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Metallurgical sludges, bio/leaching and heavy metals recovery (Zn, Cu)

Manivannan Sethurajan

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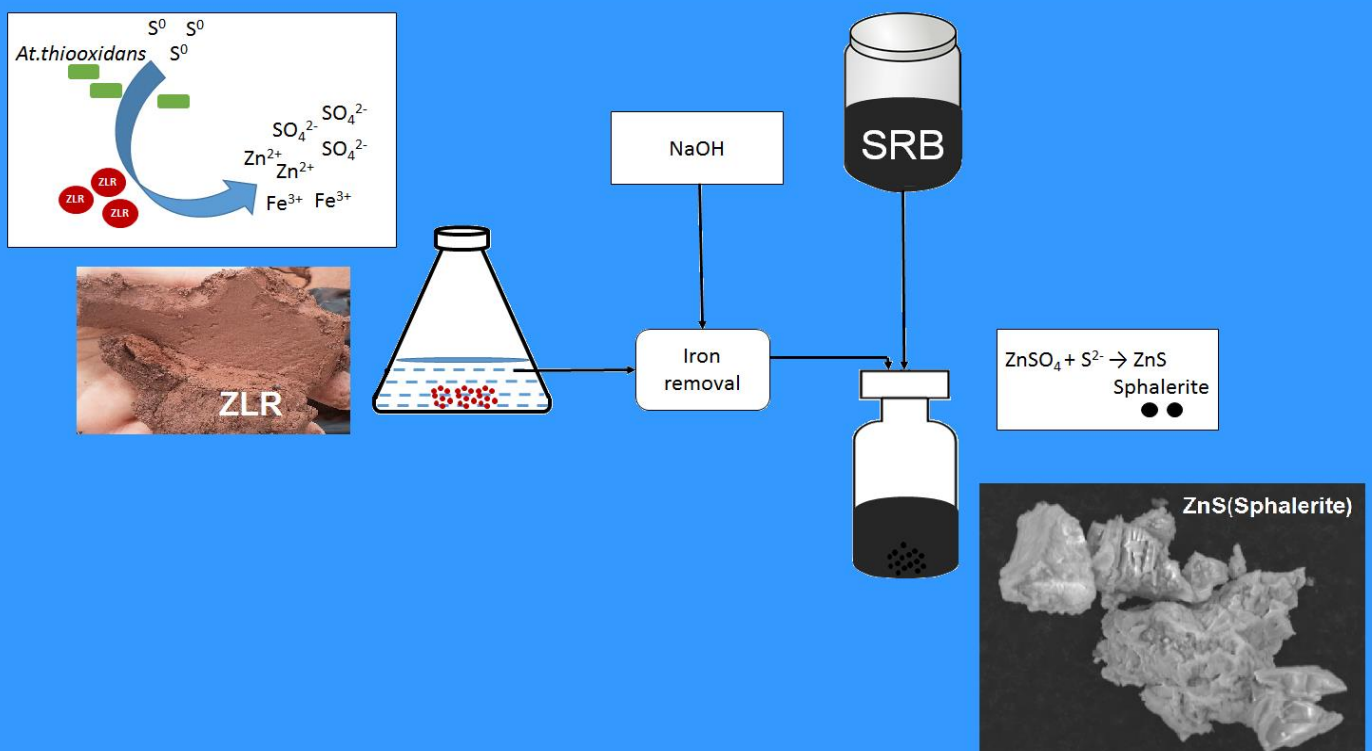
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Metallurgical sludges – Bio/leaching and heavy metals recovery (Zn & Cu)

PhD thesis
(2012-2015)

Manivannan SETHURAJAN



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(Zn & Cu)**

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— **PARIS-EST**



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Degree of Doctor in Environmental Technology

Thèse – Tesi di Dottorato – PhD thesis

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**Metallurgical sludges – Bio/leaching and heavy metals recovery
(Zn & Cu)**

To be defended December 11nd, 2015

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



Table of contents

Table of contents.....	viii
List of Figures.....	xiv
List of Tables.....	xix
List of abbreviations.....	xxi
Acknowledgements.....	xxiv
Abstract.....	xxvii
Résumé.....	xxix
Samenvatting.....	xxxix
Sintesi.....	xxxiii
Chapter 1. Introduction.....	1
1.1. Problem description.....	1
1.2. Objectives of the thesis	4
1.3. Structure of the thesis	4
1.4. Thesis outline.....	6
1.5. References	9
Chapter 2. Leaching and recovery of metals from metallic industrial sludges, dusts and residues	12
2.1. Introduction	15
2.1.1. Wastes as secondary resources.....	15
2.1.2. Metallurgical sludges, dusts and residues as secondary resources.....	16
2.2 Metal producing industrial wastes.....	20
2.2.1. Dusts.....	22
2.2.2. Sludges.....	23
2.2.3. Residues.....	23
2.3. Leaching	24
2.3.1. Hydrometallurgical processes.....	24
2.3.2. Bio-hydrometallurgical processes.....	25
2.3.2.1. Microbe and metal Interaction.....	26
2.3.2.2. Bioleaching.....	27
2.3.3. (Bio)Hydrometallurgical treatment of wastes from metal industries.....	29
2.3.3.1. Dusts.....	29
2.3.3.2. Sludges.....	32

2.3.3.3. Residues.....	34
2.4. Recovery of metals from metallurgical wastes leachates	36
2.4.1. Metals recovery by precipitation	38
2.4.1.1. Hydroxide precipitation.....	39
2.4.1.2. Carbonate Precipitation.....	40
2.4.1.3. Sulfide precipitation	40
2.4.1.6. Biogenic sulfide precipitation.....	42
2.4.2. Solvent extraction.....	43
2.4.3. Electrowinning.....	45
2.4.4. (Bio)sorption.....	47
2.5. Conclusions.....	49
2.6. References.....	50
Chapter 3. Fractionation and leachability of heavy metals from aged and recent Zn-	
metallurgical leach residues from Três Marias zinc plant (MG, Brazil).....	68
3.1. Introduction.....	71
3.2. Materials and methods.....	73
3.2.1. Solid samples.....	73
3.2.2. Physico-chemical and mineralogical characterization of the samples.....	73
3.2.2.1. pH, total solids, volatile and fixed solids.....	73
3.2.2.2. Total metal content.....	74
3.2.2.3. X-Ray Diffraction.....	74
3.2.2.4. X-Ray fluorescence.....	74
3.2.3. Toxicological characteristics leaching procedure (TCLP).....	74
3.2.4. Sequential extraction.....	75
3.2.5. Influence of pH on the leaching of heavy metals	76
3.2.5.1. pH stat leaching experiments.....	76
3.2.5.2. Geochemical modelling of heavy metals leaching	76
3.2.6. Analytical methods and statistical analysis.....	77
3.3. Results	77
3.3.1. Physico-chemical and mineralogical characterization.....	77
3.3.2. Toxicity characteristics leaching procedure.....	79
3.3.3. Sequential extraction.....	80
3.3.4. Leachability of major and trace elements.....	81
3.4. Discussion.....	84

3.4.1. Physico-chemical and mineralogical characterization of the samples.....	84
3.4.2. Fractionation and mechanisms controlling the leaching and solubility of trace and major elements from ZLRs	88
3.5. Conclusions	91
3.6. References.....	93

Chapter 4. Leaching and selective zinc recovery from acidic leachates of zinc

metallurgical leach residues	100
4.1.Introduction.....	103
4.2.Materials and Methods.....	104
4.2.1. Zinc plant leaching residues.....	104
4.2.2. Phase composition of Zn in ZLRs.....	105
4.2.2.1.Chemical extraction procedure.....	105
4.2.2.2.X-ray absorption near edge spectroscopy.....	106
4.2.3. Leaching experiments.....	106
4.2.4. Kinetic analyses.....	106
4.2.5. Selective precipitation of Zn from ZLR leachates.....	108
4.2.5.1.Prediction of selective sulfide precipitation.....	108
4.2.5.2.Sulfide precipitation experiments.....	109
4.2.5.3.Characterization of the ZnS precipitates.....	109
4.3.Results.....	110
4.3.1. Chemical phase composition of Zn in ZLRs.....	110
4.3.2. Factors influencing Zn leaching from ZLRs.....	111
4.3.3. Kinetic analysis of Zn leaching from the ZLRs investigated.....	115
4.3.4. Selective recovery of Zn from ZLR leachates.....	117
4.4.Discussion.....	122
4.4.1. ZLRs as secondary Zn resource and its environmental significance.....	122
4.4.2. Zinc leaching mechanisms from ZLR.....	123
4.4.3. Selective Zn precipitation from the ZLR leachates.....	125
4.5.Conclusions and perspectives.....	126
4.6.References.....	128

Chapter 5. Bioleaching and selective biorecovery of Zn from zinc metallurgical leach residues.....	134
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5.1. Introduction.....	136
5.2. Materials and methods.....	137
5.2.1. Zinc-metallurgical leach residues.....	137
5.2.2. Micro-organisms.....	138
5.2.3. Bioleaching experiments.....	138
5.2.3.1. Process optimization – Response surface methodology CCD approach.....	138
5.2.3.2. Bioleaching under optimum conditions.....	140
5.2.3.3. Biogenic sulfuric acid Vs chemical sulfuric acid leaching.....	140
5.2.3.4. Kinetic analysis	140
5.2.4. Fe and Zn biorecovery experiments.....	141
5.2.4.1. Sulfate reducing bacteria enrichment and biogenic sulfide production.....	141
5.2.4.2. Biogenic metal sulfide precipitation.....	141
5.2.5. Analytical methods and statistical analysis	142
5.3. Results.....	142
5.3.1. Bioleachability of Zn from ZLR by <i>A. thiooxidans</i>	142
5.3.2. Optimization of bioleaching parameters by response surface methodology.....	145
5.3.3. Bioleaching kinetics.....	148
5.3.4. Selective Zn biorecovery from the acidic bioleachates.....	150
5.3.4.1. Fe removal from the acidic bioleachate.....	150
5.3.4.2. Zn biorecovery from Fe depleted bioleachate.....	150
5.4. Discussion.....	152
5.4.1. Biohydrometallurgy for the selective Zn recovery from ZLRs.....	152
5.4.2. Bioleaching of Zn from ZLR and its kinetics.....	153
5.4.3. Selective biorecovery of Zn from the bioleachates.....	154
5.5. Conclusions	155
5.6. References	157

Chapter 6. Leaching and selective copper recovery from acidic leachates of Três Marias zinc plant (MG, Brazil) metallurgical purification residues.....162

6.1. Introduction.....	165
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6.2. Materials and methods.....	167
6.2.1. Samples.....	167
6.2.2. Characterization of the ZPR.....	167
6.2.3. Fractionation and potential toxicity of the ZPR.....	168
6.2.4. Leaching experiments.....	169
6.2.5. Metal sulfide precipitation.....	170
6.2.6. Analytical methods and statistical analysis.....	171
6.3. Results	171
6.3.1. Total metal contents of ZPR	171
6.3.2. TCLP	172
6.3.3. Sequential extraction	173
6.3.4. pH stat leaching experiments	174
6.3.5. Optimization of leaching parameters	175
6.3.6. Copper sulfide precipitation	178
6.4. Discussion.....	180
6.4.1. ZPR as an alternative resource for heavy metals.....	180
6.4.2. Characteristics of the ZPR	182
6.4.3. Cu leaching from ZPR.....	184
6.4.4. Selective Cu recovery from the acidic ZPR leachates.....	185
6.5. Conclusions.....	186
6.6. References.....	188
Chapter 7. General discussion, conclusions and perspectives.....	194
7.1. General overview of the research	196
7.1.1. Characterization of the sludges.....	197
7.1.2 Acid leachability of heavy metals from the sludges.....	197
7.1.2.1. Fractionation and pH dependent leaching.....	197
7.1.2.2. Optimization of leaching parameters	198
7.1.3. Recovery of the heavy metals from the polymetallic sludge leachates.....	201
7.2. Conclusions.....	203
7.3. Perspectives.....	205
7.3.1. Recycling perspectives.....	205
7.3.2. Potential secondary source for lead.....	208
7.4. References.....	212
Supplementary information.....	215

List of Figures

Figure 1.1. Pictorial representation of the problems associated with metallurgical industrial processes.

Figure 1.2. Schematic flow chart depicting the various unit operations to produce zinc from the zinc silicates and sulfides and the stages where zinc plant leach and purification being generated.

Figure 1.3. PhD thesis structure.

Figure 2.1. Schematic product and waste streams from mining to metal refining (adapted from Lottermoser, 2010). Note the generation of wastes at each and every step of mining and metallurgical processes.

Figure 2.2. Simplified flow charts of (a) pyrometallurgical and (b) hydrometallurgical operations, in which ore is treated to yield metals accompanied with the generation of wastes (redrawn from Lottermoser, 2010)

Figure 2.3. Basic unit processes in hydrometallurgy (redrawn from Gupta, 2006)

Figure 2.4. Bioleaching process and commercial bioheap leaching plants (a) schematic representation of bioheap leaching process, (b) bioleaching plant in Zijinshan copper mine, China (Reinman et al., 2006), (c) bioheapleaching plant in Talvivarva mining company, Finland (Reikkola-Vanhanen, 2010) and (d) bioheapleaching plant in Kasese mine, Uganda (Gahan et al., 2012)

Figure 2.5. Microbe-metal interactions that can be engineered to develop enhanced bioleaching processes (reproduced from Upadhyay, 2002)

Figure 2.6. Mechanisms of bioleaching (adapted from Uroz et al., 2009)

Figure 2.7. Various stages in the recovery of metals by precipitation

Figure 2.8. pH dependence of metal sulfide and metal hydroxide solubilities (resimulated from Lewis, 2010)

Figure 2.9. (a) Simplified flowsheet of the leaching and metal recovery by solvent extraction - electrowinning plant at Konkola Copper Mines, Zambia (Sole et al., 2005) and (b) solvent extraction plant Morenci, Arizona (Marsden, 2006)

Figure 2.10. Flow sheet of recovery of metals by solvent extraction (redrawn from Wilson et al., 2014)

Figure 2.11.(a) Solution extraction and electrowinning plant and (b) Direct copper electrowinning facility, Bagdad (Arizona, USA) (Marsden, 2006)

Figure 2.12. A simple electrolytic cell used for the recovery of metals by electrowinning

Figure 2.13. Metals recovery by (bio)sorption

Figure 3.1. Fractionation of heavy metals in (a) ZLR1, (b) ZLR2 and (c) ZLR3 determined by the accelerated BCR procedure.

Figure 3.2. Leaching behaviour of metals from (a) ZLR1, (b) ZLR2 and (c) ZLR3 and Visual MINTEQ model for the leach metals solubility features from (d) ZLR1, (e) ZLR2 and (f) ZLR3 as a function of pH.

Figure 4.1. A schematic diagram depicting the various shrinking core kinetics phenomena.

Figure 4.2. Zn K-edge XANES spectra for selected samples of (a) the Zn(II) ZLR harboring samples; (b) Zn(II) reference compounds.

Figure 4.3. Effect of agitation rates on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (Pulp density – 2%, Temperature – 80 °C, 1 M Sulfuric acid) (Legends shown inside panel (a)).

Figure 4.4. Effect of temperature on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (Pulp density – 2%, Agitation – 150 rpm, 1 M Sulfuric acid) (Legends shown inside panel (a)).

Figure 4.5. Effect of sulfuric acid concentration on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (Pulp density – 2%, Temperature – 80 °C, Agitation 150 rpm) (Legends shown inside panel (a)).

Figure 4.6. Effect of solid to liquid phase ratio on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (1 M sulfuric acid, Temperature – 80 °C, Agitation 150 rpm) (Legends shown inside panel (a)).

Figure 4.7. Kinetic model fits of ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) to experimental results of Zn leaching at temperature – 80 °C, agitation speed – 250 rpm, acid concentration – 1.5 M H₂SO₄ and pulp density – 2 %).

Figure 4.8. (a) Arrhenius plot for the determination of activation energy and (b) plot for the order of sulfuric acid concentration.

Figure 4.9. Metal precipitation versus initial pH, from ZLR1 leachate, a – percentage of metal hydroxide precipitated after initial pH adjusted with 10 M NaOH, b – percentage of metals precipitated after the addition of 100 mg/L of dissolved sulfide.

Figure 4.10. Schematic hydrometallurgical flow chart for the selective recovery of Zn from the Zn-plant leach residues.

Figure 4.11. Zn-sulfide precipitation Vs Time in the ZLR (Cd, Cu, Fe, Pb free) leachates at pH 4 (100 mg L⁻¹ of dissolved sulfide).

Figure 4.12. SEM-EDS micrographs of the Zn-sulfide precipitates of (a) ZLR1, (b) ZLR2 and (c) ZLR3.

Figure 4.13. XRD spectrum of Zn-sulfide precipitate from (a) ZLR1, (b) ZLR2 and (c) ZLR3 leachate.

Figure 5.1. (a) Bioleaching of Zn from ZLR by *A. thiooxidans* and (b) pH profile of the preliminary bioleaching studies on ZLR by *A. thiooxidans* (legends, blank 1 = MS medium + 50 g L⁻¹ ZLR, Test 1 = MS medium + *A. thiooxidans* + 50 g L⁻¹ ZLR, blank 2 = MS medium + 50 g L⁻¹ ZLR + 10 g L⁻¹ elemental sulfur, test 2 = MS medium + *A. thiooxidans* + 50 g L⁻¹ ZLR + 10 g L⁻¹ elemental sulfur).

Figure 5.2. Bioleaching efficiency of Zn from ZLR as a function of (a) sulfur concentration, (b) pulp density and (c) pH using *A. thiooxidans*.

Figure 5.3. 3-D surface plots for the optimization of Zn bioleaching from ZLR (a) sulfur concentration vs pH, (b) sulfur concentration vs pulp density and (c) pulp density vs pH.

Figure 5.4. Bioleaching yield of Zn and Fe (from ZLR) by *A. thiooxidans* under optimized conditions (sulfur concentration 25.1 g L⁻¹, pulp density 21.5 g L⁻¹, initial pH 3.3, temperature 30 °C and agitation at 150 rpm).

Figure 5.5. Zn leaching efficiency of chemical sulfuric acid vs biogenic sulfuric acid (pulp density 2%, acid concentration 0.2 M, temperature 30 °C and agitation at 150 rpm).

Figure 5.6. Kinetic model fits of ZLR to experimental results of Zn bioleaching (sulfur - 2.51 g L⁻¹, pulp density 2.15%, initial pH 3.3, temperature 30 °C and agitation at 150 rpm).

Figure 5.7. (a) SEM-EDS analysis of the Fe-precipitates, (b) SEM-EDS analysis of the Zn-sulfide precipitates and (c) XRD spectrum of Zn-sulfide precipitate from ZLR bioleachate.

Figure 6.1. XRD spectra of ZPR: (i) raw ZPR and (ii) ZPR leached at pH 2.5 (HNO₃).

Figure 6.2. Heavy metal fractionation in Três Marias ZPR evaluated by the accelerated BCR procedure.

Figure 6.3. Heavy metals leaching from the ZPR as a function of pH.

Figure 6.4. Effect of (a) agitation, (c) temperature, (e) acid concentration and (g) pulp density on Cu leachability against time and effect of (b) agitation, (d) temperature, (f) acid concentration and (h) pulp density on metal (Cd, Cu and Zn) leachability after 6 hours of leaching.

Figure 6.5. Metal sulfide precipitation versus initial pH of the leachate (100 mg L⁻¹ of dissolved sulfide in 0.1 M NaOH, temperature 20 °C and agitation 150 rpm for 1 h).

Figure 6.6. Effect of sulfide dosage on metal sulfide precipitation from the polymetallic ZPR leachate (at initial pH 1.5, temperature 20 °C and agitation 150 rpm for 1 h).

Figure 6.7. XRD spectrum of the Cu precipitates.

Figure 6.8. Hydrometallurgical flow chart for the selective recovery of Cu as covellite from ZPR.

Figure 7.1. Overview of PhD research components.

Figure 7.2. Characterization of the Zn-plant residues performed in this study.

Figure 7.3. A schematic representation of the experiments performed in phase 2.

Figure 7.4. Details of the parameters investigated for the optimization of Zn and Cu leaching from ZLRs and ZPR.

Figure 7.5. Pictorial representation of the stepwise approach for the selective recovery of metals (Cu & Zn) from the ZLR/ZPR leachates.

Figure 7.6. Alternative metal recovery strategy proposed in this PhD research.

Figure 7.7. Recycling unit operations to produce Zn from the ZnS precipitates.

Figure 7.8. Proposed process diagram for the lab scale heap leaching and recovery of the metals from the precipitates.

Figure 7.9. Total Pb content present in the investigated samples.

Figure 7.10. Effect of pulp density on Pb extraction from ZLRs, (a) ZLR1, (b) ZLR2 and (c) ZLR3 (temperature – 20 °C, agitation – 150 rpm, 1 M HCl) (legends shown inside panel (a)).

