step forward prior to its commercialization.

## 8.4.3 Chemical leaching and metal recovery: opportunities and limitations

Chemical leaching (Figure 8.10) is surely feasible for extracting metals from slags. Based on literature review it has been already shown that various leaching agents can extract metals efficiently whereby sulfuric acid has been one of the most frequently used (review: Potysz et al., 2015 and references therein). In spite of being unrivalled in its leaching duration compared to biological leaching, there are many obstacles that can be a limiting factors for technology development. Since the principal components of most Cu-slag are silicate phases (*e.g.* olivine, pyroxene, glass), the content of Si is definitely expected to be high. As mentioned above, that might bring an important limitation of silica gel formation which can entrap metals leached out (Anand et al., 1983; Banza et al., 2002; Deng & Ling, 2007; Yang et al., 2010). Some effort have been devoted to overcome this problem, therefore a main perspective arising from chemical treatment is silica removal from the leachate. An interesting approach would be to develop combined high pressure and high temperature sulfuric acid leaching. As noted by He et al. (2010), sulfuric acid coupled with air pressure supply allows to form dehydrated $SiO_2$ instead of silica gel. Additional output of this approach is minimizing Fe extraction (Anand et al., 1983; Banza et al., 2002) which might be a challenging factor in the metal (*e.g.* Cu) separation from the leachate. Microwave assisted leaching has recently been proposed as the technology which could improve the extraction efficiency in terms of time needed for treatment as well as the metal gain (Al-Harahsheh & Kingman, 2004). Furthermore, selective leaching could also be applied depending on slag composition. For example, Yin et al. (2014b) have recently proposed magnetic separation following leaching as the method for selective Cu ad Co recovery. Nevertheless, the main prerequisite of such an approach is the presence of metals of interest in the minerals displaying different magnetic properties.

The next challenging aspect in chemical approach is separation of the metals. There are many methods to be implemented depending on metal targeted and impurities present. The main possibilities are precipitation, electrochemical treatment and biosoprtion, each of them with its own advantages and limitations. Chemical approach could be based on hydrogen sulfide use, while biologically produced compound is also of possible application (Alvarez et al., 2007). This technology enables generation of metal bearing (sulfide) final product in form usable for further treatment. Sulfide precipitation embraces number of parameters which affect the efficiency and purity of the precipitate. Those include: reagent dosage as well as optimal pH which are the very important variables whose appropriate combination ensures successful recovery (Lewis, 2010). Moreover, the competition effect in polymetallic leachate is also likely to happen. Therefore, the interference between the desired metal and other accompanying elements (competition effect) in the leachate is challenging to overcome. Copper has been found to be one the most difficult metals targeted to become precipitate. That is because of formation of intermediate species. However, achievement of amorphous

precipitate and further aging can lead to formation of crystalline product with the composition approximated to this of traditionally/naturally formed sulfides such as e.g. covellite. This approach also displays many advantages such as fast precipitation rate, low solubility of final precipitate as well as selectivity of the method (Lewis, 2010). Electrowinning is a method at which metal of interest is deposed on cathode. In some cases possible solution pretreatment at which interfering metal is removed by cementation, solvent extraction or ion exchange might be needed. Cation exchange resins (CER) have found their foremost application in wastewater treatment (Dabrowski et al., 2004). Nevertheless the good performance of this method towards metal removal from liquid solution makes it appealing to use CER for leachates purification. Chemical methods have already been well investigated and reviewed and clearly indicate feasibility of selective copper recovery by means of chemical treatment. However, in regards of environmental-friendly concept, biological metal recovery approach would be the most desired. Biosorption is a "green" recovery method of removal metals from aqueous solutions. Wide variety of biosorbens might be used for metal separation and display an ability to uptake metals due to their physiological functions. The uptake pathways utilized include adsorption, ion exchange, complexation and chelation. Biomass that can be employed includes algae, bacteria and fungi, however the extent of uptake varies from one biosorbent to another and does also depend on competition effect caused by the presence of other metal ions in the solution (Vijayaraghavan & Balasubramanian, 2015). The studies concerning efficiency of individual biosorbents mostly focus on artificial leachates that has been indicated as one of the major challenges on development of the process. However, as mentioned leachate from slag treatment contains many other elements, some of them lacking biological functions but entering the sorption system. The presence of anions which exhibit complexing ability towards metals and consequently decreasing their affinity to biosorbent itself may also limit the process efficiency. Another imperative aspect to be taken into consideration is regeneration of biomass that decreases significantly the operational cost (Vijayaraghavan & Balasubramanian, 2015; Robalds et al., 2016). Combining both, bioleaching and biosorption would be the most desired approach of fully friendly specificity. However, there are still many steps forward to improve the processes designs that would ensure entirely successful copper recovery under economically viable conditions.