List of Tables

- Table 2.1 Chemical, mineralogical and toxicological characteristics of metallurgical wastes.
- Table 2.2 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from metallurgical dusts.
- Table 2.3 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from metallurgical sludges.
- Table 2.4 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from the metallurgical residues.
- Table 2.5 Different techniques used for the recovery of metals from metallurgical waste leachates.
- Table 3.1. Stepwise information (on the extractant and ultrasound acceleration time) of the BCR sequential extraction procedure (Perez-Cid et al., 1998).
- Table 3.2. Physico-chemical characteristics of the ZLRs.
- Table 3.3. Elemental oxide composition (weight %) obtained from XRF analysis.
- Table 3.4. Elemental composition (by hot plate aqua regia digestion) of the ZLRs investigated.
- Table 3.5. TCLP test results for the ZLRs investigated.
- Table 3.6. Mineralogy, metal content and potential toxicity of ZLRs from different hydrometallurgical plants.
- Table 3.7. Fractionation of metals (Cd, Cu, Pb and Zn) from ZLRs under different acidic conditions.
- Table 4.1. Extracting agent and reaction conditions of the sequential chemical phase extraction of zinc from the ZLRs (Zhang, 1992; Li et al., 2013).
- Table 4.2. Zn - Chemical phase composition of the ZLRs investigated.
- Table 4.3. Composition of leachate (ZLR1) and amounts of metals precipitated (%) at each step
- Table 4.4. Elemental composition of the ZLR precipitates by hot-plate aqua-regia digestion.
- Table 5.1. Optimization window of the bioleaching process parameters based response surface methodology (CCD approach).
- Table 5.2. Regression results from the data of central composite designed experiments
- Table 6.1. Ultrasound assisted BCR sequential extraction procedure (Perez-Cid et al., 1998).
- Table 6.2. Total metal content of the ZPR from the Três Marias Zn plant.
- Table 6.3. Potential toxicity of the ZPR.
- Table 7.1. Various studies reported on the leaching of Pb from ZLRs.

List of abbreviations

AAS – Atomic absorption spectroscopy
ATCC - American Type Culture Collection
ANOVA – Analysis of Variance
AUBR – Air up-lift bioreactor
BCR - Community Bureau of Reference
BFS – Blast furnace sldges
BOFS - Basic oxygen furnaces sludges
CCD - central composite design
CSTR – Continuous stirred tank reactor
D2EHPA - Di-(2-ethylhexyl)phosphoric acid
DIN - Deutsches Institut für Normung
DSMZ - Deutsche Sammlung von Mikroorganismen und Zellkulturen
EAFD – Electric arc furnace dust
EDTA - Ethylenediaminetetraacetic acid
EU – European Union
EW – Electrowinning
ICP-OES - Inductively coupled plasma optical emission spectroscopy
ILZSG - International Lead and Zinc Study Group
ISO - International Organization for Standardization
MG (Brazil) – Minas Gerais (Brazil)
MSP – Metal sulfide precipitation
PSD – Particle size distribution
RLE - Roasting-Leaching-Electrolysis
rpm – Rotation per minute
RSM - Response surface methodology
SEM - EDS - Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometry
SCM – Shrinking core model
S/L – Solid to liquid ratio
SX - Solvent extraction
TCLP – Toxicity characteristics leaching procedure
USEPA – United States Environmental Protection Agency
USGS – United States geological Survey

XAFS - X-ray absorption fine structure

XANES - X-ray absorption near edge structure

XRD - X-ray diffraction

XRF - X-ray fluorescence

ZLR – Zinc-metallurgical leach residues

ZPR – Zinc-metallurgical purification residues

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**Dedicated to my
parents**

Metallurgical sludges - bio/leaching and heavy metals recovery

Abstract

This research was carried out in order to develop a technology to demonstrate the metallurgical residues as a potential secondary source for heavy metals (Cu and Zn). Three different (based on their age of generation and deposition) zinc leach residues (ZLR1, ZLR2 & ZLR3) and zinc purification residue (ZPR) were collected from a Zn-metallurgical industry located in Brazil. The characterization of ZLRs and ZPR were examined for their mineralogical, physico-chemical, bulk chemical features. Fractionation of heavy metals and liquid-solid partitioning with respect to pH were also determined. Geo-chemical modelling was done to understand the mechanisms affecting the mineral solubilities of these residues.

Following the above, the residues were subjected to (bio)leachability tests to optimize the maximal extraction of heavy metals. The effects of experimental factors such as temperature, leachant concentration, pulp density and agitation speed have been optimized in shake flasks. The mass transfer kinetics of these solid-fluid heterogeneous leaching processes were examined by shrinking core kinetic models. Later, the recovery of Zn (ZLRs) and Cu (ZPR) from the polymetallic acidic leachates were investigated. The selective recovery of metals from the acidic leachates was achieved by metal sulfide precipitation (MSP). MSP process parameters such as initial pH and metal - sulfide dosage were also optimized for the selective recovery. The metal sulfide precipitates were characterized for mineralogy, purity and particle size distribution. Finally, hydrometallurgical flow charts for the selective recovery of Cu and Zn were proposed.

The results reveal that the ZLRs contain significant concentration of Zn (2.5% to 5%), Pb (1.7% to 2.3%) and metals such as Mn, Cu, and Al in detectable fractions. The ZPRs contain high concentration of Cu (47%), Zn (28%), Cd (9%) and Pb (5%). Fractionation with acetic and nitric acid suggest that both the leach and purification residues are hazardous wastes, releasing higher concentration of Pb and Cd into the environment, than the permissible concentration suggested by U.S. EPA. Leaching of metals from the residues is highly pH dependent. Heavy metals leaching (Zn & Cu) is high at low pH and the release of metals was decreased with increase in pH. Sulfated and carbonated mineral phases were predicted to be the solubility controlling minerals.

The leaching of Zn from ZLRs was highly influenced by temperature and acid concentration. The leaching kinetics of ZLRs results state that more than 92%, 85% and 70% of zinc can be extracted from ZLR1, ZLR2 and ZLR3 by H₂SO₄ (1.5 M) leaching (at 80 °C for 6 hours with a pulp density 2%, while the agitation speed was maintained 250 RPM). The

sulfuric acid leaching kinetics of ZLRs follow the shrinking core diffusion model. The activation energy required to leach zinc from the ZLR1, ZLR2 and ZLR were estimated to be 2.24 Kcal/mol, 6.63 Kcal/mol and 11.7 Kcal/mol respectively, by Arrhenius equation. Order of the reaction with respect to the sulfuric acid concentration was also determined as 0.2, 0.56, and 0.87 for ZLR1, ZLR2 and ZLR3, respectively. Selective precipitation of Zn (as sphalerite) from the leachates was achieved by the combination of hydroxide and sulfide precipitation. Biohydrometallurgy is also as effective as the chemical hydrometallurgy for the selective Zn recovery from the ZLRs. Cu leaching from ZPR was highly influenced by solid to liquid phase ratio and agitation speed, suggesting that the mass transfer depends on the diffusion. The leaching of Cu from the ZPR also follows the shrinking core diffusion model and requires apparently 2.9 Kcal/mol activation energy throughout the leaching process. More than, more than 50%, 70% and 60% of the total Cd, Cu and Zn can be leached from ZPR by 1M H₂SO₄ with 2% pulp density continuously shaken at 450 rpm at 80 °C. Covellite was selectively recovered from the acid multi-metallic (Cd, Cu & Zn) leachates were investigated by optimizing the initial pH and Cu to sulfide ratio.

In conclusion, these hazardous metallurgical residues can be seen as potential alternative resource for Zn and Cu. Not only the capital costs and environmental issues associated with the storage/disposal of these ZLRs & ZPR but also the gradual depletion of high grade sulfidic ores (for Zn and Cu) can be addressed. The study also leaves a perspective of investigating the leached ZLR & ZPR, for the selective leaching and recovery of Pb. Bioleaching and biorecovery of the heavy metals from these residues are interesting to investigate for future applications.

Key words: Metallurgical wastes; Metals recovery; Secondary resources; Biohydrometallurgy; Metal sulfide precipitation

Boues métallurgiques - bio / lixiviation et récupération des métaux lourds (Zn et Cu)

Résumé

Ce travail de recherche a été réalisé dans le but de développer une technologie pour démontrer le potentiel des résidus métallurgiques comme une source secondaire de métaux lourds (Cu et Zn). Trois résidus de lixiviation de zinc différents (en fonction de leur âge de génération et de dépôt) (ZLR1, ZLR2 & ZLR3) et des résidus d'épuration du zinc (ZPR) ont été recueillis sur un site industriel de la métallurgie du zinc localisé au Brésil. Les échantillons de ZLRs et ZPR ont été analysés pour déterminer leurs caractéristiques minéralogiques et physico-chimiques. Le fractionnement de métaux lourds par extraction séquentielle et leur mobilité en fonction du pH ont été déterminés. La modélisation géochimique a été réalisée pour déterminer les mécanismes qui affectent la mobilisation des métaux lourds à partir de ces résidus.

Ensuite, les résidus ont été soumis à des tests de lixiviation afin d'optimiser l'extraction de métaux lourds. Les effets de facteurs expérimentaux tels que la température, la concentration de l'agent de lavage, la densité de la pâte et la vitesse d'agitation ont été optimisées dans des flacons agités. Les cinétiques de transfert de masse de ces procédés de lixiviation hétérogènes solides-liquide ont été examinées par le modèle cinétique à cœur rétrécissant.

Par la suite, la récupération de Zn (ZLRs) et Cu (ZPR) à partir des (bio)lixiviats acides polymétalliques ont été étudiés. La récupération sélective de métaux à partir des lixiviviats acides a été obtenue par précipitation de sulfures métalliques (MSP). Les paramètres du procédé MSP tels que le pH initial et le ratio massique métal-sulfure ont été optimisés pour la récupération sélective. Les précipités de sulfure métallique ont été caractérisés par analyse minéralogique ainsi que la pureté et la distribution de taille de particule. Enfin, des séquences de procédés pour la récupération sélective de Cu et Zn ont été proposées.

Les résultats révèlent que ZLRs contient une concentration importante de Zn (2,5% à 5%), Pb (1,7% à 2,3%) et des métaux tels que Mn, Cu, Al dans des fractions détectables. Les ZPRs contiennent une forte concentration de Cu (47%), Zn (28%), Cd (9%) et Pb (5%). Le fractionnement à l'aide d'acide acétique ou d'acide nitrique suggère que les résidus de lixiviation et de purification sont des déchets dangereux, qui libèrent une concentration de plomb et de cadmium dans l'environnement supérieure à la concentration admissible proposée par l'USEPA. La lixiviation des métaux à partir des résidus est très dépendante du pH. La lixiviation des métaux lourds (Zn & Cu) est élevée à pH acide et la libération des métaux

diminue avec l'augmentation du pH. Les phases minérales sulfatées et carbonatées ont été identifiées comme celles contrôlant la solubilité des métaux.

La lixiviation de Zn à partir de ZLRs est fortement influencée par la température et la concentration en acide. La cinétique de lixiviation des ZLRs indiquent que plus de 92%, 85% et 70% du zinc peut être extrait de ZLR1, ZLR2 et ZLR3 par lixiviation à l'aide de H₂SO₄ (1,5 M) (à 80 °C pendant 6 heures avec une densité de pulpe de 2%, tandis que la vitesse d'agitation a été maintenue à 250 tours par minute). Les cinétiques de lixiviation de ZLRs avec l'acide sulfurique suivent le modèle cinétique à cœur rétrécissant. L'énergie d'activation nécessaire pour lixivier le zinc contenu dans ZLR1, ZLR2 et ZLR a été estimées à 2,24 kcal / mol, 6,63 kcal / mol et 11,7 kcal / mol, respectivement, à l'aide de l'équation d'Arrhenius. Les ordres de la réaction par rapport à la concentration en acide sulfurique ont également été déterminé comme étant respectivement de 0,2, 0,56, et 0,87 pour ZLR1, ZLR2 et ZLR3. La précipitation sélective du zinc (comme la sphalérite) à partir des lixiviats a été obtenue par la combinaison d'une co-précipitation avec de l'hydroxyde et du sulfure. La biohydrométallurgie est aussi efficace que l'hydrométallurgie chimique pour la récupération sélective de Zn des ZLRs. La lixiviation de Cu à partir de ZPR a été fortement influencée par le rapport solide-liquide et la vitesse d'agitation, ce qui suggère que le transfert de masse est contrôlé par la diffusion. Plus de 50%, 70% et 60% de Cd, Cu et Zn peuvent être lessivés à partir de ZPR en utilisant de l'H₂SO₄ 1M pour une densité de pâte de 2% agité à 450 tours par minute en continu à 80 ° C. La covellite a été récupéré sélectivement à partir des lixiviats acides multi-métalliques (Cd, Cu et Zn) et les lixiviats ont été étudiés en optimisant le pH initial et le rapport massique Cuivre-sulfure.

En conclusion, ces résidus métallurgiques dangereux peuvent être considérés comme une ressource alternative potentielle de Zn et Cu. Non seulement les coûts d'investissement et les questions environnementales liées au stockage / élimination de ces ZLRs & ZPR mais aussi à l'épuisement progressif des minerais sulfurés de haute qualité (pour Zn et Cu) peuvent être abordés. L'étude ouvre aussi une perspective de valorisation de ZLR & ZPR lessivés, pour la lixiviation sélective et de récupération de Pb. La biolixiviation et la biorécupération des métaux lourds provenant de ces résidus sont intéressants à étudier pour les applications futures.

Mots clés: déchets métallurgiques; récupération des métaux; ressources secondaires; biohydrométallurgie; précipitation de sulfures métalliques.

Metallurgische slib - bio / uitspoeling en zware metalen herstel

Samenvatting

Dit onderzoek werd uitgevoerd om een technologie te ontwikkelen die toelaat residuen van de metallurgische industrie als potentiële secundaire bron voor zware metalen (Cu en Zn) te benutten. Drie verschillende (op basis van hun productie en depositie leeftijd) zink uitloogresiduen (Zinc Leaching Residue - ZLR1, ZLR2 & ZLR3) en één zink zuiveringsresidu (Zinc Purification Redidue - ZPR) werden verzameld bij een Zn-metallurgische industrie in Brazilië. De mineralogische, fysisch-chemische en bulk chemische eigenschappen van de ZLR en ZPR werden gekarakteriseerd. Fractionering van zware metalen en vloeistof-vaste stof partitionering als functie van de pH werd ook bepaald. Geo-chemisch modellering gaf inzicht in de mechanismen die de minerale oplosbaarheid van deze mineraalresten bepalen.

Gezien het bovenstaande werden de zink residuen onderworpen aan uitloogbaarheid tests om de extractie van zware metalen te optimaliseren. De effecten van experimentele parameters zoals temperatuur, concentratie van de uitloogstof, pulpdichtheid en roersnelheid werden in schudkolven geoptimaliseerd. De massa-overdracht kinetiek van deze vaste stof-vloeistof heterogene uitloogprocessen werden onderzocht aan de hand van `krimpende kern` (shrinking core) kinetische modellen. Later werd het terugwinnen van Zn (ZLRs) en Cu (ZPR) uit de polymetallische zure percolaten onderzocht. De selectieve terugwinning van metalen uit de zure percolaten werd bereikt door metaalsulfide neerslag (MSP). MSP procesparameters zoals de initiële pH en metaal - sulfide dosering werden geoptimaliseerd voor de selectieve terugwinning. De mineralogie, zuiverheid en deeltjesgrootteverdeling van de metaalsulfide neerslagen werden gekarakteriseerd. Tenslotte werden hydrometallurgische stroomdiagrammen voor de selectieve terugwinning van Cu en Zn uitgewerkt.

De resultaten toonden aan dat de ZLRs significante concentraties van Zn (2,5% tot 5%), Pb (1,7% tot 2,3%) en detecteerbare fracties van de metalen Mn, Cu en Al bevatten. De ZPR bevatten hoge concentraties van Cu (47%), Zn (28%), Cd (9%) en Pb (5%). Fractionering met azijn- en salpeterzuur suggereren dat zowel de ZLR als de ZPR hoge concentraties van Pb en Cd in het milieu vrijgeven, deze concentraties zijn hoger dan de toegestane concentraties voorgesteld door de Amerikaanse EPA. Uitloging van metalen uit de residuen is sterk pH afhankelijk. Uitloging van zware metalen (Zn en Cu) was fors bij lage pH en de afgifte van

metalen verminderde bij toenemende pH. De oplosbaarheid controlerende mineralen waren gesulfateerde en koolzuurhoudende minerale fasen.

De uitloging van Zn uit ZLRs werd sterk beïnvloed door de temperatuur en de zuurconcentratie. De resultaten van de kinetische eigenschappen van metaal uitloging uit ZLR lieten zien dat meer dan 92%, 85% en 70% zink uit ZLR1, ZLR2 en ZLR3 kan worden geëxtraheerd bij het uitloggen met sterk H₂SO₄ (1,5 M) bij 80 °C gedurende 6 uur met een pulpdichtheid van 2% en een roersnelheid van 250 rpm). De zwavelzuur uitloging kinetiek van de ZLR volgt het 'krimpende kern' (shrinking core) diffusiemodel. De activeringsenergie nodig voor zink uitloging van ZLR1, ZLR2 en ZLR3 werden door middel van de Arrhenius vergelijking geschat op, respectievelijk, 2,24 Kcal/mol, 6,63 Kcal/mol en 11,7 kcal/mol. De reactieorde met betrekking tot de zwavelzuur concentratie werd bepaald als 0,2, 0,56 en 0,87 voor, respectievelijk, ZLR1, ZLR2 en ZLR3. Selectieve precipitatie van Zn (als spharaliet) uit het percolaat werd bekomen door de combinatie van hydroxide en sulfide neerslagvorming. Biohydrometallurgie was even efficiënt als chemische hydrometallurgie voor de selectieve terugwinning van Zn uit ZLR. Uitloging van ZPR werd sterk beïnvloed door de vaste stof / vloeibare fase ratio en de agitatie snelheid, wat suggereert dat de massa-overdracht diffusieafhankelijk was. De uitloging van Cu uit de ZPR volgt ook het 'krimpende kern' diffusiemodel en vereiste 2,9 Kcal/mol activeringsenergie gedurende het uitloogproces. Meer dan 50%, 70% en 60% van de totale Cd, Cu en Zn concentratie kon worden uitgelooft uit de ZPR met behulp van 1 M H₂SO₄ bij een 2% pulpdichtheid, bij 80 °C en het continu schudden bij 450 rpm. Door het optimaliseren van de initiële pH en Cu verhouding sulfide kon covelliet selectief teruggewonnen worden uit het zure multi-metalen (Cd, Cu en Zn) percolaat.

Concluderend kunnen metallurgische residuen beschouwd worden als een potentiële alternatieve bron voor Zn en Cu. Daardoor worden niet alleen de investeringskosten en milieu problemen in verband met de opslag/dumpen van de ZLR en ZPR aangepakt, maar ook de geleidelijke uitputting van hoogwaardige sulfide houdende (Zn en Cu) ertsen. Dit PhD onderzoek geeft perspectief voor studies naar het uitloggen van ZLR en ZPR voor de selectieve uitloging en het terugwinnen van Pb. Ook onderzoek naar het uitloggen en de biologische terugwinning van andere zware metalen uit deze residuen is interessant voor toekomstige toepassingen.

Sleutelwoorden: Metallurgisch afval; Metalen terugwinning; Secundaire grondstoffen; Biohydrometallurgie; Metal sulfide neerslagen.

Bio/lisciviazione di fanghi metallurgici e recupero di metalli pesanti

Sintesi

La ricerca oggetto del presente elaborato è stata condotta allo scopo di sviluppare una tecnologia finalizzata al riutilizzo dei residui dell'industria metallurgica, come potenziale risorsa secondaria di metalli pesanti (Cu e Zn). Tre diversi (sulla base del periodo di generazione e stoccaggio) residui di liscivia dello zinco (ZLR1, ZLR2 e ZLR3) e un residuo di purificazione dello zinco (ZPR) sono stati raccolti da una industria metallurgica specializzata nella produzione di zinco in Brasile. ZLR e ZPR sono stati caratterizzati ed esaminati dal punto di vista delle proprietà mineralogiche, chimiche e chimico-fisiche. Sono stati inoltre determinati il frazionamento dei metalli pesanti e la ripartizione solido-liquido al variare del pH. È stato inoltre implementato un modello geochimico finalizzato a spiegare i meccanismi coinvolti nella solubilizzazione di tali residui.

I residui sono quindi stati sottoposti a test di rilascio in scala laboratorio al fine di massimizzare l'estrazione di metalli pesanti. Sono stati ottimizzati i parametri di processo e, in dettaglio, la temperatura, la concentrazione dell'agente lisciviante, la densità del solido e la velocità di agitazione. Le cinetiche di trasferimento di massa solido-liquido di tali sistemi eterogenei sono state, inoltre, esaminate utilizzando i modelli cinetici "shrinking core". In seguito, si è proceduto ad investigare una soluzione tecnologica per il recupero di Zn (ZLR) e di Cu (ZPR) dai lisciviati polimetallici acidi. Il recupero selettivo dei metalli da tali matrici acide si è potuto ottenere attraverso precipitazione come solfuri metallici (MSP). Il processo MSP è stato ottimizzato nei suoi parametri essenziali quali pH iniziale e dosaggio di solfuri al fine di poter ottenere un recupero effettivamente selettivo. I solfuri metallici precipitati sono stati quindi caratterizzati dal punto di vista mineralogico, della purezza, e granulometrico. Infine i trattamenti idrometallurgici per il recupero selettivo di Cu e Zn sono stati proposti in forma di diagrammi di flusso.

Dai risultati ottenuti, è possibile evincere che i ZLR contengono elevate concentrazioni di Zn (dal 2.5% al 5%), Pb (dal 1.7% al 2.3%) principalmente, ed altri metalli come Mn, Cu e Al in quantità comunque rilevabili. Lo ZPR contiene elevatissime concentrazioni di Cu (47%), Zn (28%), Cd (9%) e Pb (5%). I frazionamenti ottenuti usando gli acidi acetico e nitrico come agenti liscivianti, suggeriscono che sia i lisciviati che i residui di purificazione, siano da ritenersi come rifiuti speciali pericolosi, in grado di rilasciare concentrazioni di Pb e Cd nell'ambiente ben al di sopra dei limiti suggeriti dall'U.S. EPA. Il rilascio di metalli a partire dai residui è

fortemente dipendente dal pH. Esso è infatti elevato a pH bassi e decresce con l'aumentare del pH. Le fasi minerali solfatiche e carbonatiche sono quindi coinvolte nel controllo della solubilità. Il rilascio di Zn dai ZLR si è mostrato fortemente sensibile alla temperatura, così come alla concentrazione di acido.

Le cinetiche di liscivia dei ZLR hanno mostrato come più del 92%, 85% e 70% dello Zn possa essere estratto dai campioni ZLR1, ZLR2 e ZLR3 utilizzando H₂SO₄ (1.5 M) come agente estraente (ad 80 °C per 6 ore con una densità di solidi del 2%, e agitazione a 250 RPM). Le cinetiche di rilascio dei ZLR seguono il modello di diffusione dello shrinking core. Le energie di attivazione richieste per rilasciare lo zinco dai ZLR1, ZLR2 e ZLR3 sono state stimate, secondo l'equazione di Arrhenius, pari a 2.24 Kcal/mol, 6.63 Kcal/mol e 11.7 Kcal/mol, rispettivamente. L'ordine di reazione rispetto alla concentrazione di acido solforico è risultato essere 0.2, 0.56, e 0.87 per ZLR1, ZLR2 e ZLR3. La precipitazione selettiva dello zinco (come sfalerite) è stata ottenuta attraverso la precipitazione combinata di idrossidi e solfuri. Il rilascio di Cu dai ZPR è risultato fortemente influenzato dal rapporto solido-liquido e dalla velocità di agitazione, indicando come il trasferimento di massa dipenda principalmente dalla diffusione. Il rilascio di Cu dai ZPR segue anch'esso il modello diffusivo dello shrinking core e richiede un'energia di attivazione apparente pari a 2.9 Kcal/mol. Inoltre più del 50%, 70% e 60% di Cd, Cu e Zn totali, possono essere rimossi dai ZPR con H₂SO₄ 1M, 2% di densità di solidi e agitazione in continuo a 80°C. Dai percolati multimetallici (Cd, Cu e Zn) acidi, è stato possibile recuperare selettivamente il minerale covellite ottimizzando il pH iniziale e il rapporto tra Cu e solfuri.

In conclusione, tali residui metallurgici pericolosi possono essere considerati una potenziale risorsa alternativa di Zn e Cu. In questo modo è possibile ottenere non solo l'abbattimento dei costi necessari all'immagazzinamento/smaltimento dei ZLR e del ZPR, ma anche il graduale recupero di minerali solforici di alta qualità. In prospettiva, lo studio apre alla possibilità di investigare ulteriormente i ZLR e ZPR già trattati per Cd e Zn, per la lisciviazione selettiva e il recupero finale del Pb. Biolisciviazione e biorecupero dei metalli pesanti da questo tipo di residui potrebbero, inoltre, essere interessanti alternative da investigare per future applicazioni.

Key words: Rifiuti Metallurgici; Recupero di metalli; Risorse secondarie; Bioidrometallurgia; Precipitazione di solfuri metallici.

Chapter 1

Introduction

1. INTRODUCTION

1.1. Problem statement

In the recent years, the demand for metals such as Al, Cu, Zn etc have been increasing significantly. Metallurgical industries produce metals from the naturally occurring primary ores through various mineral processes. These metallurgical industries not only produce metals but also generate a lot of different metal bearing waste materials (Fig. 1) (Lottermoser, 2010). According to a survey by EU statistics, the wastes generated from mining and quarrying industries play a big contribution (> 50%) in the total wastes generated in the EU (Eurostat, 2012). These metallurgical wastes are usually deposited in a storage deposit or dams in metal production industries. The storage dams can act as a potential reservoir of toxic heavy metals. Accidental collapse and leakage in the storage dam is a serious environmental threat (Fig. 1). For example, dam collapses of Aznalcóllar (Spain, 1998), Baia Mare and Baia Borsa (Romania, 2000) caused harmful adverse effects on the environment (Clemente et al., 2003; Hilson and Monhemius, 2006). Also due to natural weathering, the release of toxic heavy metals causes adverse effects in the environment, contaminating the surrounding soil, the surface water and also the ground water (Keith et al., 2001; Gieré et al., 2003; Kachur et al., 2003; Kierczak et al., 2009; Johnson, 2009). On the other hand, high-grade resources of these metals are depleting considerably in order to meet market demand (Fig. 1) (Anjum et al., 2012). Exploring the ways of recycling, recovery and remediation strategies of these metallurgical wastes are very much important, as it would help not only to protect the environment but also sustainable resource management.

A Zn-plant located in Três Marias (Minas Gerais) in the southeastern sub-division of Brazil close to the São Francisco river, is one of the largest zinc producers in the world (leading producers in zinc oxide and zinc powder). It has business units in Brazil and in other countries. The production capacity of the plant is 730,000 tons of zinc per year. Figure 2 displays the various mineral processing operations employed by the industry to produce pure metallic zinc from zinc sulfide and zinc silicates ores. Most of the primary zinc ores are mined from the underground mines in Vazante and Morro Agudo (MG, Brazil). They are prepared for a floatation process to produce zinc concentrates and also to remove impurities by a series of operations like crushing, homogenization and grinding. The floatation products are subjected to “thickening and filtration” to produce solid zinc silicate concentrate and zinc sulfide concentrate. Lead concentrate is also generated as a by-product at this stage.

The zinc silicate concentrate and the zinc sulfide concentrate are subjected to traditional “Roasting-Leaching-Electrolysis (RLE)” processes (Feneau, 2002). Zinc silicate concentrate

willemite (Zn_2SiO_4) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) is first treated with a washing solution of zinc sulfate mainly to remove excess magnesium and also calcium while an alkaline zinc sulfate $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ solution is produced as a slurry (Chen and Dutrizac, 2003).

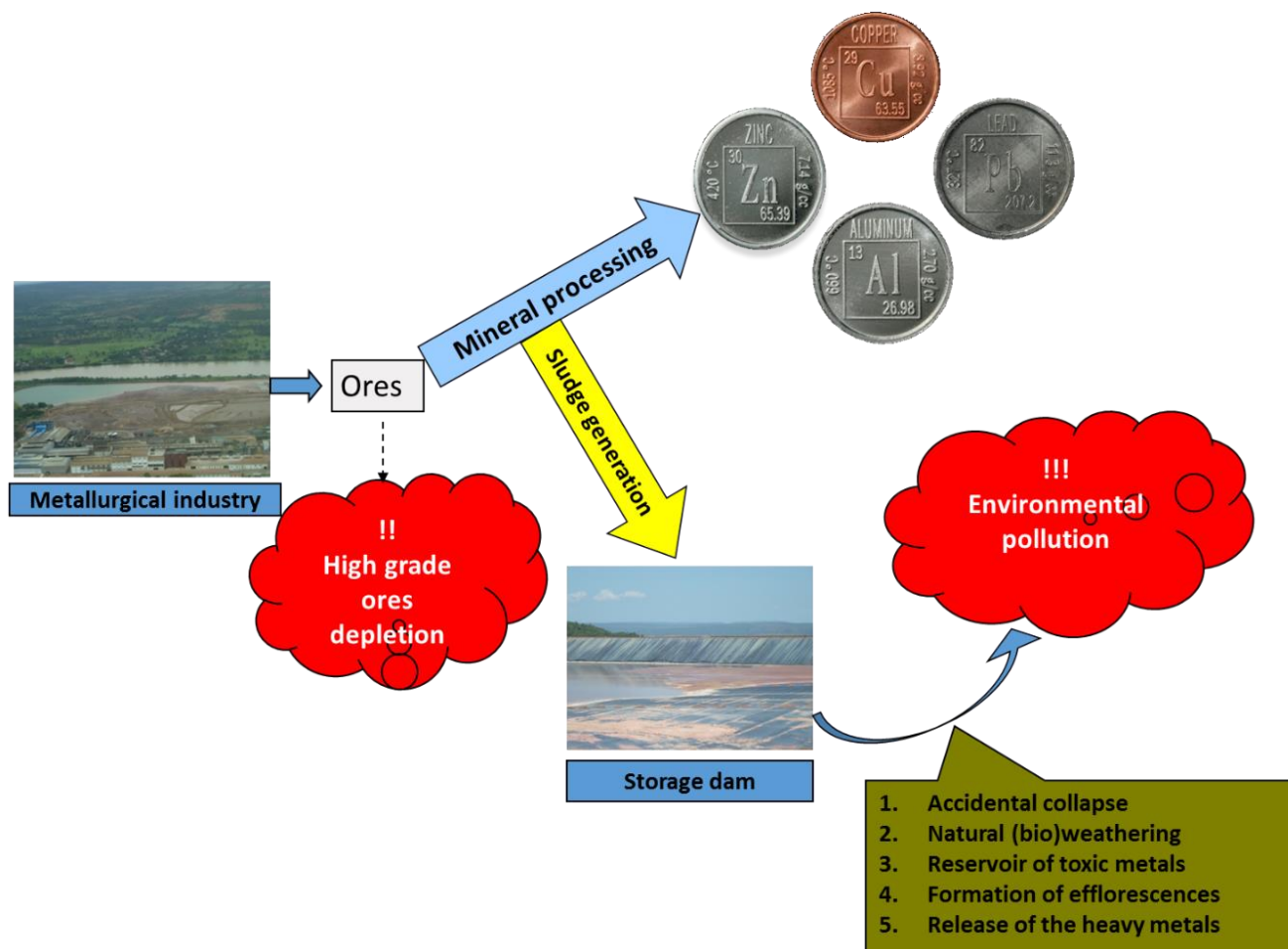
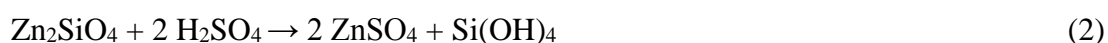
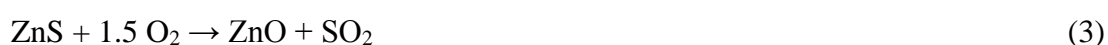


Figure 1. Pictorial representation of the problems associated with metallurgical industrial processes.

Direct acidic leaching (at high pressure) of willemite and hemimorphite mineral phases which produce soluble ZnSO_4 (and unwanted silica is coagulated, filtered and removed) can be explained by reactions 1 and 2, respectively (Souza et al., 2007):



Zinc sulfide is first treated with air or oxygen at high temperature. This process is referred as calcination/roasting to produce zinc oxide and to remove any excess sulfur (3):



During roasting, sulfuric acid and sulfur-dioxide are also generated. After the removal of magnesium and excess sulfur, the zinc silicate and sulfide concentrates are leached with acid

to remove zinc (Souza et al., 2007). Acid leaching of zinc oxide and ferrites of iron precipitation is explained in reactions 4 and 5, respectively (Souza, 2000):

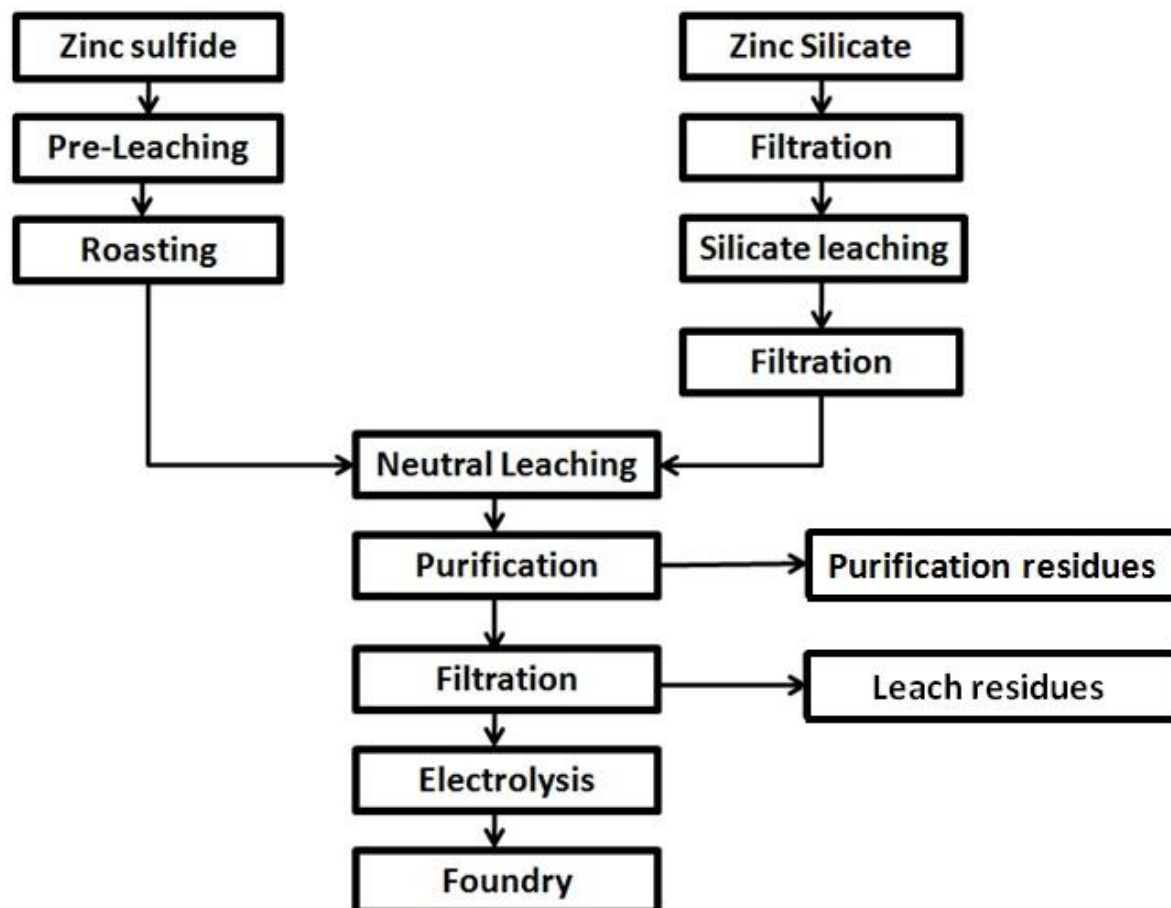


Figure 2. Schematic flow chart depicting the various unit operations to produce zinc from the zinc silicates and sulfides and the stages where zinc plant leach and purification being generated.

The leachates are purified to remove the impurities (cadmium, cobalt, copper and lead) leached alongside zinc. A processing waste is generated at this stage, which is called as zinc purification residue investigated in this research. Then the purified product is again subjected to filtration to concentrate pure zinc oxide, which is then fed to electrolytic production of zinc metal. During filtration, another sludge is generated which is the zinc plant leach residue investigated in this research. These leach residues were stored in a dam since 1969. They also had a separate dam (deposit), in which the purification residues were stored. But due to a failure of this storage dams, two other dams were constructed in 2002 and in 2011, respectively. Later

both the all the leach residues were stored in a same dam and purification residues were stored in another dam. These leach and purification residues contain significant amounts of Zn, Cu, Cd and Pb at elevated concentrations. These residues were never studied before. Hence, these wastes are interesting to explore the possibilities of extracting valuable metals.

In order to design a greener metal recovery process from these metallurgical residues, it is necessary to study the following (i) to understand the mineralogy of these wastes, the leaching kinetic and weathering mechanisms of heavy metals, (ii) to determine the leachability (also bioleachability) of the metals from the wastes and most importantly (iii) to investigate recovery of the heavy metals from these residues.

1.2. Aims and objectives:

The ultimate aim of this research project is to recover the valuable metals from the metallurgical wastes. In order to achieve the above-mentioned aim, the research plan was divided into the following sub-objectives:

- To study about the various characteristics (physico-chemistry, potential toxicity and mineralogy) of the metallurgical residues generated
- To understand about the fractionation and release of heavy metals from metallurgical residues under various environmental conditions.
- To investigate in detail about the leachability (chemical and bioleaching) of the heavy metals from the metallurgical residues.
- To study about the selective recovery (chemical and biorecovery) of the metals from the acidic polymetallic leachates.

1.3. Technical challenges and research questions

The following are the specific research questions that will be addressed during the course of the research,

- ❖ The nature of the sample, its physical and chemical properties, different mineral phases and chemical forms of the metals in the metallurgical residues?
- ❖ Are there any environmentally toxic elements present in the residues? Are these metallurgical residues hazardous to the environment?
- ❖ The acid/base titration and the buffering capacity of the samples and how far will it affect the release of metals and its kinetics with respect to pH?
- ❖ The total concentration of the metals and what is the amount of exchangeable metals, reducible and oxidizable fractions of the metals and their residual concentrations?

❖ Organic ligands (acetic and citric acid) and strong acids (HCl, HNO₃, H₂SO₄) – do they influence metal dissolution in these residues? If so, what could be the concentration of the acid required? Whether temperature will have any influence in leaching? Whether stirring do have any significant impact on the leaching?

❖ Microorganisms play a role in bioleaching of these residues, don't they? If so what are they? Chemolithotrophs – As these samples are oxidized, they do not have sulfidic moieties accessible for them to bioleach the metals. Whether external supply of any nutrients like inorganic sulfur would influence?

❖ Is it possible to scale-up the leaching process to industrial scale? If so, what about the kinetic constraints of these leaching processes i.e. activation energy, reaction order with respect to different parameters such acid concentration, solid to liquid ratio etc.?

❖ How to recover the metals metallurgical waste leachates? Which methodology will be suitable for these iron and sulfate rich polymetallic leachates? Any possibility to selectively recover the metals of interest?

The following technical challenges exist while developing the process for recovering economically valuable metals from the metallurgical residues,

➤ Lack of fundamental studies in the literature in the context of using metallurgical residues as the secondary resource of metal recovery.

➤ Metallurgical residues were found in the zone of oxidization, so metals cannot be extracted by conventional oxidative dissolution.

➤ Lack of fundamental studies on the speciation and solubility controlling mineral phases in these kinds of metallurgical wastes.

➤ Presence of complex minerals such as franklinite, goethite, hematite etc will be release a lot of iron in the leachates. Is there any possibility of selective leaching?

➤ No sulfidic forms of metals (like pyrite, chalcopyrite, sphalerite) are present, which hinders the usage of metal solubilisation by chemolithotrophic bacteria.

➤ Selective metal sulfide precipitation from the polymetallic leachates will be challenging because of the presence higher concentration of iron. Lack of fundamental studies on the selective metal recovery from the real leachates.

➤ Lower pH and higher sulfate concentration in the leachates will also be a barrier for the selective recovery of metals, as it is necessary to adjust the pH which will cause metal losses in the form of hydroxides.

1.4. Thesis outline

This doctoral thesis contains seven chapters (Fig. 3),

Chapter 1: Introduction

This chapter deals with the general introduction and overview of the research. The specific information about the samples and the associated problems were introduced. The major and specific objectives of this PhD research were stated. The research questions that could be addressed and the technological barriers to achieve the objectives were discussed. Finally, the research components and the structure of the thesis are provided.

Chapter 2: Leaching and recovery of metals from metallic industrial sludges, dusts and residues

This chapter is devoted to the literature that was already reported on the various metal bearing wastes. Three types of metal bearing solid wastes such as dusts, sludges and residues were selected and bibliographic study was carried out. The chapter was constructed in such a way that firstly mineralogical knowledge on the metallurgical wastes was updated. Secondly, information on the various chemical leaching and bioleaching on these waste materials were listed and criticized. Finally, various recovery techniques such as solvent extraction, electrowinning, precipitation and (bio)sorption etc. reported for the recovery of the metals from the leachates were discussed. Commercially available (industrial scale) examples were also provided.

Chapter 3: Fractionation and leachability of heavy metals from aged and recent Zn-metallurgical leach residues from the Três Marias zinc plant (Minas Gerais, Brazil)

This chapter is dedicated to the detailed characterization of the leach residues. Various physico-chemical characteristics such as pH, total solids, fixed solids and volatile solids, moisture and carbonate content were investigated. Mineralogy and total metal content of the leach residues were studied and discussed. Potential toxicity and fractionation of heavy metals under various environmental conditions were also discussed. Effect pH on the liquid-solid portioning was investigated and the solubility controlling mineral phases were theoretically predicted.

Chapter 4: Leaching and selective zinc recovery from acidic leachates of zinc metallurgical leach residues

This chapter deals with the selective recovery of Zn from the leach residues. Detailed mineral phase composition and speciation of Zn in the leach residues were investigated. Various parameters affecting the Zn leaching from the leach residues such as temperature, leachant concentration, agitation rate and the solid to the liquid ratio were studied and optimized. Zn leaching kinetics and kinetic parameters were investigated. Selective Zn recovery from the polymetallic leachates was investigated by adjusting the initial pH. A hydrometallurgical route for the selective sphalerite recovery was proposed.