According to the data collected during this PhD work slags exhibited good leachability under exposure to nitric acid (Chapter 4; Potysz et al., 2016b). Other chemical treatment such as metal extraction with sulfuric acid could be even more efficient due to higher corrosion property of this extractant. Moreover, extraction kinetic could be investigated in order to optimize the time needed for efficient leaching. As formation of silica gel was evident for granulated slag, a combination of sulfuric acid with oxidant (*e.g.* hydrogen peroxide) could be interesting for Cu leaching from this slag. Furthermore, a high $Fe_2O_3$ content (up to 51 wt.%) also indicates the perspective of Fe recovery from such materials.
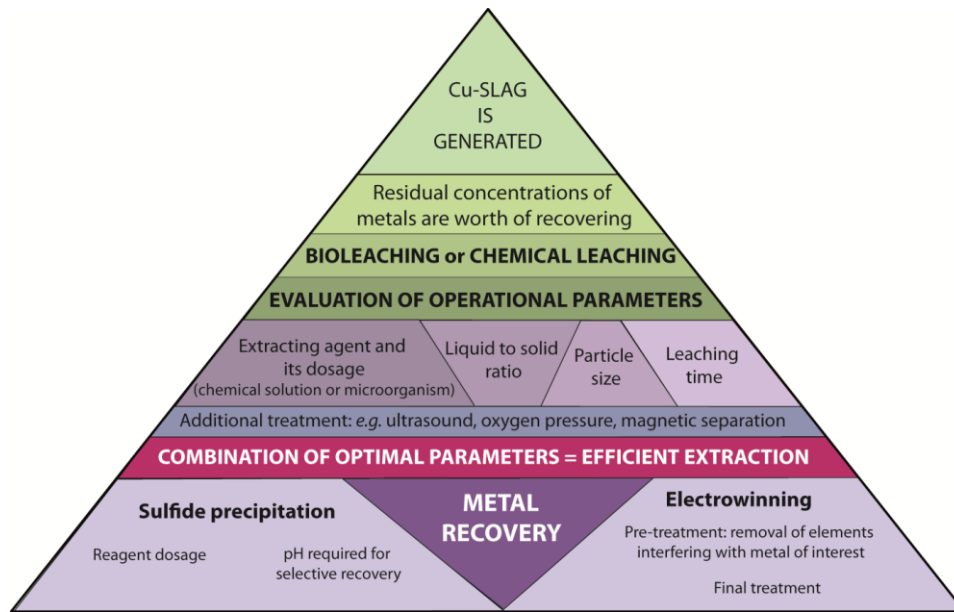
**FIGURE 8.10 Ultimate stages to be passed through prior to implement metal recovery.**

## 8.5 Engineering applications

An application of slags as supplementary materials for civil and hydraulic purposes has been practiced in last years (Shi & Qian, 2000; Al-Jabri et al., 2006; Moura et al., 2007; Shi et al., 2008; Najimi et al., 2011; Schmukat et al., 2012). It has to be highlighted that any of those application require a deep evaluation of slag stability depending on potential method to be applied. As pointed out leaching test are useful screening tools for the preliminary assessment of environmental hazard. Nevertheless, more advanced studies predicting more reliable long-term behavior of slag might be required (Schmukat et al., 2012). Using the slags as the replacement of aggregates or road bed filling materials arises critical concern about long-term stability. For this reason, adequate verification methodology related to slag stability should be far advanced.

According to pH-stat leaching the release of metals entrapped in the studied slags was rather low under alkaline conditions, therefore an application of these slags as potential raw materials appears to be feasible. Nevertheless, a deeper study would be required to see their long-term behavior.

## 8.6 Cu isotopes in biogeoscience: current application and perspectives

Anthropogenic origin of Cu in the environment occurs in a wide range of concentrations, whereby an industrial input carries an important responsibility. Its natural abundance occurs nevertheless at ppm level in the earth crust (Parker, 1967). In spite of essential involvement in many geological and biological processes, its distribution in the environment might affect microbial and plant communities. Undesirable effect of Cu on biotic systems might be an example, especially when its concentrations reach abnormal content above the metabolic requirements or exceeds accumulation capacity and becomes toxic. In order to decipher the origin of Cu in the environment as well as the biogeochemical processes that drive its migration, isotopic techniques can be used. Two stable isotopes of Cu (63 and 65) present in the environment are being fractionated depending on the conditions and processes involved. For this reason, Cu fingerprinting isotopic fractionation has already been applied in environmental sciences and emerged wide range of aspects dedicated to: complexation with organic ligands (Ryan et al., 2014), adsorption onto bacteria/algae and (oxy)hydroxides (Pokrovsky et al., 2008), precipitation, bacterial intracellular incorporation (Mathur et al., 2005; Navarrete et al., 2011), acid mine drainage (Kimball et al., 2009), mineral dissolution (Wall et al., 2011), rock weathering (Fernandez and Borrok, 2009), ore formation (Larson et al., 2003), plant assimilation (Jouvin et al., 2009; Navarrete et al., 2011; Weinstein et al., 2011), ocean and river processes (Vance et al., 2008; Borrok et al., 2008) and soil contamination (Ettler et al., 2011).

Therefore, an application of isotopic technique for tracking back Cu of industrial and slag-released origin could be interesting for understanding its mobility path, biotic acquisition mechanisms and other processes included. Furthermore, an application of Cu-slags as supplementary materials in hydraulic structures might affect aquatic environment through metal release (Schmukat et al., 2012). Thus, implementation of isotopic approach could be a prospective for capability of tracing critical load of Cu in water resulting from engineering Cu-slag reuse.

## 8.7 Concluding remarks

The studies carried out in a frame of this PhD dissertation focused on environmental risk and future application of Cu-slag. The gathered results have equally high importance for historical and modern slags. First of all, the importance lies in determining the environmental behavior of such wastes since similar Cu-slags might be found elsewhere. Furthermore, historical slags were collected from real dumping site at which potential risk assessment was needed. The relevance of research undertaken for modern slags is justified by number of reasons such as high production volume and strong need of appropriate management of these slags from generation stage onwards. Moreover, modern slag might contain even higher content of residual metals as compared to historical slags, hence environmental risk can be of even greater concern.