Chapter 5: Bioleaching and selective biorecovery of zinc from zinc metallurgical leach residues from the Três Marias zinc plant (Minas Gerais, Brazil)

This chapter deals with the biohydrometallurgical recovery of Zn from ZLR (ZLR3). The process parameters affect the bioleaching of Zn from the ZLR3 by *A. thiooxidans*, such as (i) sulfur supplementation, (ii) solid to liquid ratio and (iii) initial pH were optimized. Response surface methodology (central composite design) was used for the bioprocess optimization. The leaching efficiencies of chemical and sulfuric acid were compared. The Zn bioleaching kinetics were investigated. Selective biorecovery of Zn from the bioleachates were demonstrated by biogenic sulfides. Finally, a biohydrometallurgical route for the selective biorecovery of Zn from ZLRs was proposed.

Chapter 6: Leaching and selective copper recovery from acidic leachates of Três Marias zinc plant (MG, Brazil) metallurgical purification residues

This chapter is devoted to the Zn-plant purification residues. The purification residues were characterized for its total metal content and mineralogy. Physico-chemical characteristics were also investigated. Potential toxicity, fractionation of heavy metals under different environmental conditions and the effect of pH on the heavy metals leachability were studied in detail. Heavy metals leaching (especially Cu) were optimized by studying different process variables such as temperature, leachant concentration (sulfuric acid), agitation rate and the solid to the liquid ratio. Selective copper recovery from the polymetallic leachates was investigated by optimizing the initial pH and the Cu to sulfide molar ratio. A hydrometallurgical route for the selective covellite recovery was proposed.

Chapter 7: General discussions, conclusions and perspectives

In this chapter, general discussions and conclusions of the various studies carried out on the leach and purification residues were discussed. The scientific information obtained from the different experiments and their global conclusions were presented. Scientific perspectives of the research carried out were proposed. (Bio)hydrometallurgy for the heavy metals recovery and selective recovery of lead from the metallurgical wastes were given special emphasis and some case studies were also discussed.

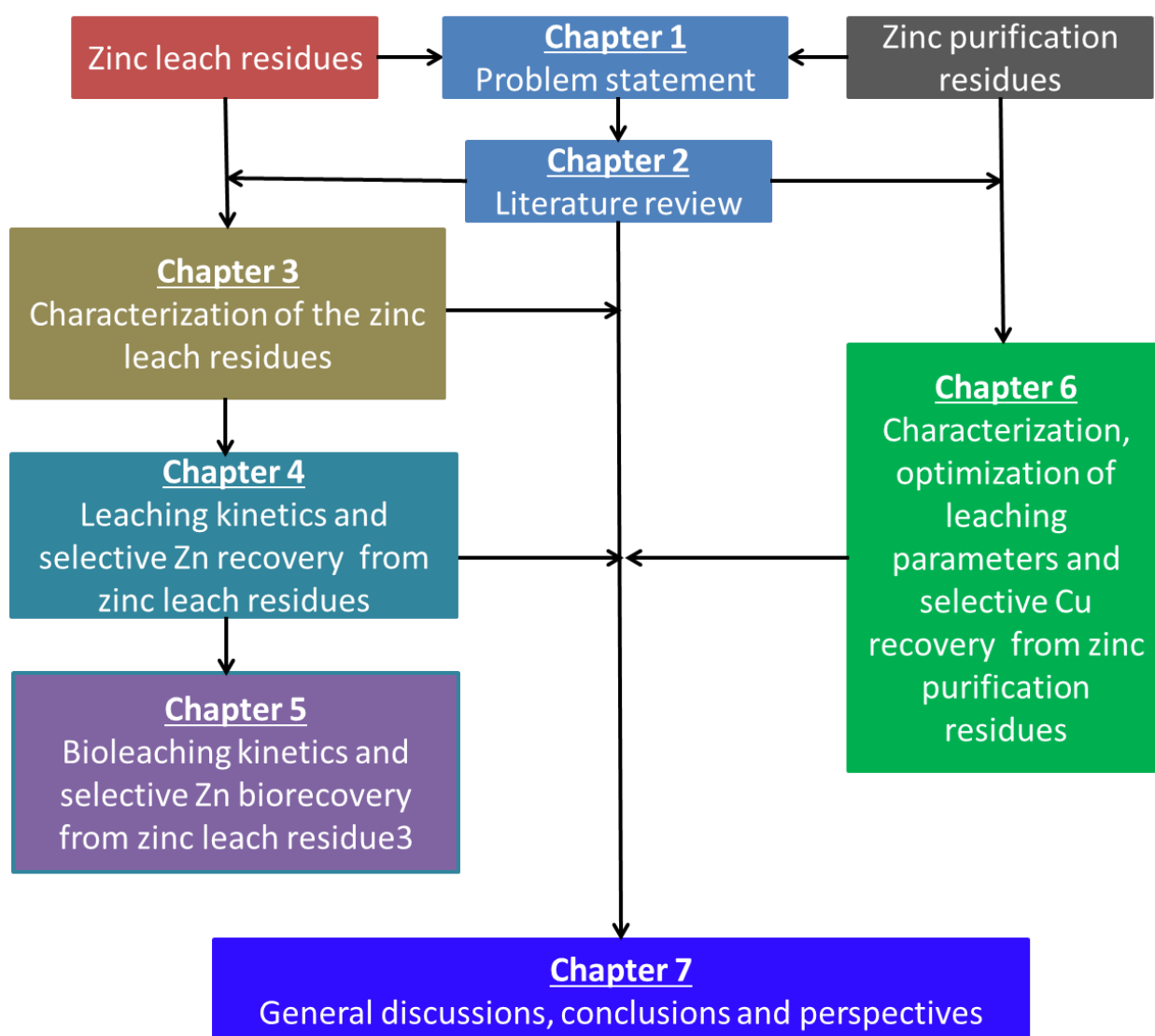


Figure 3. PhD thesis structure.

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Chapter 2

Leaching and recovery of metals from metallic industrial sludges, dusts and residues – A review

This chapter is in press for a book chapter: M. Sethurajan, H.A Horn, H.A.F. Figueiredo, P.N.L Lens, E.D van Hullebusch* (2015), “Leaching and recovery of metals from metallic industrial sludges, dusts and residues – A review.” Sustainable Technologies For Heavy Metal Removal From Soils, Solid Wastes And Wastewater, Springer (in press).

Abstract

Sludges, dusts, residues and other wastes originating from ferrous and non-ferrous metallic industries pose a serious environmental threat, if not disposed properly. Disposal of these wastes is expensive and remediation is a necessary step to be implemented to control the adverse environmental effects if disposal is done improperly. Since the past couple of decades, the world's high-grade metal reserves have been depleted considerably, but the demand for metals in day-to-day life in this electronic era is growing rapidly. The depletion of the high-grade ores urges the mineral industry to look for alternative resources for metal extraction. Sludges, dusts, and other wastes generated in the metallurgical industries are interesting options as they still contain significant amounts of valuable base and heavy metals, sometimes even precious metals like gold and silver and also rare earth elements, depending on the nature of the mining site and composition of the primary ores used. This chapter overviews various hydrometallurgical and bio-hydrometallurgical leaching processes for the extraction of metals from these wastes. Different strategies of metals recovery (solvent extraction, electrowinning, (bio)sorption and (microbial) precipitation) from the wastes generated by various ferrous and non-ferrous metallic industries are overviewed.

Key-words: Metallurgical Wastes • Secondary resources • Bio-hydrometallurgy • Metal recovery

2.1. Introduction

Due to the enormous increase in the usage of metals in the day-to-day life in the form of electronics, households, ornaments and accessories, the demand for metals is also increasing enormously (Ajnum et al., 2012; Gahan et al., 2012). Metals are usually produced from mined mineral ores by ferrous and non-ferrous industries. These metallurgical industries are not only producing metals, but generate also bulk quantities of wastes, which are either stored in reservoirs or disposed off in the environment. There are a lot of environmental issues associated with this practice (Lottermoser, 2010). This review discusses in detail these different types of wastes, their composition and the environmental considerations. Due to the rapid industrialization and the demand for metals, there is also a huge depletion of high-grade primary metal resources, which urges the metal producing industries to look for secondary alternative sources for metal extraction (Anjum et al., 2012). Metal bearing wastes from different industries can be such alternative resources for the recovery of metals, as some of the wastes still contain significant levels of valuable metals. In addition, also the adverse effects of the metals on the environment can thus be reduced. The importance of waste utilization and recycling has widely increased nowadays in view of sustainable resource supply, waste management and environmental protection. Secondary resources utilization refers to the usage of waste as the feedstock for the manufacturing of products. This strategy helps the society in two ways: (i) the generation of waste is greatly reduced; consequently their disposal into the environment will also be reduced and (ii) it enables sustainable resource management as well as yields economic benefits (Rao, 2011).

In this chapter, up-to-date available methodologies for the extraction and recovery of base and heavy metals from different metallurgical wastes will be discussed. Metal bearing wastes such as dusts and sludges from steel making industries and smelting processes, sludges and leach residues from metallurgical industries will be given a special focus, and their potential to be used as a secondary source for metals extraction will be highlighted. Their nature, element and mineralogical composition and various hydrometallurgical (chemical and biological) processes used for metal leaching and recovery will be overviewed.

2.1.1. Solid wastes as secondary resources

There are a lot of studies on the effective utilization of low grade ores to extract valuable metals in an economic as well as environment friendly manner (Anjum et al., 2012). Different

approaches have been proposed for the extraction of heavy metals from industrial wastes (solid wastes and slurry wastes), such as metal rich wastewaters, fly ashes, spent liquors, spent catalysts, spent batteries, slags, shales and sludges, some of them have been patented (Brombacher et al., 1997). Jha et al. (2001) studied the proposed processes to recover zinc from various industrial wastes. Techniques for the utilization of slags (Shen and Forsberg 2003) and sludges from the steel industries were reviewed by Das et al. (2006). Cui and Zhang (2008) overviewed the different pyrometallurgical and hydrometallurgical processes for the extraction of precious metals from electronic wastes. Lee and Pandey (2012) discussed the available methods for the extraction of various metals (Cu, Zn and Ni) from different industrial wastes by microbial assisted leaching processes. Erust et al. (2013) reviewed the possible applications of biohydrometallurgy to recover metals from spent batteries and spent catalysts. Hennebel et al. (2013) pointed out the scarcity of resources and crucial demand of raw materials, even for the basic requirements such as energy and water. They overviewed biological approaches for the utilization of secondary resources to supply some of the critical materials, e.g. platinum group elements and rare earths. Kaksonen et al. (2014) reported the ability of microbes to process and recover of gold. Johnson (2014) discussed about biomining and the possible biotechnological applications to extract metals from ores and waste materials.

2.1.2. Metallurgical sludges, dusts and residues as secondary resources

Chemical and mineralogical characteristics and toxicity levels of metallurgical wastes are listed in Table 2.1. Table 2.1 clearly shows the high metal content (above sub-economic) of these waste materials. Also, the toxicity characteristic leaching procedure (TCLP) figures from Table 2.1 suggest that at least one of the metal values fails to comply with environmental regulations, making them as “hazardous” and preventing them to be disposed in the environment (Laforest and Duchesne, 2006; Özverdi and Erdem, 2010; Erdem and Özverdi, 2011; Li et al., 2013; Tutor et al., 2013). In a few instances, Portland cement, ferrous sulfate or glass cullets are mixed with these metallurgical wastes to make them more stable and solidified (Pereira et al., 2001; Pelino et al., 2002; Salihoglu et al., 2007; Bulut et al., 2009). In any case, the valuable metals harboured by these solid wastes are wasted. The toxicity levels of these metallurgical wastes form the basic necessity to find a solution to treat or to reuse them in order to reduce their environmental impacts. Moreover, the mineralogical characteristics indicate the potential of these metallurgical solid wastes to be a secondary resource for metal recovery.

Table 2.1 Chemical, mineralogical and toxicological characteristics of metallurgical wastes

Source	Major mineral phases	Chemical composition and Metal content (%)	Potential toxicity	Binders	Reference
Electric arc furnace dust (steel industry)	Fe ₃ O ₄ Fe ₂ O ₃ MgO FeCr ₂ O ₄ ZnFe ₂ O ₄	Cr - 10.9 Ni - 4.1 Pb - 1.4 Zn - 5.2	(TCLP, US EPA 1311, pH 2.88) Cr _{total} - 9.7 mg L ⁻¹ Cr (VI) - 6.1 mg L ⁻¹ Ni - 2.3 mg L ⁻¹ Pb - 0.4 mg L ⁻¹ Zn - 93.9 mg L ⁻¹	-	Laforest and Duchesne, (2006)
Electric arc furnace dust (steel industry)	-	As - 0.29 Cd - 0.08 Cr - 0.95 Ni - 0.20 Pb - 1.30 Zn - 26.0	(TCLP, DIN 38414-S4, pH 7) Cd - 0.5 mg L ⁻¹ Cr - 5 mg L ⁻¹ Pb - 5 mg L ⁻¹ Zn - 300 mg L ⁻¹	-	Pereira et al. (2001)
Ferrochrome arc furnace dust (steel industry)	-	Mg - 17.18 Cr - 13.90 Si - 10.13 Fe - 5.19 Al - 2.83 Zn - 1.50 Ca - 0.99 Cu - 0.03 Mn - 0.18 Ni - 0.13 Pb - 0.02	(TCLP, US EPA 1311, pH 2.88) Cr - 9.81 mg L ⁻¹ Zn - 103.85 mg L ⁻¹	PC – sand – FeSO ₄ mixture (5 stoichiometric: 30%: 16%) is used with the dust to make environmentally stable	Bulut et al. (2009)

		Ti - 0.07			
Arsenopyrite mining sludge (Abandoned mining site)	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ $\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot (6-7)\text{H}_2\text{O}$ $\alpha\text{-FeOOH}$	As - 0.015	As - 11.2 mg L ⁻¹	-	Tutor et al. (2013)
Zinc extraction residue (Zinc industry)	PbSO_4 Fe_2O_3 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	Pb - 19.02 Zn - 7.98 Fe - 5.44 Cu - 0.065 Cd - 0.024	(TCLP, US EPA 1311, pH 2.88) Zn - 362 mg L ⁻¹ Pb - 65.10 mg L ⁻¹ Cd - 2.88 mg L ⁻¹ Mn - 3.47 mg L ⁻¹	-	Özverdi and Erdem, (2010)
Zinc extraction residue (Zinc industry)	PbSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$	Pb - 19.02 Zn - 7.98 Fe - 5.44 Cu - 0.065 Cd - 0.024	-	Minimum 40% of Portland cement (PC) should be blended to the residue to make stable and solidified	Erdemand Özverdi, (2011)
Zinc leach residue (Zinc industry)	ZnFe_2O_4 ZnSO_4 CaSO_4 PbS PbSO_4 Pb_3SiO_5 Zn_2SiO_4	Fe - 24.02 Zn - 19.57 Ca - 1.97 Pb - 4.18 Mn - 1.41 Cu - 0.91 Mg - 0.37	(TCLP, US EPA 1311, pH 2.88) Zn - 4589 mg L ⁻¹ Pb - 1.4 mg L ⁻¹ Cd - 93.5 mg L ⁻¹ As - 0.3 mg L ⁻¹	-	Li et al. (2013)
Zinc leach residue (Zinc industry)	-	Fe -13.6 Zn -5.0 Ca -3.3 Pb -5.40	(TCLP, US EPA 1311, pH 2.88)	Neutralization sludge (NS) mixed to the zinc leach residue in the mass	Ke et al. (2014)

		Cd-0.15 Cu - 0.26	Zn -3499.5 mg L ⁻¹ Pb-5.17 mg L ⁻¹ Cd -67.75 mg L ⁻¹ Cu-82.35 mg L ⁻¹	ratio of 8:2 to make the residue stable.	
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“-” = Not available

2.2. Metal producing industrial wastes

Natural ores consist of the desired metal present in high concentrations in combination with inherent waste compounds, i.e. metals or elements not important for the production process and usually present in lower concentrations. For example, nearly 50% of a zinc concentrate consists of unwanted elements like sulfur, iron, lead, titanium, silicon, copper, calcium, manganese, cadmium, magnesium, arsenic and mercury (Reuter et al., 2003). The metal of interest can be found in its oxidic or sulfidic form, as primary or secondary metallic phases or any other form in the natural ore. Many metallurgical processes, starting from open pit mining to final purification, have to be done to separate the pure metal from the ore. Usually some kind of waste is generated at each step of the metallurgical process; thus the metallurgical industries not only produce metals, but deposit also a huge load of waste materials in the environment (Leonard, 1978; Chandrappa and Das, 2012). The wastes generated by the metallurgical industries are huge and they are mostly disposed off in the environment (Fig. 2.1). Certain wastes contain not only unwanted elements, but have also considerable quantities of metals, mostly as oxides or sulfides.

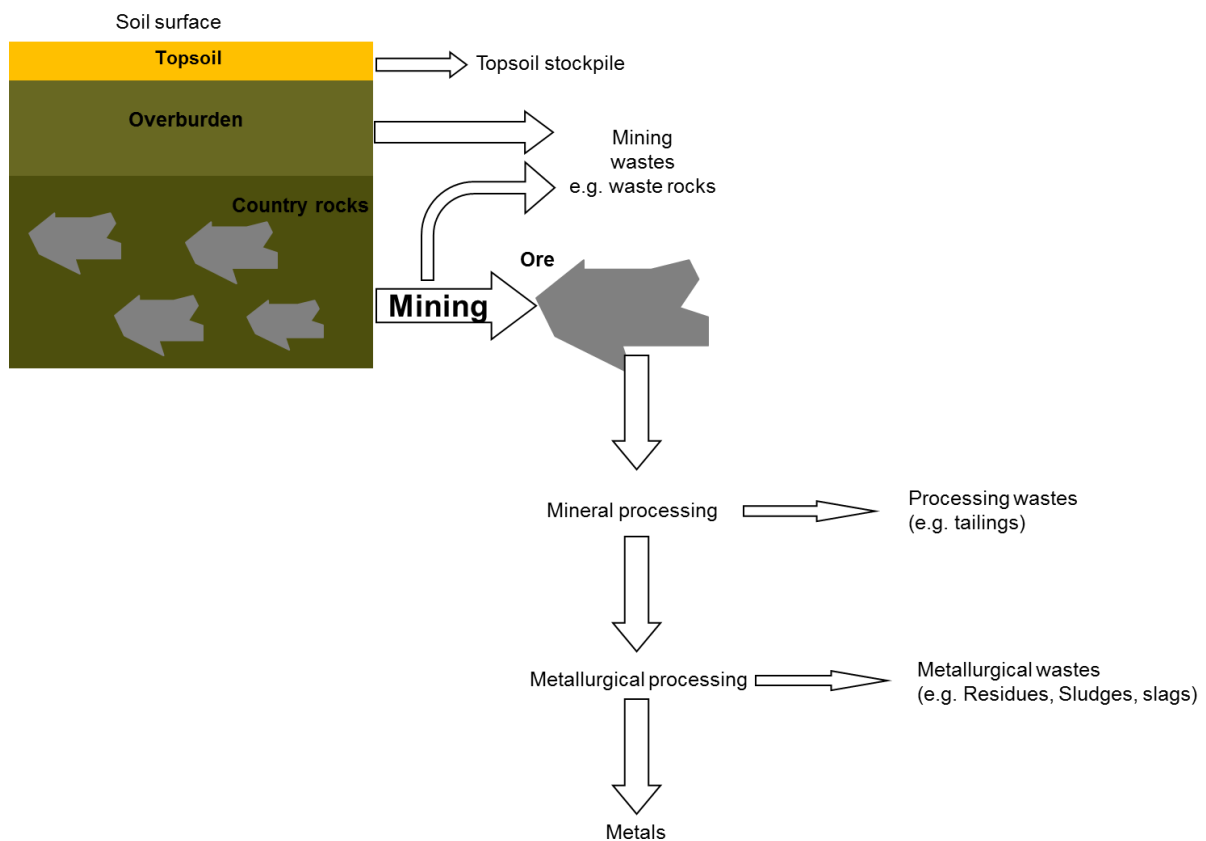


Fig. 2.1. Schematic product and waste streams from mining to metal refining (adapted from Lottermoser, 2010). Note the generation of wastes at each and every step of mining and metallurgical processes.

Metallurgical industries produce solid, liquid and gaseous wastes. These can be classified as (i) mining wastes, (ii) processing wastes and (iii) metallurgical wastes (Lottermoser 2010). Mining wastes are produced during the initial stages of mining operations like “open pit” or “underground” mining. These operations usually produce waste rocks, overburden, spoil and atmospheric emissions. These mining wastes contain very low levels of or even no metals. Processing wastes are wastes generated by physical ore processing processes applied prior to the extraction of metals, like washing, magnetic separation, gravity separation, crushing, milling, size reduction and floatation (Leonard 1978; Lottermoser 2010). Wastewater streams resulting from the washing and also the mine tailings are categorized as processing wastes. Some of the mine tailings contain significant concentrations of metals and are prone to the extraction of metals. Most of them are used for backfilling working sites or reclamation and reconstruction of the mining areas, as they do not contain economic levels of metals (Wong 1986).