Since historical slag was found to be highly-leachable, the consideration should be given to removal of the materials from dumping site and preferably metal recovery. For example, subjection to bioleaching process could be a good alternative to disposal. In spite of low concentrations of Cu, its total amount to be recovered might be of economical profit considering the volume of slags disposed. Nevertheless, the main challenge that would be faced at the very initial stage is slags collection since they are dispersed widely across the site as shown in Figure 8.6. On the other hand there are many spots where slags could be easily collected since heaps covered by soil layer are fairly often present as shown in Figure 8.6. Undoubtedly, the investment outlay of this approach would be necessary in order to make sure that the profit gained outstrips the expenses to be carried. Modern slags should be dealt with a special caution since concentrations of metals might be even higher as compared to historical slags.

As the result of this PhD thesis following general conclusions can be drawn:

1) Metallurgical slags should be considered as hazardous materials since remaining metals can be released into the environment. For this reason harmonization of legislation concerning metal discharge limits and handling these wastes is necessary.

2) Characterization of slags including not only bulk chemical, but also phase composition as well as evaluation of leaching susceptibility are needed prior selecting appropriate management method to be put into practice.

3) Slags are susceptible to dissolution when exposed to organic compounds (artificial root exudates, humic and fulvic acids). Therefore, the disposal sites lacking physical impermeable

barriers preventing migration of metallic contaminants may require urgent implementation of such a lining blockage. An evaluation of remediation methods which could repress or more preferably exclude already existing metal contaminations of dumping sites is of critical demand.

4) Bacteria (*Pseudomonas aeruginosa)* considerably enhances the release of major (Si and Fe) and metallic (Cu, Zn, Pb) elements relative to effects of abiotic solutions (ultrapure water and growth medium) regardless of the slags chemistry and structure. Therefore, bio-weathering at industrial dumping sites cannot be ignored.

5) Bacteria *A. thiooxidans* was found to be a good leaching agent catalyzing the release of metals from both, amorphous granulated and crystalline massive slags, whereas contribution of *P. fluorescens* to metal extraction was rather marginal presumably due to higher pH conditions at which *P. fluorescens* acted. Optimization of operating parameters for bioleaching following development of industrial scale technology is an incentive scheme for future management of metallurgical slags.

An appropriate choice of future slag management requires critical appraisal of various technologies along with methodological advantages and disadvantages. An overview of technological approaches given in this chapter highlights the opportunities arising from treatment of Cu-slags. Many attractive routes can be undertaken for Cu-recovery with simultaneous downscaling of environmental impact. An application of Cu-slags for any treatment should base on suitability of the method whereby the alleviation of concern regarding environmental hazard has to be prioritized. A particular emphasis is given to bio-extraction methods which are found to be highly attractive. Biological treatment offers number of advantages; therefore the importance of technology development has been recognized. Nevertheless, there are still many technological problems to be obviated prior its commercial application.

# REFERENCES

1.  **Akcil A., Ciftci H., Deveci H. (2007):** *„Role and contribution of pure and mixed cultures of mesophiles in bioleaching of a pyritic chalcopyrite concentrate".* Minerals Engineering 20 (3), 310-318.

2.  **Al-Harahsheh M. & Kingman S.W. (2004):** *„Microwave-assisted leaching—a review".* Hydrometallurgy *73* (3), 189-203.

3.  **Al-Jabri K.S., Taha R.A., Al-Hashmi A., Al-Harthy A.S. (2006):** *„Effect of copper slag and cement by-pass dust addition on mechanical properties of concrete".* Construction and Building Materials 20 (5), 322–331.

4.  **Alvarez M.T., Crespo C., Mattiasson B. (2007):** *„Precipitation of Zn (II), Cu (II) and Pb (II) at bench-scale using biogenic hydrogen sulfide from the utilization of volatile fatty acids".* Chemosphere 66 (9), 1677-1683.

5.  **Anand S., Rao K.S., Jena P.K. (1983):** *„Pressure leaching of copper converter slag using dilute sulphuric acid for the extraction of cobalt, nickel and copper values".* Hydrometallurgy 10 (3), 305-312.

6.  **Anjum F., Bhatti H.N., Ghauri, M.A. (2010):** *„Enhanced bioleaching of metals from black shale using ultrasonics".* Hydrometallurgy 100(3), 122-128.

7.  **Banza A.N., Gock E., Kongolo K. (2002):** *„Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction".* Hydrometallurgy 67 (1), 63-69.

8.  **Borrok D.M., Nimick D.A., Wanty R.B., Ridley W.I. (2008):** *„Isotopic variations of dissolved copper and zinc in stream waters affected by historical mining".* Geochimica et Cosmochimica Acta 72 (2), 329-344.

9.  **Boularbah, A., Schwartz, C., Bitton, G., Aboudrar, W., Ouhammou, A., Morel, J.L. (2006):** *„Heavy metal contamination from mining sites in South Morocco: 2. Assessment of metal accumulation and toxicity in plants.Chemosphere"* 63 (5), 811-817.

10. **Bridge G. (2000):** *„The social regulation of resource access and environmental impact: production, nature and contradiction in the US copper industry".* Geoforum 31 (2), 237-256.

11. **Bunzl K., Trautmannsheimer M., Schramel P., Reifenhäuser W. (2001):** *„Availability of arsenic, copper, lead, thallium, and zinc to various vegetables grown in slag-contaminated soils".* Journal of Environmental Quality 30 (3), 934-939.

12. **Buss H.L., Lüttge A., Brantley, S.L. (2007):** *„Etch pit formation on iron silicate surfaces during siderophore-promoted dissolution".* Chemical Geology 240(3), 326-342.

13. **Carranza F., Romero R., Mazuelos A., Iglesias N, Forcat. O. (2009):** *„Biorecovery of copper from converter slags: Slags characterization and exploratory ferric leaching tests".* Hydrometallurgy 97 (1-2), 39-45.

14. **Casper S.T., Mehra A., Farago M.E., Gill R.A. (2004):** *„Contamination of surface soils, river water and sediments by trace metals from copper processing industry in the Churnet River Valley, Staffordshire, UK".* Environmental Geochemistry and Health 26(1), 59-67.

15. **Cheng Y., Guo Z., Liu X., Yin H., Qiu G., Pan F., Liu H. (2009):** *„The bioleaching feasibility for Pb/Zn smelting slag and community characteristics of indigenous moderate-thermophilic bacteria".* Bioresource Technology, 100 (10), 2737-2740.

16. **Conesa H.M., Faz Á., Arnaldos R. (2006):** *„Heavy metal accumulation and tolerance in plants from mine tailings of the semiarid Cartagena–La Unión mining district (SE Spain)."* Science of the Total Environment 366 (1), 1-11.

17. **Çubukçu A. & Tüysüz N. (2007):** *„Trace element concentrations of soils, plants and waters caused by a copper smelting plant and other industries, Northeast Turkey".* Environmental geology 52(1), 93-108.

18. **Dabrowski A., Hubicki Z., Podkościelny P. Robens, E. (2004):** *„Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method".* Chemosphere 56(2), 91-106.

19. **Deng H., Ye Z.H., Wong, M.H. (2004):** *„Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metal-contaminated sites in China".* Environmental Pollution 132 (1), 29-40.

20. **Deng T. & Ling Y. (2007):** *„Processing of copper converter slag for metal reclamation. Part I: extraction and recovery of copper and cobalt".* Waste Management and Research 25, 440-448.

21. **Dimitrijević M., Kostov A., Tasić V., Milosević, N. (2009):** *„Influence of pyrometallurgical copper production on the environment".* Journal of Hazardous Materials 164 (2), 892-899.

22. **Dong Y., Lin H., Xu X., Zhang Y., Gao Y., Zhou S. (2013):** *„Comparative study on the bioleaching, biosorption and passivation of copper sulfide minerals".* International Biodeterioration & Biodegradation 84, 29-34.

23. **Dopson, M., Halinen, A.K., Rahunen, N., Boström, D., Sundkvist, J.E., Riekkola-Vanhanen, M. Puhakka J.A. (2008):** *„Silicate mineral dissolution during heap bioleaching".* Biotechnology and bioengineering 99 (4), 811-820.

24. **Ehrlich H.L. (1998):** *„Geomicrobiology: its significance for geology".* Earth-Science Reviews 45 (1) 45-60.

25. **Ernst W. (1974):** *„Schwermetallvegetation der erde"* (p. 863). Stuttgart.: Gustav Fischer Verlag.

26. **Ettler V. & Johan Z. (2014):** *„12 years of leaching of contaminants from Pb smelter slags: geochemical/mineralogical controls and slag recycling potential".* Applied Geochemistry 40, 97-103.

27. **Ettler V. (2016):** *„Soil contamination near non-ferrous metal smelters: A review".* Applied Geochemistry 64, 56-74.

28. **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 (1), 73-84.

29. **Ettler V., Piantone P., Touray J.C. (2003):** *„Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long- term assessment".* Mineralogical Magazine 67 (6), 1269-1283.

30. **Faucon M.P., Shutcha M.N., Meerts P. (2007):** *„Revisiting copper and cobalt concentrations in supposed hyperaccumulators from SC Africa: influence of washing and metal concentrations in soil".* Plant and Soil 301 (1), 29-36.

31. **Fernandez A. & Borrok D.M. (2009):** *„Fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks".* Chemical Geology 264 (1), 1-12.

32. **Gadd G.M. (2010):** *„Metals, minerals and microbes: geomicrobiology and bioremediation".* Microbiology 156, 609-643.

33. **Gardea-Torresdey J.L., Peralta-Videa J.R., Montes M., De la Rosa G., Corral-Diaz B. (2004):** *„Bioaccumulation of cadmium, chromium and copper by Convolvulus arvensis L.: impact on plant growth and uptake of nutritional elements".* Bioresource Technology 92 (3), 229-235.

34. **Gee C., Ramsey M.H., Maskall J., Thornton I. (1997):** *„Mineralogy and weathering processes in historical smelting slags and their effect on the mobilisation of lead".* Journal of Geochemical Exploration 58 (2-3), 249-257.

35. **Ghaderian S.M., Ravandi A.A.G. (2012):** *„Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran".* Journal of Geochemical Exploration 123, 25-32.

36. **Gonzalez C., Parra R., Klenovcanova A., Imris I., Sanchez M. (2005):** *„Reduction of Chilean copper slags: a case of waste management project".* Scandinavian journal of metallurgy 34 (2), 143-149.