Metallurgical wastes are mostly residues or muds which are produced at the final stage of the extractive metallurgy and cannot be treated commercially. Extractive metallurgy can be hydrometallurgy, pyrometallurgy or electrometallurgy. Hydrometallurgy involves solvents for the metal extraction, whereas pyrometallurgy involves heat. These processes separate the metals from their processed ores and also generate vast amounts of metallurgical wastes, like gaseous emissions, dust, slags, sludges, muds, spent ore and residues (Fig. 2.2).

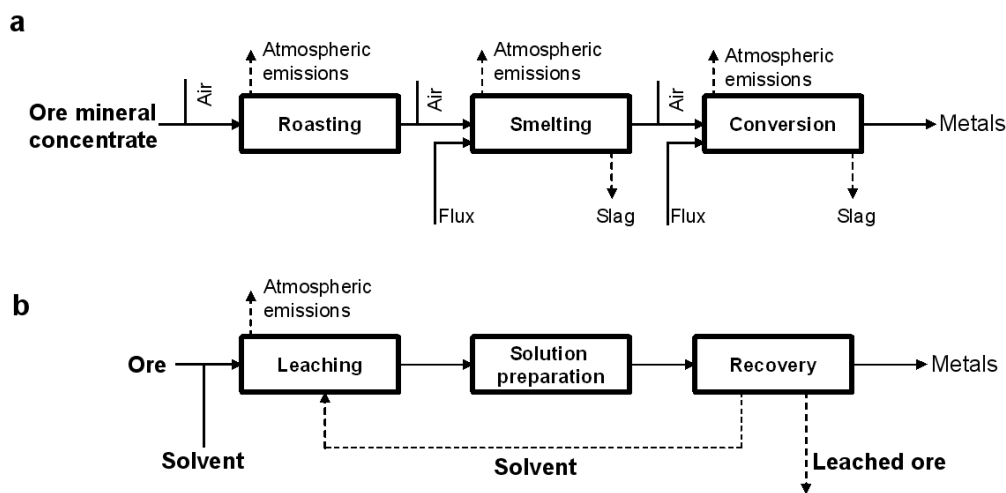


Fig. 2.2. Simplified flow charts of (a) pyrometallurgical and (b) hydrometallurgical operations, in which ore is treated to yield metals accompanied with the generation of wastes (redrawn from Lottermoser, 2010)

Metallurgical wastes contain considerable concentrations of metals, depending on the mineralogy of the ore and geography of the ore mining site. Disposal or storage of these wastes needs to be done carefully because of the adverse environmental impacts such as release of heavy metals by weathering (Gieré et al., 2003; Kierczak et al., 2009), contamination of water bodies (Johnson, 2009), metal incorporation into the food chain (Kachur et al., 2003), formation of efflorescences i.e. metal hydrosulfates as a result of evaporation (Keith et al., 2001; Sánchez España et al., 2005; Romero et al., 2006) or creating acidic environments (Hammarstrom et al., 2005).

2.2.1. Dusts

Flue dusts are fine, metal containing dust particles collected at the gas exhaust of smelters or any other furnace during metallurgical processing. Copper and zinc producing industries are the major sources of dust waste generation. According to Davenport et al. (2002), dusts emanating from copper smelters consist of 20 - 40 mass percent of Cu and can be either recycled with concentrates or can be treated by hydrometallurgy for further metal recovery. Massinaie et al. (2006) reported that these wastes originating from copper industries are mostly rich in chalcocite (Cu_2S), chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) and covellite (CuS).

Similarly, there are metallic dusts generated during the steel making processes like electric arc furnace (EAF) smelters. These EAF dusts are rich in zinc and iron oxides and are generated during the heating and cooling of the smelting processes and collected at the gas cleaning system of scraps (Jha et al., 2001). Electric arc furnaces dusts from steel industries typically contain 19.4% Zn, 24.6% Fe, 4.5% Pb, 0.42% Cu, 0.1% Cd, 2.2% Mn, 1.2% Mg, 0.4% Ca, 0.3% Cr, 1.4% Si and 6.8% Cl (Caravaca et al., 1994).

Blast furnace (BF) dusts are similar to EAF, generated during the wet cleaning of the gases in blast furnace mediated steel production. These emission dusts agglomerate after long-term exposure to the earth's atmosphere because of its inherent moisture content. Elemental analysis revealed that these BF dusts mostly contain iron and carbon in high concentrations. The typical

composition of BF dusts is carbon (~ 30%), Fe₂O₃ (~ 51%), SiO₂ (~ 7%), Al₂O₃ (~3%) and other metals such as Zn, Pb and Mn (Zeydabadi et al., 1997; Das et al., 2002).

2.2.2. Sludges

Sludges are co-products generated during various stages in ferrous and non-ferrous industries. They can be blast furnace sludges (BFS), electric arc furnace sludges (EAFS), converter sludges, basic oxygen furnaces sludges (BOFS) from steel making industries, sludges from plating industries and also sludges from metal producing industries. Steel making industries generate significant quantities of sludge (2-4 tonnes of wastes per tonne of steel (Das et al., 2006)), which consists of approximately 2.5% of Zn and 61% of Fe (Trung et al., 2011). Mansfeldt and Dohrmann (2004) studied the mineralogical and chemical composition of the pig iron making sludges and found that apart from the iron mineral phases magnetite (Fe₃O₄, 3%), hematite (Fe₂O₃, 4%), wuestite (FeO, 2%), they also contain primary and secondary phases of the metals Zn (3%), Pb (1%), Cd (0.01%), and As (0.1). The sludges from the metallurgical industries are also polymetallic, containing significant mass concentrations of Fe 44%, S 28%, As 0.38%, and Zn 0.13% (Hita et al., 2006, 2008). The mineralogical and elemental composition of the metallurgical sludge depends on the nature of the ores. Due to their multi-metallic nature, recycling of this type of waste is not feasible (Bayat et al., 2008).

2.2.3. Residues

The residues can be mainly classified as leach residues and purification residues, based on their generation during the operational processes. Purification residues are produced during the separation of the pure zinc metal from its impurities (for e.g. copper and cobalt) while leach residues are derived during the filtration of the purified acid (mostly sulfuric acid) leached products prior electrolysis. Recovery of metals from plant residues, like zinc plant residues (ZPR), gained importance in recent years. Copper and cobalt are often found in the residues generated at the end of zinc production processes.

There were a few investigations on the extraction of these metals from ZPR. Min et al. (2013) investigated the chemical and mineralogical composition of the leaching residues generated during zinc and lead hydrometallurgical operations. They found that ZPR consists of (mass fractions) 5.35 % Zn, 4.66 % Pb, 0.24 % Cu, 0.15 % Cd, 0.25 % As and 13.54 % Fe. Usually

the presence of zinc ferrites, which is a spinel ($ZnFe_2O_4$), resulting from the desulfurization of iron containing sphalerite ores in the final leach residues make the extraction of metals tedious because of its very stable and insoluble nature.

2.3 Leaching

Leaching is the key unit operation in metallurgical processes. It is the dissolution of metals from their natural ores into a liquid medium. Leaching processes are classified based on the method used for the leaching of metals, i.e. hydrometallurgy (chemicals) or bio-hydrometallurgy (microbial mediated leaching). Different leaching processes and the leaching of metals from various metal bearing solid wastes are discussed in detail below.

2.3.1. Hydrometallurgical processes

Hydrometallurgy is the extraction of metals from resources with the help of aqueous chemicals. Hydrometallurgical processes have a few advantages over pyrometallurgy, as they are more eco-friendly and economic for low-grade metal reserves. A general process flow diagram of hydrometallurgy is illustrated in Fig. 2.3. Hydrometallurgy is a general term which refers to a range of processes, including chemical leaching or mediated by oxidizing agents, higher oxygen partial pressure or microbial activity (National research council, 2002).

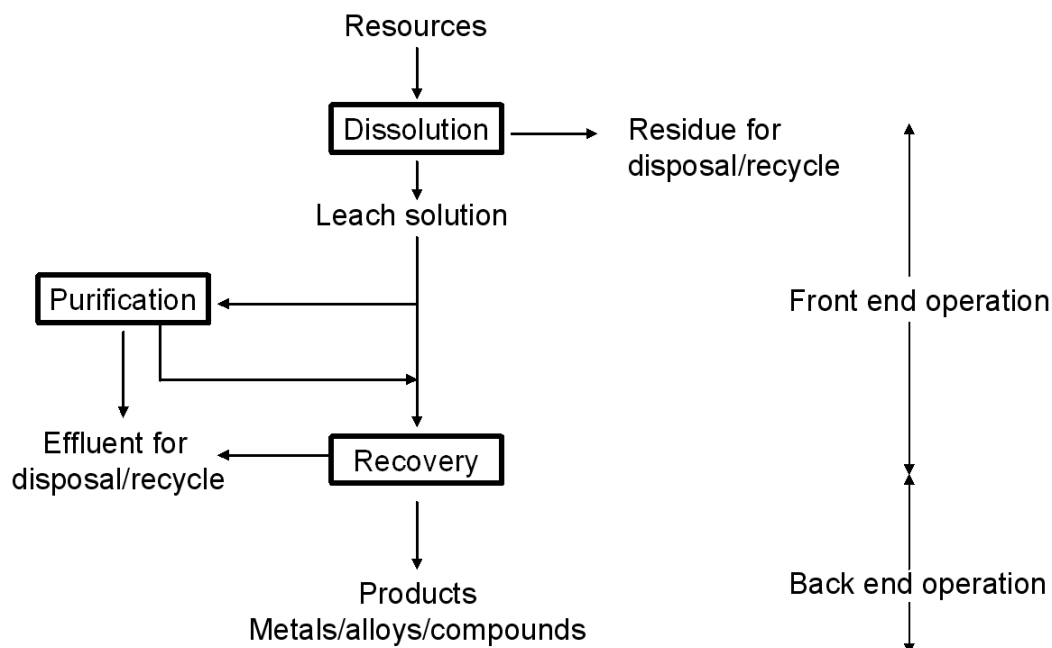


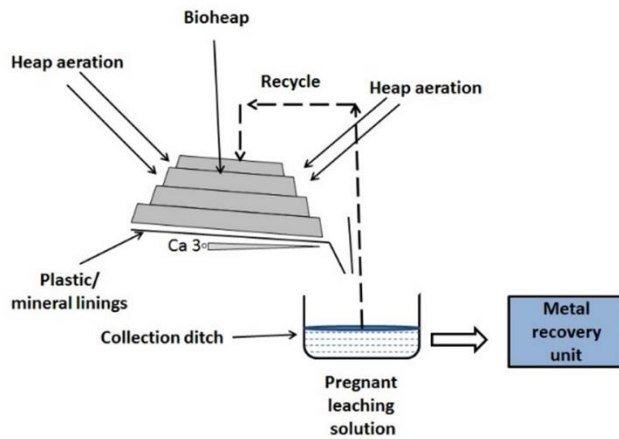
Fig. 2.3. Basic unit processes in hydrometallurgy (redrawn from Gupta, 2006)

Hydrometallurgical processes consist of different steps: (i) leaching of metals from the source and dissolution into the leachate, (ii) separation of the metal loaded leachate from the residues, (iii) recovery of the metals from the leach solution and (iv) regeneration and reuse of the leachate (Ghosh and Ray, 1991). Leaching processes can be done *in situ* (heaps or dumps) or *ex situ* (reactors or vessels). There are various parameters which affect the leaching behaviour of metals from their parent material: (i) pH, (ii) temperature, (iii) concentration of the leaching agent(s), (iv) solid to liquid phase ratio and (v) particle size of the parent material. The efficiency of hydrometallurgical processes is increased by using improved leaching conditions coupled to high pressure leaching and ultra-fine grinding (Malhotra et al., 2009). Selective leaching of metals can also be achieved by adjusting the pH or working at elevated temperatures and pressures (Trefry et al., 1984; National Research Council, 2002; Havlik et al., 2004).

2.3.2. Biohydrometallurgical processes

Biohydrometallurgy is a recent advancement in the mining industry where microorganisms are used to enhance the leaching of metals and biotechnological processes are used for the recovery of the dissolved metals. Biohydrometallurgy is the conversion of insoluble metals in ores (or other sources like metallurgical wastes) to the soluble form with the help of microorganisms. Microbial extraction and recovery of metals like Cu has received considerable attention in the past three decades due to its relative simplicity, eco-friendly operation and low capital requirement when compared to those of the conventional chemical/heat treatment processes (Olson et al., 2003; Watling, 2006; Johnson, 2013). Commercial applications of bioleaching were also reported in many instances (Brierley and Brierley, 1999, 2001; Brierley, 2008, Neale et al., 2011; Gahan et al., 2012). A simplified bioheap leaching process and commercial bioleaching plants are given in Fig. 2.4.

Knowledge and understanding the metal - microbe interactions and the mechanisms of bioleaching is much needed for the effective recovery of metals from metallurgical wastes.



(a)



(b)



(c)



(d)

Fig. 2.4. Bioleaching process and commercial bioheap leaching plants (a) schematic representation of bioheap leaching process, (b) bioleaching plant in Zijinshan copper mine, China (Reinman et al., 2006), (c) bioheapleaching plant in Talvivaara mining company, Finland (Reikkola-Vanhanen, 2010) and (d) bioheapleaching plant in Kasese mine, Uganda (Gahan et al., 2012)

2.3.2.1. Microbe - metal interactions

Bacteria and fungi are able to extract metals from metal contaminated soils and metal wastes. These micro-organisms use one of the processes (Fig. 2.5): (i) non-specific interaction of metal ions with cationic binding sites present outside the cell wall, (ii) specific interactions at the periplasmic sites of the cell wall, (iii) metallo-chemical complex (chemicals secreted by the microbes in the surrounding medium and the metals form a complex) uptake by the cells, (iv)

bioaccumulation, (v) metal precipitation by the microbial metabolites or (vi) metal volatilization (Upadhyay, 2002).

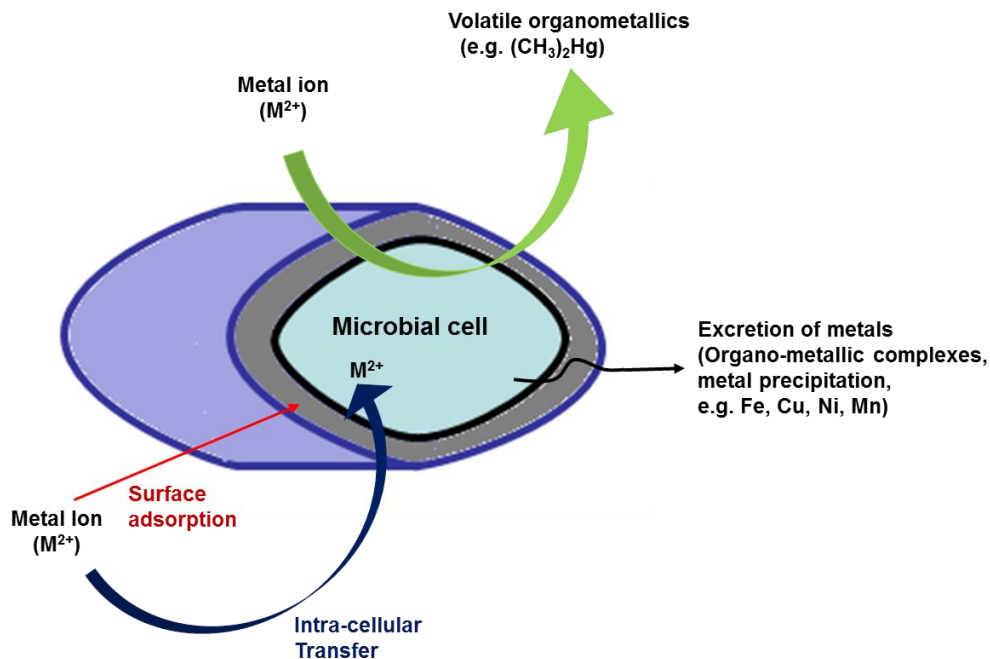


Fig. 2.5. Microbe-metal interactions that can be engineered to develop enhanced bioleaching processes (reproduced from Upadhyay, 2002)

2.3.2.2. Bioleaching

Microbes leach metals via various processes (Fig. 2.6): (i) acidolysis, (ii) redoxolysis, (iii) complexolysis and (iv) bioaccumulation (Schinner and Burgstaller, 1989; Bosshard et al., 1996; Brandl, 2001; Wu and Ting, 2006). Recently, reductive dissolution of oxidized Ni-laterites ores was also reported (Johnson et al., 2013).

The most commonly used genera to catalyze the biooxidation of sulfides and liberate the desired metals into the liquid phase are chemo-litho-autotrophic bacteria oxidizing iron, e.g. *Leptospirillum* spp. (Sand et al., 1992; Falco et al., 2003; Sethurajan et al., 2012), *Ferroplasma* spp. (Edwards et al., 2000; Golyshina et al., 2000) and *Ferrimicrobium* spp. or sulfur, e.g. *Acidithiobacillus* spp. (Kelly and Wood, 2000; Falco et al., 2003), *Thiomonas* spp. (Han et al., 2013) and *Sulfolobus* spp. (Norris et al., 2000). These microbes obtain energy by oxidizing ferrous into ferric ion and elemental sulfur to sulfuric acid (Rawlings, 2005), thereby leach the reduced sulfide minerals. Consequently, the supply of the ferric ion and sulfuric acid for the oxidative dissolution and acidolysis is the role of bacteria.

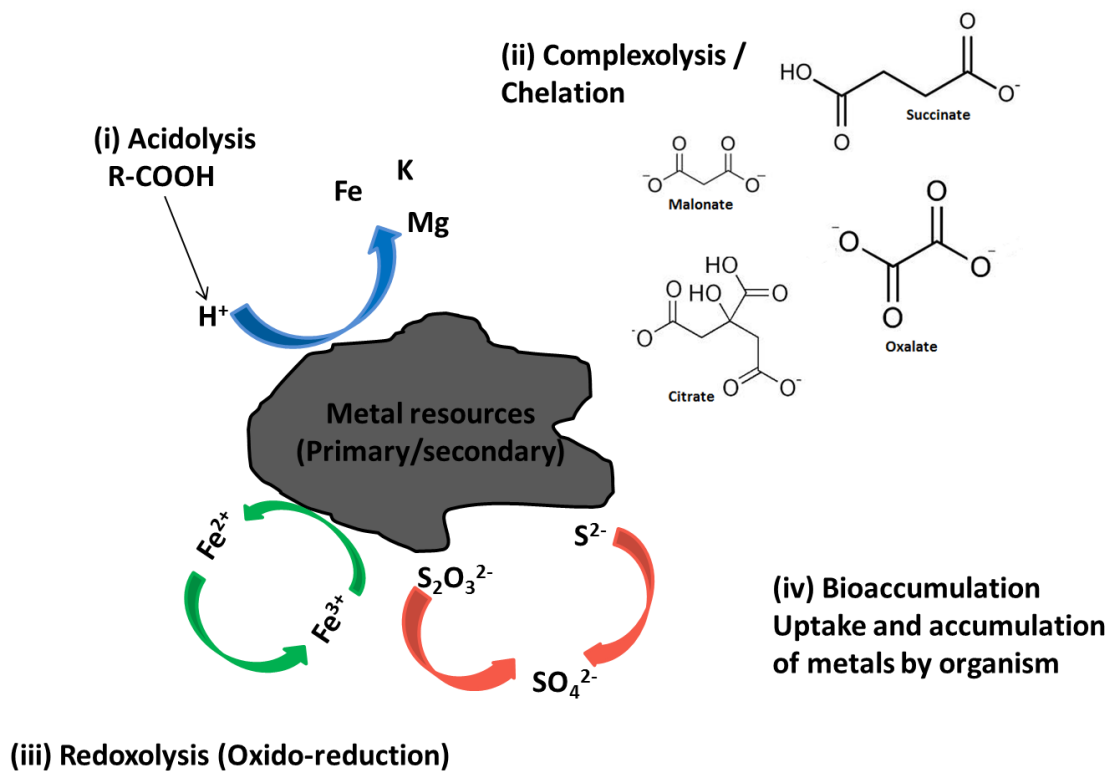
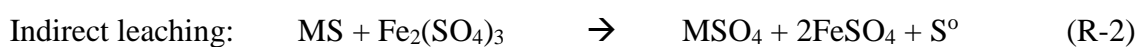
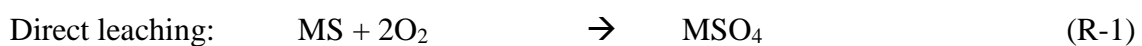


Fig. 2.6. Mechanisms of bioleaching (adapted from Uroz et al., 2009)

The mechanisms by which *Acidithiobacillus ferrooxidans* leach out the metal constituents are (Crundwell 2003): (i) direct bioleaching, (bacteria adhere on the surface of the ores and oxidize the reduced sulfides), (ii) indirect bioleaching, (bacteria oxidize the ferrous ion to ferric ion thereby contribute to the leaching of minerals). This indirect bioleaching by ferric ion can be subdivided into two phenomena: the produced ferric ions will either be released into the bulk solution or inside the layer between bacteria and exopolymeric material and thus leach out minerals.

The generalized reactions (R-1 and R-2) for the bio-oxidation of mineral sulfides leading to (precious) metal leaching are:



Where, M is a bivalent metal.,

Various heterotrophic bacteria, e.g. *Pseudomonas* spp. (Müller et al., 1995; Lingling et al., 2012; Pradhan and Kumar, 2012) and *Bacillus* spp. (Farbiszewska-Kiczma et al., 2004) as well as fungi, e.g. *Aspergillus* spp. (Mulligan et al., 2000; Rao et al., 2002; Mulligan et al., 2004), *Penicillium* spp. (Acharya et al., 2002; Amiri et al., 2011; Ilyas et al., 2013) and *Ganoderma* spp. (Nouren et al., 2011) have also been investigated for their ability to bioleach metals. Mixed cultures of two or more bacteria or indigenous enrichments of microbes from metal contaminated sites were studied for metal solubilization from the ores and have been reported to have a higher efficiency than the pure cultures (Sandstrom and Petersson, 1997; Fu et al., 2008; Plumb et al., 2008).

Fungal bioleaching mechanisms follow mainly acidolysis, i.e. solubilisation of the metals by the acidic dissolution (protonation of oxygen atom) from the parent material (Burgstaller and Schinner, 1993). These fungi produce organic acids like citric, oxalic, malic or gluconic acid (Mulligan et al., 2004; Johnson, 2006). *Aspergillus* spp are the most studied fungi for the bioleaching processes, because of their capacity to produce higher levels of organic acids (Catherine et al., 2004). Acharya et al. (2002) and Sukla (1993) studied *Penicillium* sp. for the bioleaching of valuable metals from low grade ores.

2.3.3. (Bio)hydrometallurgical treatment of wastes from metal industries

2.3.3.1. Dusts

Dusts from the metallurgical industries contain significant amounts of metals. Various researchers used chemical and microbial mediated leaching procedures for the release of heavy metals from these wastes. Different (bio)hydrometallurgical approaches to process these dusts from the metal industry for the leaching of metals were developed (Table 2.2). Cole et al. (1987) and Gabler et al. (1988) studied the possibilities of re-using Zn from Brass smelter flue dust and secondary copper converter dust by sulfuric acid and ammonium carbonate, respectively. The recovered Zn was suitable for electrogalvanizing and the ZnO can be re-fed to the furnace. Vítková et al. (2011) investigated the effect of pH on the leachability of metals from Cu smelter dusts and found that an acidic pH (pH 3) favours the maximum leaching of the metals. As these dusts from the copper industries mainly consist of reduced mineral phases of metals, bioleaching is considered as an eco-friendly approach (Rossi, 1990; Schnell, 1997; Oliazadeh et al., 2005). *Acidithiobacillus* spp. and *Leptospirillum* spp. are the genera widely used for the biological leaching of metals from metallurgical dusts. More than 70% of Zn was extracted by

Thiobacillus ferrooxidans from industrial Fe-Mn alloy dust (Solisio et al., 2002). Mixed populations of iron oxidizing and sulfur oxidizing bacteria were proposed to be more efficient than the pure cultures solely. Bakhtiari et al. (2008a, 2008b, 2011) investigated the leaching efficiency of mixed cultures of *A. ferrooxidans*, *A. thiooxidans* and *L. ferrooxidans* in different bioreactor configurations like continuous stirred tank reactors (CSTR) and air-lift bioreactors (ALBR) from different metal bearing dust samples and reported that a maximum of 90% of Cu was leached within 2 days at lower solid to liquid phase ratios (2.7%) in ALBR configurations.

Table 2.2 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from metallurgical dusts.

Dust type (metal content - %)	Treatment	Leaching yield	Reference
Brass smelter flue dust Zn - 66% Cu - 0.88% Fe - 0.24%	H ₂ SO ₄ leaching	More than 90% of Zn was dissolved by using 0.18 kg L ⁻¹ of H ₂ SO ₄ (pH 4-5, temperature 90°C) in 1 hour. Leached Zn used for electrogalvanizing	Cole et al. (1987)
Secondary Copper Converter Dust Zn - 40.4% Cu - 0.86% Fe - 0.16% Pb - 16%	(NH ₄) ₂ CO ₃ and NH ₄ OH leaching	66% of Zn was dissolved by using 117 mg L ⁻¹ of NH ₃ , 94 g L ⁻¹ of CO ₂ at room temperature, in 15 minutes leaching. Reusable ZnO and metal values from secondary copper smelter flue dusts were achieved	Gabler et al. (1988)
Cu smelter dust Zn - 0.22 % Cu - 27.2% Fe - 19.3% Pb - 0.21%	CEN/TS 14997:2006 protocol	80% of the total Cd, 30 – 40% Cu, Zn and Co, 17% Ni and only 2% Pb were released at pH 3 (HNO ₃) in 48 hours	Vítková et al. (2011)
Fe-Mn alloy industrial dust Zn - 5.5% Cu - 0.052% Pb - 0.29%	Bioleaching by <i>Thiobacillus ferrooxidans</i>	Maximum of 76% of Zn recovered, when the conditions were: 1% pulp density, pH 2, 250 rpm, and temperature 30°C	Solisio et al. (2002)
Copper smelter flue dust	Mixed mesophilic (<i>A. ferrooxidans</i> , <i>A. thiooxidans</i> and <i>L.</i>	Maximum 85.5% of Cu after 23 days at 2.7% pulp density	Bakhtiari et al. (2010)

Zn - 1.67% Cu - 22.2% Fe - 5.9% Pb - 1.54%	<i>ferrooxidans</i>) bioleaching in CSTR		
Flue dust of the Sarcheshmeh copper smelter Cu - 35.8% Fe - 15.3%	Mixed culture of <i>A. ferrooxidans</i> , <i>A. thiooxidans</i> and <i>L. ferrooxidans</i> airlift bioreactors	Maximum 90% of Cu at 2.7% pulp density after 2 days	Bakhtiari et al. (2008)
Copper flue dust Cu - 35.8% Fe - 15.3%	<i>A. ferrooxidans</i> , <i>Acidithiobacillus thiooxidans</i> and <i>Leptospirillum</i> mixed cultures in CSTR's	Maximum 89% of Cu at 2% pulp density after 2.7 days	Bakhtiari et al. (2008)
Copper mining flue dust Cu - 29.15% Fe - 22.23%	Mixed culture of <i>A. ferrooxidans</i> and <i>A. thiooxidans</i> in an agitated bioreactor	Cu recovery was 87% after 22 days in shake flask and 91% in bioreactor after 6.5 days	Massinaie et al. (2006)
Copper mining flue dust Cu - 29.15% Fe - 22.23%	Mixed culture of <i>A. ferrooxidans</i> and <i>A. thiooxidans</i>	Maximum 87% of Cu after 22 days at 5% pulp density	Oliazadeh et al. (2006)

The bioleaching efficiency of copper from smelter dusts (combined with floatation concentrate) was higher in the stirred tank reactors than in airlift bioreactors (Vakylabad et al., 2012) and thermophilic lithotrophs were slightly better bioleaching bacteria than mesophilic bacteria, although the impact of temperature was not very high as observed in the case of primary (chalcopyrite) ores (Vakylabad, 2011; Vakylabad et al., 2012).

Alike Cu dusts, there are numerous hydrometallurgical processes developed for the utilization of EAF dusts. Conventionally these dusts are treated by sulfuric acid (Duyvesteyn et al., 1979; Pearson, 1981; Duyvesteyn et al., 1986; Cruells et al., 1992). The efficiency of acidic leaching is greatly affected by the iron/zinc ratio and the presence of halogens, as these will interfere during the electrolysis (Havlik et al., 2004; Havlik et al., 2006). Alkaline leaching is an alternative strategy to overcome these problems. Xia and Picklesi (2000) proposed microwave assisted caustic leaching for the recovery of zinc from EAF dust and were able to extract more

than 90% of Zn at 8 M NaOH at 117 °C. Dutra et al. (2006) demonstrated that 6 M NaOH at 90°C recovered 74% of Zn within 4 hours from EAF dusts.

2.3.3.2. Sludges

Different hydrometallurgical approaches to process metallurgical sludges for the effective and economic extraction of metals have been developed (Table 2.3). The use of hydrometallurgical operations for the effective extraction of Zn and Pb from BFS was reported by Van Herck et al. (2000) who focused on the effect of the pH and redox potential., Silva et al. (2005) investigated various factors (pulp density, stirring, concentration of leachant and particle size) affecting the leaching of metals from galvanic sludges and stated that 1 M of H₂SO₄ can leach 88.6% Cu, 98.0% Ni and 99.2% Zn at room temperature in 24 hours. Trung et al. (2011) reported that at high temperature (80°C), approximately 70% of Zn can be leached within 15 minutes by using 1 M H₂SO₄. Vereš et al. (2012) investigated the extraction of Zn from blast furnace sludge by microwave-assisted procedures. Cantarino et al. (2012) reported the selective leaching of zinc from basic oxygen furnace sludge with a three step leaching procedure (5 M NaOH) coupled to a thermal treatment and extracted 95% of Zn.

Table 2.3 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from metallurgical sludges.

Sludge type (metal content - %)	Treatment	Leaching yield	Reference
Basic oxygen furnace sludge Zn - 1.35% Fe - 55.9% Pb - 0.65%	H ₂ SO ₄ leaching	81% of Zn recovered from the sludge (particle size >38 µm) by sulfuric acid (pH 2) and 18% of Fe recovered with H ₂ SO ₄ (at pH 2) within 15 minutes	Kelebek et al. (2004)
Basic oxygen furnace sludge Zn - 2.74% Cu - 0.1% Fe - 47.7%	H ₂ SO ₄ leaching	70% of Zn leached by 1 M H ₂ SO ₄ at 80°C within 15 minutes	Trung et al. (2011)

<p>Basic oxygen furnace sludge</p> <p>Zn - 4.37% Fe - 50.65% Pb - 0.068% Cr - 0.023% Cd - <0.02%</p>	<p>5 M NaOH</p>	<p>Approximately 95% of the zinc was selectively removed after 3 leaching steps of the treated sludge with NaOH, at 400 °C</p>	<p>Cantarino et al. (2012)</p>
<p>Converter sludge from steel production</p> <p>Zn - 1.7% Cu - 0.02% Fe - 60.2% Pb - 0.09%</p>	<p>Bioleaching with mixed culture of <i>Acidithiobacillus</i> spp. and <i>Leptospirillum</i> spp.</p>	<p>100% Zn leached after 79 days at pH 0.5</p>	<p>Vestola et al. (2010)</p>
<p>Sludge from Ni/Cr plating plant</p> <p>Zn - 2.96% Cu - 4.2% Fe - 1.53% Pb - 0.36%</p>	<p>Sulfuric acid and ammoniacal leaching</p>	<p>88.6% Cu and 99.2% Zn by acid leaching</p>	<p>Silva et al. (2005)</p>
<p>Pyritic sludge – (Aznalcóllar, Spain)</p> <p>Zn - 0.132% Fe - 44%</p>	<p>Bioleaching with iron oxidizing bacteria (<i>Acidithiobacillus ferrooxidans</i>, <i>Acidithiobacillus caldus</i>), and archaea (<i>Sulfolobus metallicus</i>)</p>	<p>Approximately 90% of total Zn was recovered in 10 days, pH 2, temperature 65°C by <i>Sulfolobus metallicus</i></p>	<p>Hita et al. (2008)</p>

Bioleaching of a steel plant sludge using *Acidithiobacillus ferrooxidans* was studied by Bayat et al. (2009). *Acidithiobacillus ferrooxidans* extracted comparatively less metals (35% of Zn and 37% of Fe), which might be due to the oxidized mineral phases present in the metallurgical sludge (Fe₃O₄, Fe₂O₃). Metallurgical sludges containing sulfidic minerals can be treated by microbial processing by oxidative dissolution, as acidic leaching involves concentrated acids and high temperature and is thus expensive. Hita et al. (2008) reported the possibility of bacterial leaching (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus caldus*, and *Sulfolobus metallicus*) of Fe, Zn and As from pyritic metallurgical sludge.

2.3.3.3. Residues

Hydrometallurgical extraction of zinc, especially from sulfidic ores results in the generation of leach and purification residues. Different pyrometallurgical and hydrometallurgical leaching processes have been developed for the extraction of metals from these metallurgical residues (Table 2.4). Ngenda et al. (2009) proposed a new thermal treatment coupled to a high concentrated acid leaching for the extraction of Zn from the zinc plant residues (ZPR) obtained from the Kolwezi Zinc Plant (Republic of Congo). Safarzadeh et al. (2009) extracted almost 99% of Zn from the zinc residues by 1.7 M sulfuric acid. Lu et al. (2014) demonstrated that 99% of Zn, Cd and Co could be extracted from purification residues by 48 g L⁻¹ sulfuric acid.

Table 2.4 Different (bio)hydrometallurgical approaches proposed for the leaching of heavy metals from the metallurgical residues

Residue type (metal content - %)	Treatment	Leaching yield	Reference
Zinc plant residues - Kolwezi Zinc Plant Zn - 19.47% Cu - 2.7% Pb - 2.1% Fe - 26.6%	Thermal treatment coupled with high concentrated acid leaching	98.7% Zn, 99.9% Cu, and 6.4% Fe obtained after of series of treatment (I. 48% H ₂ SO ₄ , II. Thermal treatment at 750°C for 2 hours and III. H ₂ O leaching at 40 °C)	Ngenda et al. (2009)
Zinc plant residues - Kolwezi Zinc Plant Zn - 32.48% Cu - 0.075% Fe - 0.16% Pb - 0.39%	Acid leaching	More than 90% of Zn and Cd and 80% of Ni extracted at conditions maintained in 1.7 M sulfuric acid concentration, pulp density of 1/8, 400 rpm and 25 °C temperature	Safarzadeh et al. (2009)
Zinc plant residues Zn - 11.3% Fe - 8.3% Pb - 24.6%	Combination of pyrometallurgical (roasting) and hydrometallurgical processes (sulfuric acid, water and NaCl)	86% Zn was extracted after roasting at 200 °C for 30 minutes, 1:1 weight ratio of H ₂ SO ₄ : ZPR and leached at 25 °C for 60 minutes and liquid/solid ratio 20%	Turan et al. (2004)
Neutral leach residue along with zinc ferrite	Series of hydrometallurgical process includes leaching, cementation and refining	80% Zn, 80% Ag and 90% Pb were extracted after series of processes like sulfuric acid leaching (200 g L ⁻¹ H ₂ SO ₄ , 80 °C, 2 Hours), followed by brine leaching (300 g L ⁻¹ NaCl, pH 1.5 to 2.0,	Raghavan et al. (1998)

		30 minutes) and by cementation and refining.	
Zinc leach residue Zn - 9.87% Fe - 4.93%	Oxidative leaching and non-oxidative leaching	95% of zinc and 72% of Fe was recovered at pH 1.5, pulp density 1/7, temperature 75 °C and contact time 2 hours (non-oxidative leaching)	Alizadeh et al. (2011)
Zinc leaching residue Zn - 19.57% Fe - 23.91% Pb - 4.35%	Combination of reduction roasting and acid leaching	More than 60% of Zn recovered at 10% of pulp density by 90 g L ⁻¹ H ₂ SO ₄ at 35 °C and leaching time 1 hour	Yan et al. (2014)
Jarosite residue from zinc hydrometallurgy Zn - 8.97% Cu - 0.24% Fe - 23.1% Pb - 4.84%	Hydrometallurgical leaching	More than 95% of Zn, Pb, Cu, Cd and Ag at the end of leaching by NH ₄ Cl and 94% of As and 73% Si leach residue by 30 wt% NaOH	Ju et al. (2011)
Zinc plant residues Zn - 12.43% Fe - 6.27% Pb - 15.51%	Acid leaching	72% of Zn extracted at 20% of pulp density by 150 g L ⁻¹ H ₂ SO ₄ at 95 °C and leaching time 2 hours	Ruşen et al. (2008)
Zinc purification residue Zn - 29.1% Cu - 24.6% Cd - 2.62% Co - 0.39%	Acid leaching	More than 99% of Zn, Cd and Co and 58% of Cu extracted at 25% of pulp density by 48 g L ⁻¹ H ₂ SO ₄ at 20 °C and leaching time 1 hour	Lu et al. (2014)

The metal release kinetics follow the shrinking core model for the extraction of metals from ZPR (Safarzadeh et al., 2009, 2011). They propose that the addition of sulfuric acid, particle size and temperature and phenol dosage played an important role in the reductive leaching of manganese and cobalt. In some cases, e.g. residue from a Zn metallurgical plant in Çinko-Kurşun metal industry (Turkey), the residues obtained during the hydrometallurgical extraction of Zn with concentrated sulfuric acid solution, contained higher levels of Pb and Cd. Turan et al. (2004) and Yan et al. (2014) studied metallic residues from a zinc–lead plant and proposed a combination of pyrometallurgical (roasting) and hydrometallurgical (sulfuric acid, water and NaCl) processes for the extraction of Zn and Pb from these residues. Rusan et al. (2008) reported a similar hydrometallurgical extraction process for Zn and brine leaching for Pb extraction.

2.4. Recovery of metals from metallurgical wastes leachates

After the leaching of the metals with acids or microorganisms from the metallurgical wastes, the metals are distributed in the leach solution, simply referred to as leachate. Recovery of pure metals from the leachates is extremely important as it is the final and critical stage. Many strategies have been developed and applied for the extraction of metals from the leachates, with solvent extraction, precipitation, electrowinning and (bio)sorption as the most commonly applied methodologies. The established metal recovery strategies are overviewed and discussed below (Table 2.5). Each of these methods has advantages and disadvantages, so that sometimes a combination of two or three recovery techniques is required to achieve higher metal recovery efficiencies. However, the recovery of metals from metallurgical waste leachates is only in its infancy and requires lots of research and development at laboratory and pilot scale for further commercial applications.

Table 2.5 Different techniques used for the recovery of metals from metallurgical waste leachates.

Source (metal content - g L ⁻¹)	Treatment	Recovery yield	Reference
Copper converter flue dust leachates Cu - 4.5 Fe - 1.8	Solvent Extraction by LIX 860 or MOC-55TD in Iberfluid	More than 70% of Cu recovered	Martin et al. (2003)
Zinc plant residues leachates	Solvent extraction by D ₂ EHPA	More than 90% of indium was recovered from the leachates	Koleini et al. (2010)
Zinc leach residue leachates Zn - 28.80 Pb - 0.011 Fe - 0.21	Solvent extraction by D ₂ EHPA	99% of Zn was extracted by 40% of D ₂ EHPA.	Vahidi et al. (2009)
Electric arc furnace dust leachates Zn - 45.60 Pb - 3.60 Fe - 0.06 Cu - 0.06	Electrowinning	1 kg of pure zinc recovered from the Pb free leachate by using 2.4–2.7 kWh	Youcai and Stanforth (2000)
Water-jacket furnace flue dusts leachates Zn - 35 Fe - 0.05 Cu - 0.00013	Electrowinning	More than 94% of Zn is hydrolyzed at the expense of 3.5 kWh/kg energy	Mukongo et al. (2009)

Electric arc furnace dust leachates Zn - 14.0 Fe - 13.0 Cu - 0.3	Electrowinning	92% of Zn was electrolyzed	Tsakiridis et al. (2010)
Copper flue dusts leachates Zn - 35-40 Pb - 6-8 Al - 0.3-0.8 Cu - 0.2-0.5	Electrowinning	88% to 92% of Zn was electrolyzed	Qiang et al. (2014)
EAF dusts leachates Zn - 58	Carbonate precipitation	58% of Zn was precipitated at 10°C and 700 rpm.	Török et al. (2013)
EAF dust alkaline leachates Leachate 1 - 26.95 of Zn Leachate 2 - 45 of Zn Leachate 3 - 50.85 of Zn Approximately 3 of Pb in all the samples	Sulfide precipitation	More than 90% of Zn recovered from the Pb free solution	Youcai and Stanforth (2001)
EAF dust alkaline leachates Zn - 50 Pb - 2 Fe - 0.05	Sulfide precipitation	More than 90% of Zn recovered from the leachates	Lenz and Martins (2007)

2.4.1. Metal recovery by precipitation

Precipitation is a conventional methodology developed for the removal and recovery of metals from metal bearing solutions. Precipitation of metals from metal contaminated aqueous solutions, like acid mine drainage, industrial wastewaters or leaching solutions, can be achieved by the formation of their respective (i) sulfide, (ii) hydroxide and sometimes (iii) carbonate salts (Manahan, 1990). Few metals like arsenic can also be co-precipitated during flocculation with the salts of iron and aluminium. Recovery efficiencies of the metals by precipitation highly depend on the metal concentrations in the solution and also on the system pH. The major disadvantages of precipitation processes are the high requirements of chemicals to adjust the pH and the generation of a not well settling and dewaterable sludge containing toxic compounds (Ahalya et al., 2003).

Metal precipitation occurs when the concentration of ions in solution exceeds the solubility product (Wang et al., 2005), and can be induced by changes in the ionic equilibrium of the

system with the addition of the reaction products (either metal or sulfide/hydroxide). Precipitation of metals consists of various stages like (i) nucleation, (ii) growth of nucleus, and (iii) aggregation or crystallization (Fig. 2.7) (Benning and Waychunas, 2007). In some cases, certain chemicals can induce the precipitation (precipitating agents) and subsequent crystal formation (crystallisation nuclei) (Wang et al., 2005). This process is distinctly different from coagulation and flocculation.