37. **González R.C., González-Chávez M.C.A. (2006):** *„Metal accumulation in wild plants surrounding mining waste".* Environmental Pollution 144 (1), 84-92.

38. **Gorai B., Jana R.K., Premchand (2003):** *„Characteristics and utilization of copper slags-a review".* Resources, Conservation and Recycling 39 (4), 299-313.

39. **Gordon R.B. (2002):** *„Production residues in copper technological cycles".* Resources, Conservation and Recycling 36 (2), 87-106.

40. **He S., Wang J., & Yan J. (2010):** *„Pressure leaching of high silica Pb–Zn oxide ore in sulfuric acid medium".* Hydrometallurgy 104 (2), 235-240.

41. **Hong S., Candelone J.P., Soutif M. Boutron C.F (1996):** *„A reconstruction of changes in copper production and copper emissions to the atmosphere during the past 7000 years".* Science of The Total Environment 188 (2). 183-193.

42. **Houben D., Couder E., Sonnet P. (2013):** *„Leachability of cadmium, lead, and zinc in a long-term spontaneously revegetated slag heap: implications for phytostabilization".* Journal of Soils and Sediments 13 (3), 543-554.

43. **Jouvin D., Weiss D.J., Mason T.F.M., Bravin M.N., Louvat P., Zhao F., ... & Benedetti M.F. (2012):** *„Stable isotopes of Cu and Zn in higher plants: evidence for Cu reduction at the root surface and two conceptual models for isotopic fractionation processes".* Environmental Science & Technology 46 (5), 2652-2660.

44. **Kierczak J.,** Potysz A., Pietranik A., Tyszka R., Modelska M., Néel C., Ettler V., Mihaljevič M. (2013) : *„Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland).* Journal of Geochemical Exploration 124, 183-194.

45. **Kimball B. E., Mathur R., Dohnalkova A.C., Wall, A.J., Runkel R.L., Brantley S.L. (2009):** *„Copper isotope fractionation in acid mine drainage".* Geochimica et Cosmochimica Acta 73 (5), 1247-1263.

46. **Kuenen J., Pacyna J.M., Rentz O., Oertel D., Pulles T., Appelman W. (2013):** NFR: 2. C. 7. a Copper production SNAP: 040309a Copper production ISIC: 2720 Manufacture of basic precious and non-ferrous metals Version Guidebook 2013.

47. **Larson P.B., Maher K., Ramos F.C., Chang Z., Gaspar M., Meinert L.D. (2003):** *„Copper isotope ratios in magmatic and hydrothermal ore-forming environments".* Chemical Geology 201 (3), 337-350.

48. **Lewis, A.E. (2010):** *„Review of metal sulphide precipitation".* Hydrometallurgy 104 (2), 222-234.

49. **Liu Y.G., Zhou M., Zeng G.M., Wang X., Li X., Fan T., Xu W.H. (2008):** *„Bioleaching of heavy metals from mine tailings by indigenous sulfur-oxidizing bacteria: effects of substrate concentration".* Bioresource Technology 99 (10), 4124-4129

50. **Lottermoser B.G. (2002)**: *„Mobilization of heavy metals from historical smelting slag dumps, north Queensland, Australia".* Mineralogical Magazine 66 (4), 475-490.

51. **Male D.W., Leduc L.G., Ferroni G.D. (1997):** *„The potential of mining slag as a substrate for microbial growth and the microbiological analysis of slag and slag seepage".* Antonie van Leeuwenhoek 71 (4), 379-386.

52. **Manz M. & Castro L.J. (1997):** *„The environmental hazard caused by smelter slags from the Sta. Maria de la Paz Mining District, Mexico".* Environmental Pollution 98 (1), 7-13.

53. **Mathur R., Ruiz J., Titley S., Liermann L., Buss H., Brantley S. (2005):** *„Cu isotopic fractionation in the supergene environment with and without bacteria*. Geochimica et Cosmochimica Acta 69 (22), 5233-5246.

54. **Moura W.A., Gonçalves J.P., Lima M.B.L. (2007):** *„Copper slag waste as a supplementary cementing material to concrete".* Journal of Materials Science 42 (7), 2226-2230.

55. **Najimi M., Sobhani J., Pourkhorshidi A.R. (2011):** *„Durability of copper slag contained concrete exposed to sulfate attack".* Construction and Building Materials 25 (4), 1895–1905.

56. **Navarrete J.U., Borrok D.M., Viveros M., Ellzey J.T. (2011):** *„Copper isotope fractionation during surface adsorption and intracellular incorporation by bacteria".* Geochimica et cosmochimica acta 75 (3), 784-799.

57. **Navarrete J.U., Viveros M., Ellzey J.T., Borrok D.M. (2011):** *„Copper isotope fractionation by desert shrubs".* Applied Geochemistry 26, 319-321.

58. **Niu Z., Zou Y., Xin B., Chen S., Liu C., Li, Y. (2014):** *„Process controls for improving bioleaching performance of both Li and Co from spent lithium ion batteries at high pulp density and its thermodynamics and kinetics exploration".*Chemosphere 109, 92-98.

59. **Pan H.D., Yang H.Y., Tong L.L., Zhong C.B., Zhao, Y. S. (2012):** *„Control method of chalcopyrite passivation in bioleaching".* Transactions of Nonferrous Metals Society of China, 22(9), 2255-2260.

60. **Panda S., Akcil A., Pradhan N., Deveci H. (2015):** *„Current scenario of chalcopyrite bioleaching: A review on the recent advances to its heap-leach technology".* Bioresource technology 196, 694-706.

61. **Pandey S., Saha P., Barai P.K., Maiti T.K. (2010):** *„Characterization of a $Cd^{2+}$ -resistant strain of Ochrobactrum sp. isolated from slag disposal site of an iron and steel factory".* Current Microbiology 61 (2), 106-111.

62. **Pandey S., Saha P., Biswas S., Maiti T.K. (2011):** *„Characterization of two metal resistant Bacillus strains isolated from slag disposal site at Burnpur, India".* Joural of Environmental Biology 32, 773-779.

63. **Parker R.L. (1967):** *„Data of geochemistry: composition of the earth's crust".* US Government Printing Office.

64. **Parsons M.B., Bird D.K., Einaudi M.T., Alpers Ch.N. (2001):** *„Geochemical and mineralogical controls on trace element release from the Penn Mine base-metal slag dump, California".* Applied Geochemistry 16 (14), 1567–1593.

65. **Piatak N.M., Seal 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".* Applied Geochemistry 19, 1039-1064.

66. **Pokrovsky O.S., Viers J., Emnova E.E., Kompantseva E.I., Freydier R. (2008):** *„Copper isotope fractionation during its interaction with soil and aquatic microorganisms and metal oxy (hydr) oxides: possible structural control”.* Geochimica et Cosmochimica Acta 72(7), 1742-1757.

67. **Potysz A., Grybos M., Kierczak J., Guibaud G., Lens P.N.L., van Hullebusch E.D. (2016a):** *„Bacterially-mediated weathering of crystalline and amorphous Cu-slags”.* Applied Geochemistry 64, 92-106.

68. **Potysz A., Kierczak J., Fuchs Y., Grybos M., Guibaud G., Lens P.N.L. van Hullebusch E.D. (2016b):** *„Characterization and pH-dependent leaching behaviour of historical and modern copper slags”,* Journal of Geochemical Exploration 160, 1-15.

69. **Potysz A., van Hullebusch E.D., Kierczak J., Grybos M., Lens P.N.L., Guibaud G. (2015):** *„Copper Metallurgical Slags–Current Knowledge And Fate: A Review”.* Critical Reviews in Environmental Science and Technology 45 (22), 2424-2488.

70. **Rachid D. & Ahmed B. (2005):** *„Effect of iron and growth inhibitors on siderophores production by Pseudomonas fluorescens”.* African Journal of Biotechnology 4(7), 697-702.

71. **Radetzki M. (2009):** *„Seven thousand years in the service of humanity-the history of copper the red metal”.* Resources Policy 34. 176-184.

72. **Rascio N. & Navari-Izzo F. (2011):** *„Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting?”.* Plant Science 180 (2), 169-181.

73. **Robalds A., Naja G.M., Klavins M. (2016):** *„Highlighting inconsistencies regarding metal biosorption”.* Journal of hazardous materials 304, 553-556.

74. **Rogers J.R. & Bennett P.C (2004):** *„Mineral stimulation of subsurface microorganisms: release of limiting nutrients from silicates”.* Chemical Geology 203 (1), 91–108.

75. **Ruan R., Zou G., Zhong S., Wu Z., Chan B., Wang D. (2013):** *„Why Zijinshan copper bioheapleaching plant works efficiently at low microbial activity–Study on leaching kinetics of copper sulfides and its implications”.* Minerals Engineering 48, 36-43.

76. **Ryan B.M., Kirby J.K., Degryse F., Scheiderich K., McLaughlin M.J. (2014):** *„Copper isotope fractionation during equilibration with natural and synthetic ligands”.* Environmental Science & Technology 48 (15), 8620-8626.

77. **Schippers, A., Bosecker, K., Willscher, S., Spröer, C., Schumann, P., & Kroppenstedt, R. M. (2002):** *„Nocardiopsis metallicus sp. nov., a metal-leaching actinomycete isolated from an alkaline slag dump”.* International Journal of Systematic and Evolutionary Microbiology 52 (6), 2291-2295.

78. **Schmukat A., Duester L., Ecker D., Schmid H., Heil C., Heininger P., Ternes T.A. (2012):** *„Leaching of metal(loid)s from a construction material: Influence of the particle size, specific surface area and ionic strength”.* Journal of Hazardous Materials (227–228), 257–264.

79. **Sheoran V., Sheoran A.S., Poonia P. (2009):** *„Phytomining: a review”.* Minerals Engineering 22(12), 1007-1019.

80. **Shi C. & Qian J. (2000):** *„High performance cementing materials from industrial slags — a review”.* Resources, Conservation and Recycling 29 (3), 195–207.

81. **Shi C., Meyer Ch., Behnoodc A. (2008):** *„Utilization of copper slag in cement and concrete”.* Resources, Conservation and Recycling 52 (10), 1115–1120.

82. **Sobanska S., Ledésert B., Deneele D., Laboudigue A. (2000):** *„Alteration in soils of slag particles resulting from lead smelting”.* Earth and Planetary Sciences 331 (4), 271-278.

83. **Stoltz E. & Greger M. (2002):** *„Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plant species growing on submerged mine tailings”.* Environmental and Experimental Botany 47 (3), 271-280.

84. **Suzuki I. (2001):** *„Microbial leaching of metals from sulfide minerals”.* Biotechnology Advances 19, 119-132.