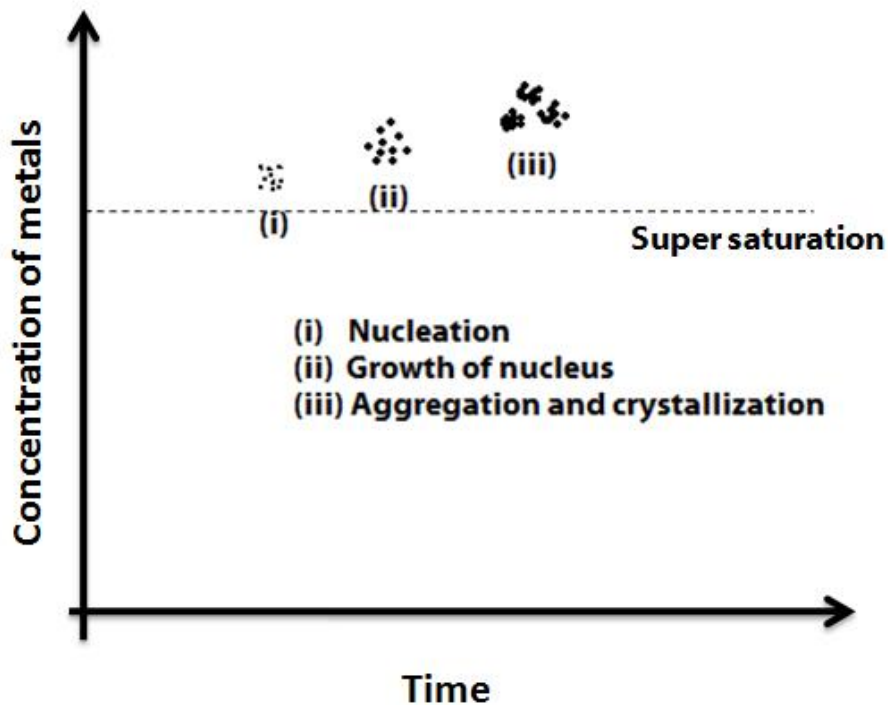


Fig. 2.7. Various stages in the recovery of metals by precipitation

2.4.1.1. Hydroxide precipitation

Sodium hydroxide (NaOH) and lime or hydrated lime (Ca(OH)₂) are the commonly applied chemicals for the precipitation of metal hydroxides. A generalised equation for the metal hydroxide precipitation can be written as:



where M is a divalent metal ion.

A major disadvantage of this process is the solubility of the precipitated metal hydroxides, when the pH is not optimum: a soluble metal complex ($M(OH)^+$) will be formed when altering the pH.

2.4.1.2. Carbonate precipitation

Carbonate precipitation is also used to precipitate metals as metal carbonates, in which straight precipitation by chemicals such as calcium carbonate is used or the conversion of hydroxides to carbonates is applied for the precipitation of metals (Wang et al., 2005). Carbonate precipitation can also be applied in combination with hydroxide precipitation. Operation at low pH, faster settling and good metal recovery are the merits of carbonate precipitation (Tunay et al., 2004).

Török et al. (2013) studied the precipitation of zinc from the EAF dusts ammoniacal leach liquors by using CO_2 (Table 2.5). The tested EAF dusts contained franklinite (49.5%), magnetite (0.5%) and zincite (29%) as the major mineral phases and these dusts were leached by ammonia and ammonium carbonate to dissolve zinc. These leachates and model synthetic solutions were studied for the precipitation of zinc carbonate by using gaseous CO_2 . 58% of Zn was precipitated from the leach liquors at 5 L min^{-1} , 700 rpm and $10\text{ }^\circ\text{C}$. The recovery of Zn from synthetic solutions was comparatively poorer (37%) and it was proposed that co-precipitation of Fe and Pb from the leachates might help in enhancing the recovery of Zn from the solutions.

2.4.1.3. Chemical sulfide precipitation

Ferrous sulfide (FeS), calcium sulfide (CaS), sodium sulfide (Na_2S), sodium hydrosulfide ($NaHS$), ammonium sulfide ($(NH_4)_2S$) and hydrogen sulfide (H_2S) are the major chemicals used for metal sulfide precipitation (MSP). MSP has various advantages over the other precipitation methods, including that metal sulfide precipitates are less soluble, reaction rates faster, settling properties better and sulfide precipitates can be combined with ores in metallurgical processes (Lewis, 2010). In addition, MSP also allows precipitating metals selectively (Sampaio et al., 2009, 2010) and can achieve extremely low (ppb range) residual metal concentrations (Kim et al., 1983). The solubility products of different metal sulfides were studied by Sampaio et al. (2009), who found the $\log K_{SP}$ values for metals such as Cu (I), Cu (II) and Zn (II) to be 48.0,

35.1, and 23.8, respectively. The operational pH (Fig. 2.8) plays an important role in the precipitation of metal sulfides, as various metal sulfides can solubilize as a function of pH (Lewis, 2010). The sulfide concentration is the other key factor in MSP (Villa-Gomez et al., 2012), if it exceeds or depletes either sulfides or metals will remain in the leachate solution (Veeken et al., 2003).

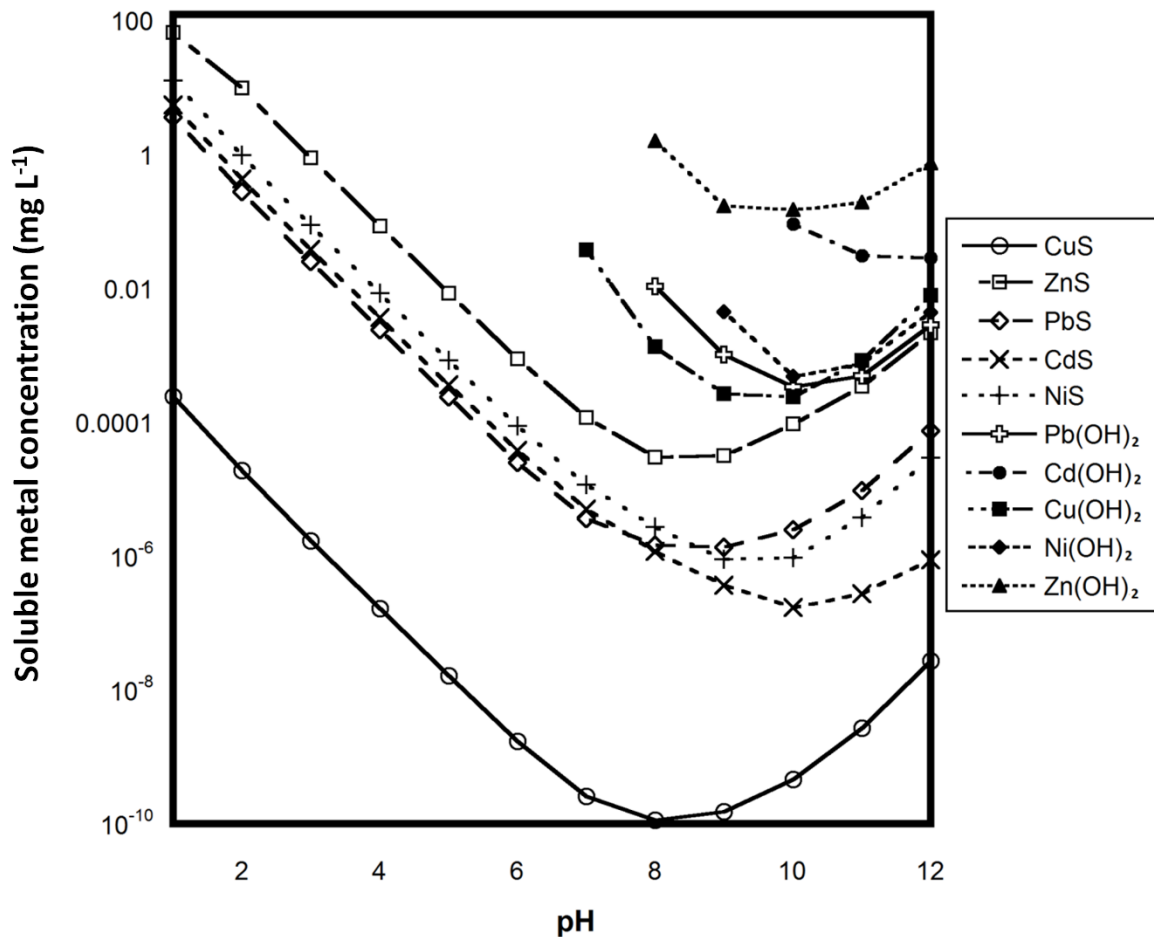


Fig. 2.8. pH dependence of metal sulfide and metal hydroxide solubilities (resimulated from Lewis, 2010)

Metal recovery by MSP has various barriers to cross such as (i) the formation of poly-sulfides due to the poor mixing of supplied sulfides, which results in excessive consumption of sulfide and low metal recovery and (ii) the low solubility of metal sulfides induces supersaturation conditions in the solution, which results in the formation of fine particles with poor solid-liquid separation (Lewis and Van Hille, 2006). By optimizing the operating pH, polysulfide formation can be minimized, while the metal recovery efficiency can be improved (Mokone et al., 2009).

Lewis and Van Hille (2006) proposed that a gaseous hydrogen sulfide source could decrease the level of supersaturation and thus control the formation of fine particles.

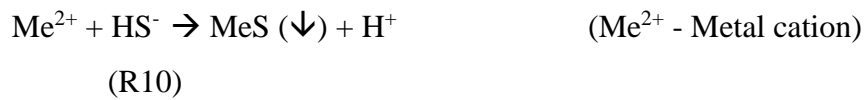
Youcai and Stanforth (2001) investigated the sulfide precipitation of EAF dusts alkaline leachates (Table 2.5), which contained 14.4 g L⁻¹ Zn, 2.98 g L⁻¹ Pb, 1 g L⁻¹ Al, and 0.05 g L⁻¹ Fe. These metals were very stable and did not precipitate, even after several months. They proposed that sodium sulfide was a better precipitant than phosphates, sulfates and carbonates. They were able to selectively precipitate lead with a molar ratio 1.5 – 1.7 and then the zinc precipitated in the lead free solution. Lenz and Martins (2007) studied the selective chemical precipitation of lead and Zn (Table 2.5) from EAF dust alkaline leachates. EAF dusts were leached after a series of steps including hydrolysis and alkaline leaching (NaOH). The final leachates contained various metals and the concentrations were 50 g L⁻¹ zinc, 2 g L⁻¹ lead, 1 g L⁻¹ Al and 0.05 g L⁻¹ Fe. Sodium sulfide with a 2.0 (w/w) and 3.0 (w/w) weight ratio could achieve almost complete precipitation of Pb in the leachates and later Zn was selectively precipitated by sodium sulfide (in the Pb free solution). According to Youcai and Stanforth (2001) chemical precipitants such as phosphates, sulfates and carbonates are less effective in the alkaline medium than in neutral media. Metal phosphates and metal carbonates are readily soluble at alkaline pH.

2.4.1.4. Biogenic sulfides precipitation

Sulfate reducing bacteria (SRB) are prokaryotes which utilize sulfate and other oxidized sulfur compounds as their terminal electron acceptor (Jorgensen, 1982). These anaerobic bacteria have not only assimilatory sulfate reduction (which synthesize sulfur compounds by reducing sulfates), but also dissimilatory sulfate reduction in which the sulfates are reduced to sulfides in the absence of molecular oxygen (Barton and Hamilton, 2007). Most of the metal wastes (solid wastes or wastewaters) contain significant amount of sulfates.

SRBs can use simple organic compounds as electron donors and sulfate as the terminal electron acceptor, and produce sulfide which can be used for MSP. The following reactions illustrate the process:

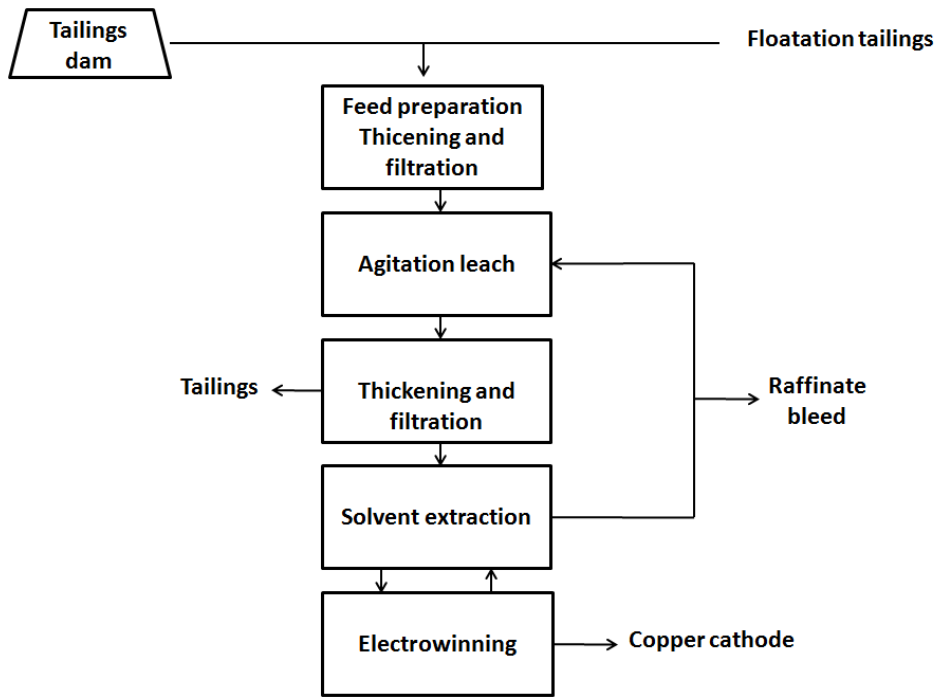




Metal sulfide precipitation by SRB occurs in two stages: (1) biological hydrogen sulfide production by SRB and (2) metal sulfide precipitation by the biologically produced H₂S. MSP has been reported for the successful recovery of pure metals from various sources like laterite pressure leaching solution (Zhang and Cheng, 2007), bioleaching solution from nickel pyrite ore (Cao et al., 2009), industrial wastewater (Kosińska and Miśkiewicz, 2012), and also various other sources (Lewis, 2010). The effect of the sulfide concentration and other macro-nutrients on MSP (Villa-Gomez et al., 2011, 2012) and the morphological characteristics of the metal sulfides precipitated were reported using inverse fluidised bed reactors (Villa-Gomez et al., 2014). This technology has been applied at full scale to treat wastewaters containing low metal concentrations ($\mu\text{g L}^{-1}$ - 0.1 g L^{-1}), but not yet to treat metal bearing solid waste leachates (metal concentrations $> 1 \text{ g L}^{-1}$) at full scale.

2.4.2. Solvent extraction

Solvent extraction (SX), also referred to as liquid-liquid distribution, requires two liquid phases that are completely immiscible with each other. The distribution of the solute between the phases greatly depends on the interaction of the solute with the aqueous and organic phases (Choppin and Morgenstern, 2000). Solvent extraction has been commercially applied to the RLE (Roasting-Leach-Electrowinning technology) liquors. Solvent extraction and electrowinning are often integrated in the commercial hydrometallurgical plants to improve the metal recovery efficiency. Prominent developments in the leaching and recovery of metals through solvent extraction and electrowinning were overviewed by Domic (2007). A simplified flow sheet of the unit operations applied in the metallurgical industry (Fig. 2.9a) and a commercial solvent extraction plant (Fig. 2.9b) are depicted below.



(a)



(b)

Fig. 2.9. (a) Simplified flowsheet of the leaching and metal recovery by solvent extraction - electrowinning plant at Konkola Copper Mines, Zambia (Sole et al., 2005) and (b) solvent extraction plant Morenci, Arizona (Marsden, 2006)

SX includes three steps to achieve the recovery of pure metals: extraction, stripping and reduction (Fig. 2.10). The major merits of the solvent extraction procedure are: (i) low energy consumption and (ii) regeneration of the solvent.

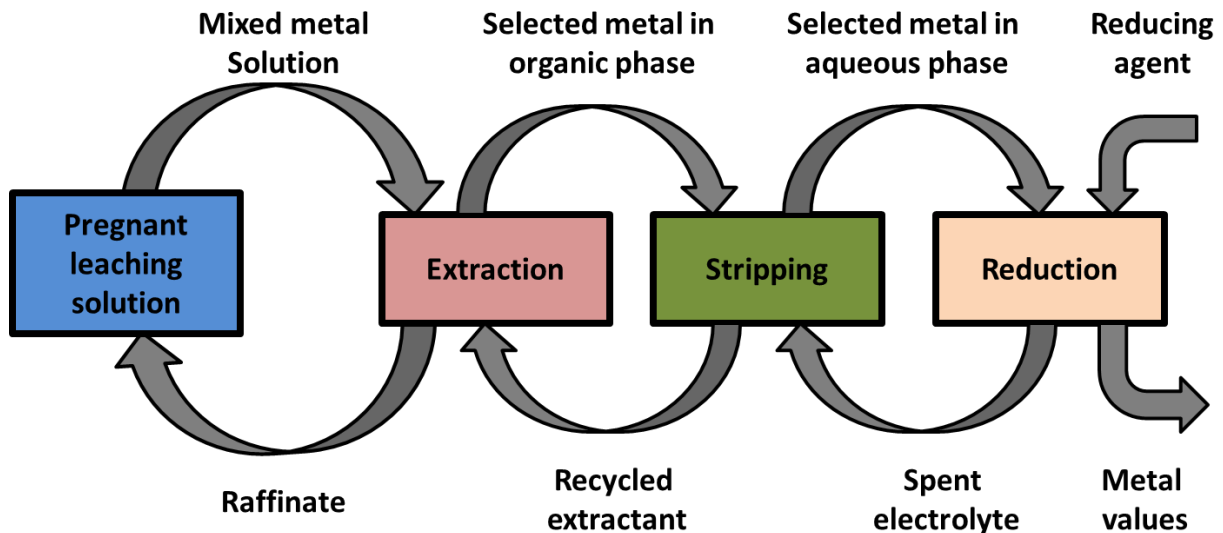


Fig. 2.10. Flow sheet of recovery of metals by solvent extraction (redrawn from Wilson et al., 2014)

Solvent extraction has been recently applied to many waste materials like galvanic sludge (Silva et al., 2005), industrial effluents (Mansur, 2011), fly ashes (Karlfeldt et al., 2012) for the extraction of Zn, Cu, In and even for rare earths (Xie et al., 2014). Martín et al. (2003) investigated the extraction of copper from converter flue dust by the combination of acid leaching and solvent extraction procedures (Table 2.5). The dust sample's mineralogical characterization reveals that they contain 30 wt % of metallic copper (cuprite (Cu_2O)), chalcocite ($\text{Cu}_{1.96}\text{S}$) and 4.5 wt% of Fe (maghemite ($\gamma\text{-Fe}_2\text{O}_3$)). Traces of As (0.18 wt %) and Mo (0.09 wt %) were also identified. Sulfuric acid was used as the leachant and a maximum of 2500 ppm of Cu was leached at 25 °C with 50 g L⁻¹ of sulfuric acid. LIX 860 or MOC-55TD was used to recover the Cu from the acidic leachate. These solvents successfully extracted the maximum of metals at the aqueous/organic phase ratio 4.7 at pH 0.5 (Martin et al., 2003).

Vahidi et al. (2009) studied the recovery of zinc by solvent extraction from the roast leach residues by using di-2-ethylhexyl phosphoric acid (D₂EHPA) (Table 2.5). They were able to extract all the zinc from the leach solution with 20% w/w D₂EHPA in the kerosene organic phase (ratio 1:1) at pH 2.5. They found that the addition of tri-butyl phosphate (TBP) (5%) or

Na_2SO_4 (0.2 M) enhanced the zinc recovery to the maximum. Interestingly, they found that none of the parameters aqueous organic phase ratio, TBP or Na_2SO_4 had a significant effect on the zinc recovery above pH 2.5 and thus the pH plays a key role in the extraction of Zn by D_2EHPA . Similarly, Koleini et al. (2010) recovered 90% of indium from the zinc plant residues using the D_2EHPA solvent extraction method. Thus, solvent extraction can also be successfully applied for the recovery of heavy metals from metallurgical leachates.

2.4.3. Electrowinning

Electrowinning (EW) is one of the successful methodologies that can be applied to recover metals from aqueous solutions. Commercial implementations of the EW in combination with SX are often exploited by the industries. Figure 2.11 shows a commercial electrowinning facility operated at Bagdad, Arizona.



(a)



(b)

Fig. 2.11.(a) Solution extraction and electrowinning plant and (b) Direct copper electrowinning facility, Bagdad (Arizona, USA) (Marsden, 2006)

The design of EW processes consists of a chamber, a cathode (negatively charged electrode), an anode (positively charged electrode) and also an electrolytic solution (Fig. 2.12). The mechanism of EW is simple by applying an electric current to the electrolytic solution (eluate), thereby migrating and depositing the dissolved positively charged metals ions on the negatively charged cathode through the electrons passage to the anode. Unlike the other recovery methods, separation of elemental metal ions is the major advantage of this process. Other highlights of EW processes are no sludge production, no hazardous chemical usage and low capital costs (Kundo et al., 1991). Though EW is a promising recovery technology, recovery of pure metals from multi-metallic solutions is tedious as non-target metals can greatly influence the metal recovery, e.g. copper influences gold extraction (Steyn and Sandenbergh, 2004) and lead affects the recovery of zinc (Youcai and Stanforth, 2001).