85. **Swamy K.M., Narayana K.L., Misra V.N. (2005):** *„Bioleaching with ultrasound”.* Ultrasonics sonochemistry 12 (4), 301-306.

86. **Themelis M.J. (1994):** *„Pyrometallurgy near the end of 20th century”.* Industrial Insight 46 (8). 51-57.

87. **Torres M.A., West A.J., Nealson K. (2014):** *„Microbial acceleration of olivine dissolution via siderophore production”.* Procedia Earth and Planetary Science 10, 118-122.

88. **Van Der Ent A., Baker A.J., Reeves R.D., Chaney R.L., Anderson C.W., Meech J.A…, Mulligan D.R. (2015):** *„Agromining: farming for metals in the future?”.* Environmental Science & Technology 49 (8), 4773-4780.

89. **van Hullebusch E. D., Yin N-H., Seignez N., Labanowski J., Gauthier A., Lens P. N. L., Avril C., Sivry Y. (2015) :** *„Bio-alteration of metallurgical wastes by Pseudomonas aeruginosa in a semi flow-through reactor".* Journal of Environmental Management 147, 297-305.

90. **Vance D., Archer C., Bermin J., Perkins J., Statham P.J., Lohan M.C., ... & Mills R.A. (2008):** *„The copper isotope geochemistry of rivers and the oceans".* Earth and Planetary Science Letters 274 (1), 204-213.

91. **Verbruggen N., Hermans C., Schat H. (2009):** *„Molecular mechanisms of metal hyperaccumulation in plants".* New Phytologist 181 (4), 759-776.

92. **Vijayaraghavan K. & Balasubramanian R. (2015):** *„Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions".* Journal of environmental management 160, 283-296.

93. **Virkutyte J., Sillanpää M., Latostenmaa P. (2002):** *„Electrokinetic soil remediation—critical overview".* Science of the Total Environment 289 (1), 97-121.

94. **Wall A.J., Mathur R., Post J.E., Heaney P.J. (2011):** *„Cu isotope fractionation during bornite dissolution: An in situ X-ray diffraction analysis.* Ore Geology Reviews 42 (1), 62-70.

95. **Watling H.R. (2006):** *„The bioleaching of sulphide minerals with emphasis on copper sulphides".* Hydrometallurgy 84 (1), 81-108.

96. **Weinstein C., Moynier F., Wang K., Paniello R., Foriel J., Catalano J., Pichat S. (2011):** *„Isotopic fractionation of Cu in plants".* Chemical Geology 286 (3), 266-271.

97. **Wenzel W.W. & Jockwer F. (1999):** *„Accumulation of heavy metals in plants grown on mineralised soils of the Austrian Alps".* Environmental Pollution 104 (1), 145-155.

98. **Willscher S. & Bosecker K. (2003):** *„Studies on the leaching behaviour of heterotrophic microorganisms isolated from an alkaline slag dump".* Hydrometallurgy 71 (1), 257-264.

99. **Yang Z., Rui-lin M., Wang-dong N. Hui W. (2010):** *„Selective leaching of base metals from copper smelter slag".* Hydrometallurgy 103 (1), 25-29.

100. **Yanqun Z., Yuan L., Schvartz C., Langlade L., Fan L. (2004):** *„Accumulation of Pb, Cd, Cu and Zn in plants and hyperaccumulator choice in Lanping lead–zinc mine area, China".* Environment International 30 (4), 567-576.

101. **Yao Z., Li J., Xie H., Yu C. (2012):** *„Review on remediation technologies of soil contaminated by heavy metals".* Procedia Environmental Sciences 16, 722-729.

102. **Yin F., Xing P., Li Q., Wang C., Wang, Z. (2014b):** *„Magnetic separation-sulphuric acid leaching of Cu–Co–Fe matte obtained from copper converter slag for recovering Cu and Co".* Hydrometallurgy 149, 189-194.

103. **Yin N.-H., Sivry Y., Avril C., Borensztajn S., Labanowski J., Malavergne V., Lens P. N. L., Rossano S., van Hullebusch E.D., (2014a):** *„Bioweathering of lead blast furnace (LBF) metallurgical slags by Pseudomonas aeruginosa",* International Biodeterioration & Biodegradation 86, 372-381.

104. **Yoon J., Cao X., Zhou Q., Ma L. Q. (2006):** *„Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site".* Science of the total environment 368 (2), 456-464.

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# Appendix 1
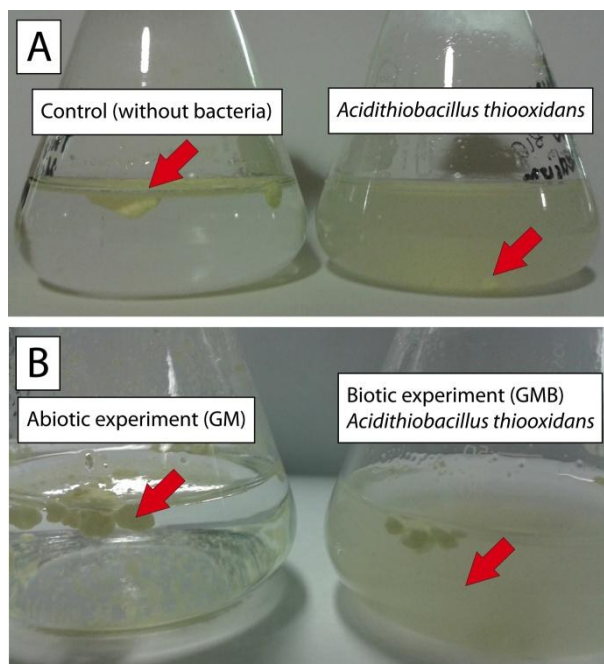


**Figure S1. Comparison of sulfur oxidation under abiotic and biotic conditions: control experiments (A). Activity test done for batch experiments (2% vol. solution from the batches transfered into growth medium). Lack of bacterial growth (solution remained transparent) in abiotic batches and positive sulfur oxidation in biotic batches (B).**
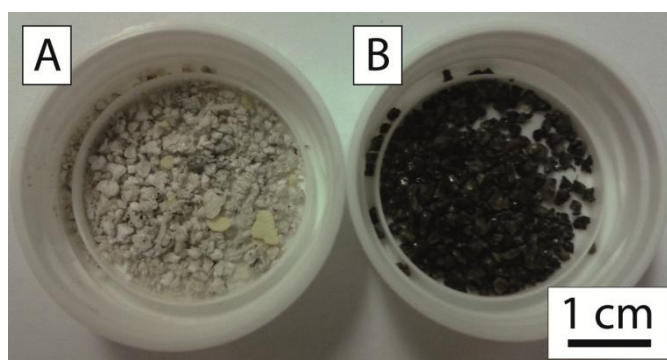


**Figure S2. Macroscopic image of A: granulated slag after bioleaching (FS: 1-2 mm, PD: 1%) and B: corresponding grains from abiotic experiment carried out under the same conditions (FS: 1-2 mm, PD: 1%).**

# Appendix 2

**Table. List of PhD activities.**

| ACTIVITY | | DATE |
|---|---|---|
| SUMMER SCHOOL | • Summer School: Contaminated Sediments-Characterization and Remediation<br>• Introductory ETeCoS$^3$ course "Environmental Technology Research in Context"<br>• Summer School: Biological Treatment of Solid Waste<br>• Summer School: Contaminated soils and remediation | 17 - 21 June, 2013, Delft (THE NETHERLANDS)<br>24-27 June, 2014, Cassino (ITALY)<br><br>June 30 - July 4, 2014, Cassino-Gaeta (ITALY)<br>22-26 June 2015, Champs-sur-Marne (France) |
| CONFERENCES | • THE XX$^{th}$ MEETING OF THE PETROLOGY GROUP OF MINERALOGICAL SOCIETY OF POLAND, Oral presentation: Modern and historical Cu-slags: from characterization to environmental impact<br>• 4$^{th}$ INTERNATIONAL CONFERENCE ON RESEARCH FRONTIERS IN CHALCOGEN CYCLE SCIENCE AND TECHNOLOGY<br>Flash presentation and poster presentation<br>• GOLDSCHMIDT CONFERENCE<br>Poster presentation: Bioweathering of crystalline and amorphous Cu-metallurgical slags | 17 – 20 October, 2013, Niemcza, Lower Silesia (POLAND)<br><br><br>28-29 May, 2015, Delft (THE NETHERLANDS)<br><br><br>16-21 August, 2015, Prague (CZECH REPUBLIC) |
| WORKSHOP/COURSE | • COURSE: "Methodology for analysis of minerals and materials" at the University Pierre et Marie Curie in Paris<br>• WORKSHOP: Environmental impacts of mining and smelting", Orsay, France: Oral presentation: *Microbially mediated mobilization of metals from copper metallurgical slags.*<br>• COURSE: Environmental processes and technologies (UNESCO-IHE)<br>• Training on High Performance Size Exclusion Chromatography (Limoges, France) | 20-21 November, 2014 Paris (FRANCE)<br><br>8-9 January, 2015, Orsay (FRANCE)<br><br><br>30 March-16 April, 2015 Delft (THE NETHERLANDS)<br><br>November-December, 2014 |

**List of papers related to PhD work:**

1. Potysz A., van Hullebusch E. D., Kierczak J., Grybos M., Lens P.N.L. & Guibaud G. (2015): *Copper Metallurgical Slags–Current Knowledge And Fate: A Review.* Critical Reviews in Environmental Science and Technology 45 (22), 2424-2488.

2. Potysz A., Kierczak J., Fuchs Y., Grybos M., Guibaud G., Lens P.N.L. & van Hullebusch E.D. (2016): *Characterization and pH-dependent leaching behaviour of historical and modern copper slags.* Journal of Geochemical Exploration 160, 1-15.

3. Potysz A., Grybos M., Kierczak J., Guibaud G., Lens P.N.L. & van Hullebusch E.D. (2016): *Bacterially-mediated weathering of crystalline and amorphous Cu-slags.* Applied Geochemistry 64, 92-106.

4. Potysz A., Grybos M., Kierczak J., Guibaud G., Fondaneche P., Lens P.N.L. & van Hullebusch E.D. (2016): *Metal mobilization from Cu-slags by soil organic acids.* Environmental Science and Pollution Research (in revision).

5. Potysz A., Lens P.N.L., van de Vossenberg J., Rene E.R., Grybos M., Kierczak J., Guibaud G. & van Hullebusch E.D. (2016): *Comparison of Cu, Zn and Fe bioleaching from Cu-metallurgical slags in the presence of Pseudomonas fluorescens and Acidithiobacillus thiooxidans.* Applied Geochemistry (in revision).