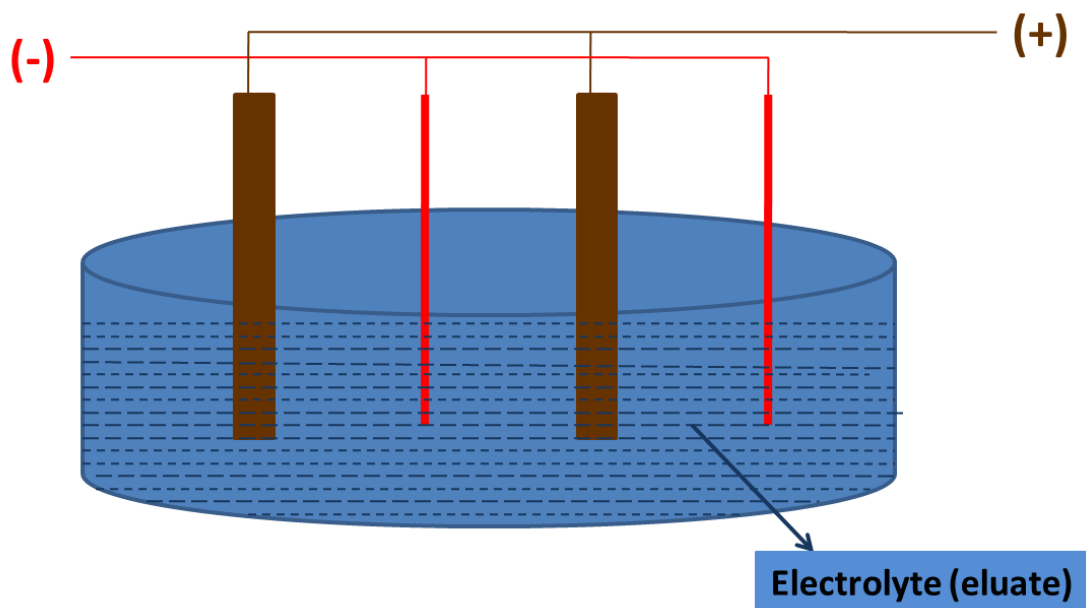


Fig. 2.12. A simple electrolytic cell used for the recovery of metals by electrowinning

The EW technology was successfully applied to recover metals from leachates of industrial wastes such as electronic scraps and fly ashes (Jha et al., 2001; Vegliò et al., 2003; Cui and Zhang, 2008). EW extraction is more cost effective (especially for the recovery of Zn) in alkaline solutions than in acidic solutions because of their high-energy requirements (St-Pierre and Piron, 1986, 1990). Youcai and Stanforth (2000) worked on the separation of pure Zn from

an alkaline medium leached EAF dust solution containing Zn 45.60 g L⁻¹, Pb 3.60 g L⁻¹, Fe 0.06 g L⁻¹, Al 1.14 g L⁻¹, Cu 0.06 g L⁻¹ and Cd 0.04 g L⁻¹ (Table 2.5). The presence of lead in the solution might affect the electrowinning process considerably and so Pb was removed by sodium sulfide precipitation. The lead depleted solution was used for the EW process to separate pure zinc. 2.4 – 2.7 kWh electricity was applied to recover 1 kg of pure zinc from the zero-Pb solution. Mukongo et al. (2009) and Tsakiridis et al. (2010) obtained similar results by applying the EW technology to furnace flue dusts (Table 2.5). They were able to electrolyse more than 90% of Zn from the dust samples at the expense of 3.5 kWh/kg energy.

2.4.4. (Bio)sorption

Sorption is a widely used and relatively cost effective metal recovery technology, which can be applied to heavy metal containing aqueous solutions. Ion-exchange and expansion properties are important in the selection of suitable sorbent materials. The mechanism of sorption involves three important phases (Das et al., 2010): (i) solid phase (which denotes the sorbent used), (ii) liquid phase (the leachate is usually used as the solvent) and (iii) dissolved phase (refers to the dissolved metal ions).

Clay minerals, biological materials, carbon nanotubes, activated carbon, metal oxides and zeolites have been used as sorbents for heavy metals (Zhao et al., 2011). Biological agents, such as bacteria, yeasts, fungi and plant materials can also be used in sorption and the process is termed as biosorption. Microorganisms accumulate metals in the cell wall based on the cell's metabolism and properties of the cell wall (Fig. 2.13) (Ahalya et al., 2003). Also plant tissues are able to accumulate metals, which take-up the metals either by active (at the expense of energy) or passive (electrostatic attachment to the cell wall) processes.

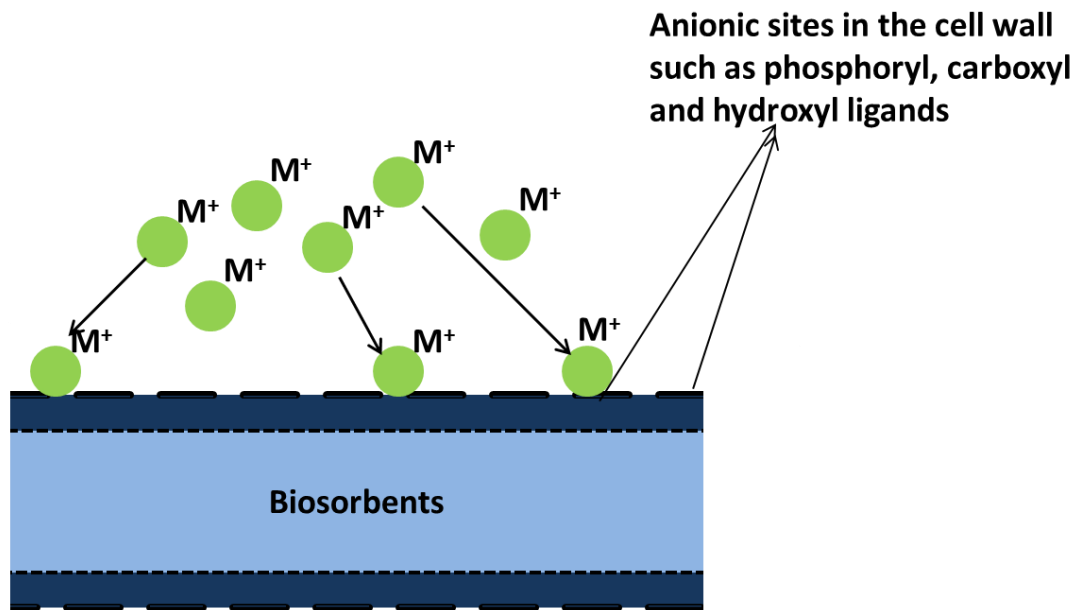


Fig. 2.13. Metals recovery by (bio)sorption

Different sorbents have been applied for the recovery of metals from the synthetic leaching solutions. The efficiency of biosorption for the recovery of metals from metal containing liquid wastes has also been studied at full scale. But there are only few studies on the biosorption of metals from metallurgical leachates. Petrisor et al. (2002) reported the biosorption from mine waste leachates. Creamer et al. (2006) and Macaskie et al. (2007) demonstrated the use of bacteria (*Desulfovibrio desulfuricans* and *Klebsiella pneumonia*, respectively) to recover precious metals like gold, silver and palladium from electronic scrap leachates. Zinc removal from leachates of solid industrial waste using hazelnut shell was reported by Turan et al. (2011). Jalili Seh-Bardan et al. (2013) investigated the biosorption of metals such as Zn, Pb, Fe, As and Mn using *Aspergillus fumigates* from gold mine tailing leachates. More rigorous lab scale studies are needed to scale-up the biosorption of metals from leachates at large scale levels. Apart from low cost, sorption has other advantages like low sludge production and multiple use of the sorbent by regeneration of the sorbent. The major limitation of this technique is the early saturation of the (biomass) sorbent (Alluri et al., 2007).

2.5 Conclusions

Huge loads of different metal bearing wastes are produced by different ferrous and non-ferrous metallurgical operations. These metallurgical dusts, sludges, residues and other solid wastes contain high metal concentrations. The two important environmental issues i.e growing demand of metals and environmental impacts caused by metallurgical wastes can be addressed by extraction and recovery of the heavy metals from these wastes. There are different leaching procedures suggested by various authors for distinctly different metal wastes, also a variety of metal recovery strategies have been developed for the successful recovery of metals from the metal containing leachates. Mineralogical phase composition (oxidized or reduced) and metal content play an important role in the selection of suitable leaching and recovery processes. The combination of the knowledge on the mineralogical composition of the waste with the various leaching and metal recovery processes will help to use these metallurgical wastes as potential secondary sources of metals.

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Chapter 3

Fractionation and leachability of heavy metals from aged and recent Zn-metallurgical leach residues from Três Marias zinc plant (MG, Brazil)

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Abstract

Various mineral processing operations to produce pure metals from mineral ores generate sludges, residues and other unwanted by-products/wastes. As a general practice, these wastes are either stored in a reservoir or disposed in the surrounding of mining/smelting areas which might cause adverse environmental impacts. Therefore, it is important to understand the various characteristics like heavy metals leaching features and potential toxicity of these metallurgical wastes. In this study, zinc plant leach residues (ZLR) were collected from a currently operating Zn metallurgical industry located in Minas Gerais (Brazil) and investigated for their potential toxicity, fractionation and leachability. Three different ZLR samples (ZLR1, ZLR2 and ZLR3) were collected, based on their age of production and deposition. They mainly consisted of Fe (6 % - 11.5 %), Zn (2.5% to 5.0%) and Pb (1.5% to 2.5%) and minor concentrations of Al, Cd, Cu and Mn, depending on the sample age. Toxicity Characteristic Leaching Procedure (TCLP) results revealed that these wastes are hazardous for the environment. Accelerated Community Bureau of Reference BCR sequential extraction clearly showed that potentially toxic heavy metals such as Cd, Cu, Pb and Zn can be released into the environment in high quantities under mild acidic conditions. The results of the liquid-solid partitioning as a function of pH showed that pH plays an important role in the leachability of metals from these residues. At low pH (pH 2.5), high concentrations of metals can be leached: 67%, 25% and 7% of Zn can be leached from leach residues ZLR1, ZLR2 and ZLR3, respectively. The release of metals decreased with increasing pH. Geochemical modeling of the pH dependent leaching was also performed to determine which geochemical process controls the leachability / solubility of the heavy metals. This study showed that the studied ZLRs contain significant concentrations of non-residual extractable fractions of Zn and can be seen as a potential secondary resource for Zn.

Key words: Geochemical modeling, metals fractionation, pH stat leaching, TCLP, zinc plant leach residues.

3.1. Introduction

Enormous amounts of metal bearing wastes are generated by various ferrous and non-ferrous industries, for instance 0.5 - 0.9 ton of hydrometallurgical residues are generated simultaneously with every ton of zinc produced (Creedy et al., 2013). As per the U.S geological survey (2014), 1.9 billion tons of zinc resources (primarily sulfidic, carbonates and silicate ores) are available and various wastes are generated depending on the mineralogy and exploration location of the mineral ores. As a general practice, these wastes are stock-piled or disposed off in the environment (Guo et al., 2010). Soil and water contamination by heavy metals released from these metal-bearing wastes is a serious environmental issue (Margui et al., 2004; Al-Jabri et al., 2006). There are several studies reporting on the various environmental and health impacts caused by toxic heavy metals present in smelting wastes (Kachur et al., 2003; Sánchez-España et al., 2005; Johnson, 2009). Mineral processing wastes such as zinc ashes, zinc dusts, zinc-bearing sludges, zinc purification residues and zinc leach residues are typical unwanted by-products produced during the pyro-metallurgical and hydro-metallurgical operations in the Zn-metallurgical industry (Jha et al., 2001; Ngenda et al., 2009).

Zinc plant leach residues (ZLR) often contain significant concentrations of toxic heavy metals such as Cd, Cr, Cu, Ni and Pb apart from Zn (Ngenda et al., 2009; Safarzadeh et al., 2009; Min et al., 2013). High concentrations of heavy metals in metallurgical wastes do not necessarily mean the wastes are toxic or metals are released into the environment. This depends on the metal leachability under different environmental conditions (i.e. pH, reducing and/or oxidizing conditions). There are different tests proposed in the literature to assess the potential toxicity and leachability of metal wastes. The Toxicity Characteristic Leaching Procedure (TCLP) suggested by the United States Environmental Protection Agency (USEPA) is widely used to evaluate the mobility of heavy metals into the environment (USEPA, 1992; Al-Abed et al., 2006). Even though TCLP is a widely followed and accepted protocol; it was also criticized for its unreliable results, since the results were assessed based on short term laboratory conditions and not on real environmental conditions (Jang and Townsend, 2003; Visvanthan et al., 2010). The mobility of heavy metals depends on their binding forms and the different chemical species and minerals in which the metals prevail. By understanding the heavy metal chemical and mineralogical forms and their specific binding characteristics, it is possible to predict the bioavailability of the heavy metals (Clevenger, 1990).

The release and the bioavailability of the metals based on their chemical fractionation can be partially assessed by sequential extraction procedures. There are different procedures

proposed to study the fractionation of heavy metals under different environmental conditions (Filgueiras et al., 2002; Bacon and Davidson, 2008). The Community Bureau of Reference (BCR) proposed a three-step sequential extraction procedure with more uniformity, reproducibility and comparability with reference materials (Quevauviller et al., 1993). As this procedure was criticized for its long duration, application of ultrasound was introduced to speed up the extraction. The ultrasound accelerated BCR procedure is a comparatively “quick” procedure and the results were validated using BCR601 reference materials (Pérez-Cid et al., 1998; Ipolyi et al., 2002).

The release of heavy metals is greatly influenced by pH. The solubility controlling mineral phases are affected by the change in pH and hence the release of heavy metals is altered accordingly (Van Herreweghe et al., 2002; Astrup et al., 2006). Therefore, it is necessary to consider the effect of pH to understand the leachability of metals. The effect of pH on the leaching characteristics of wastes was assessed by liquid/solid partitioning as a function of pH (USEPA, 2012). There are many studies reporting on the leaching of metals and inorganic constituents in controlled pH environment. The leaching of toxic and heavy metals as a function of pH from metal bearing waste materials such as fly ashes (Vitkova et al., 2009, 2011, 2013) and bottom ashes (Dijkstra et al., 2006) have been reported. In contrast, little research has been done on mineral processing wastes (Al-Abed et al., 2006, 2007, 2008) and only very few studies reported on zinc - mineral processing wastes (Li et al., 2013; Min et al., 2013). There are also few research reports that used geochemical modeling tools such as Visual MINTEQ (formerly known as MINTEQA2) (van Herck et al., 2000; van Herreweghe et al., 2002; Zhang et al., 2008; Quina et al., 2009), PHREEQC (Vitkova et al., 2009, 2011, 2013) or ORCHESTRA (Dijkstra et al., 2006) to predict the metal speciation and mineral phases that control the solubility of metals from different waste materials. Visual MINTEQ is the most often used tool for geochemical modeling (Quina et al., 2009).

The major objective of this paper was to quantify the potential toxicity and leaching characteristics of the mineral processing wastes generated by a zinc metallurgical industry. Various physico-chemical and mineralogical characteristics as well as heavy metal fractionation of ZLR produced by a Zn-metallurgical plant located in Três Marias (Minas Gerais (MG) state, Brazil) were studied. Their potential toxicological characteristics were assessed via the TCLP test. The leaching behavior of these ZLR samples was also investigated and reported as a function of pH. Geochemical modeling was done using visual MINTEQ 3.1

to understand the mechanisms that drive the leaching and identify the possible mineral phases controlling the solubility of the leached metals.

3.2. Materials and methods

3.2.1. Solid samples

Representative samples of ZLR wastes were collected from a zinc metallurgical industrial site located in Três Marias (Minas Gerais state, Brazil) in March 2013. This Zn-plant produces Zn from Zn-sulfide and Zn-silicate ores through various mineral processes (Souza, 2000; Souza et al., 2007). During filtration, a sludge is generated which is the zinc plant leach residue investigated in this paper. These zinc plant leach residues are stored in specially built storage dams. For this study, three different leach residues (based on their age of disposal) were collected from different waste storage ponds. Leach residue 1 (ZLR1) is more than 30 years old. Leach residue 2 (ZLR2) is moderate (between 2 and 30 years old), whereas leach residue 3 (ZLR3) is the most recent one (less than 2 years old).

3.2.2. Physico-chemical and mineralogical characterization of the samples

3.2.2.1. pH, total solids, volatile and fixed solids

ZLR samples were ground to ensure the homogeneity of the samples with a particle size below 1 mm. A volume of 25 mL of boiled distilled water was added to 10 g of the dried samples taken in a polyethylene flask. The flask was then agitated using an orbital shaker (IKA Labortechnik K550 Digital) for 1 h. The solution was filtered at 0.45 µm nitrocellulose filters and the filtrate pH was measured using a Horizon pH-meter (Pansu and Gautheyrou, 2007). Total solids, volatile and fixed solids as well as moisture content of the samples were determined according to the USEPA 1684 (2001) procedure.

3.2.2.2. Total metal content

Total metal content of the samples was determined by modified hotplate aqua-regia digestion (Chen and Ma, 2001). A volume of 9 mL of HCl (37%) and 3 mL of HNO₃ (65%) was added to 1.0 g of solid sample taken in a digestion flask. The flasks were placed in a digester (DigiBlock ED16S, Lab Tech) heated to a temperature of 100°C for 2 h, covered with a watch glass and left to cool at room temperature for 2 h. Then, 20 mL of HNO₃ (2%) was added on the sides of the flask to recover metals and the solid residues were separated by filtration

through Whatman grade 5 filter paper (mesh size 2.5 μm). The filtrate was then made up to 100 mL with ultrapure water. The final solution was analyzed for its metal concentrations (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Pb, Zn).

3.2.2.3. X-Ray Diffraction

Crystalline mineral phases were investigated by using an X-Ray diffractometer. X-ray diffraction (XRD) studies were carried out on a Bruker D8 Advance diffractometer equipped with an energy dispersion Sol-X detector with copper radiation ($\text{CuK}\alpha$, $\lambda = 0.15406 \text{ nm}$). The acquisition was recorded between 2° and 80° , with a 0.02° scan step and 1 s step time. Prior to XRD analysis, the samples were ground to powder using a pestle and mortar and dried at 25°C . ZLRs were pre-concentrated by magnetic fraction separation. XRD analysis was also done on the pre-concentrated fractions of the ZLRs.

3.2.2.4. X-Ray fluorescence

X-ray fluorescence (XRF) analyses were also carried out on the ZLR samples. A Panalytical X-fluorescence spectrometer equipped with an Energy Dispersive Minipal 4 (Rh X Ray tube-30 kV-9W) at a resolution of 150 eV (MnKa) was used.

3.2.3. Toxicological characteristics leaching procedure (TCLP)

The TCLP of ZLR was investigated using the USEPA 1311 protocol (1992). As for practical convenience, the procedure was slightly modified by reducing the weight of the samples and volume of extractant without changing the solid to liquid phase ratio. Air dried ZLR (0.5 g) was taken in poly-ethylene extraction bottles and the extractant solution (acetic acid) was added in a ratio of 1:20 (sample:extractant, wt/vol). The pH of the extractant liquid was $2.88 (\pm 0.1)$ for the ZLR which was selected based on the alkalinity analysis suggested by USEPA 1311 (1992). The ZLR and extractant contained polyethylene tubes were rotated in a rotary tumbler for 18 h (+2 h equilibration time) at 20°C . The final pH of the leachates was measured (Horizon pH meter) and the leachates were filtered using $0.45 \mu\text{m}$ nitrocellulose filters and the filtrate was analyzed for the soluble metal concentrations (Cd, Cu, Pb and Zn).

3.2.4. Sequential extraction

The ultrasound assisted BCR sequential extraction procedure proposed by Perez-Cid et al. (1998) was used to study the release of metals under natural environmental conditions. The detailed experimental conditions (such as the extractants, ultrasound contact time, temperature and associated metal phases) are provided in Table 3.1. The hydroxyl ammonium chloride solution was freshly prepared before the start of the experiments.

In step 1, 20 mL of 0.11 M acetic acid was added to 1 g of air-dried residues in centrifuge tubes, and an ultrasonic probe was placed inside the centrifuge tube to supply the required sonication (at room temperature for 7 min). After sonication, the samples were centrifuged at 3000 g for 10 minutes to separate the extractant from the residue. In step 2, 20 mL of 0.5 M hydroxyl ammonium chloride adjusted to pH 2 with nitric acid was added to the residues obtained from step 1, and the extraction was performed as described for step 1. The leachates were filtered using 0.45 μm nitrocellulose filters and the filtrate was analyzed for the amount of metal (Al, Cd, Cu, Fe, Mn, Pb, Zn) released.

Table 3.1. Stepwise information (on the extractant and ultrasound acceleration time) of the BCR sequential extraction procedure (Perez-Cid et al., 1998).

Fraction	Extracting agent	Extraction conditions	
		Ultrasound time	Temperature
F1. Acid soluble	20 mL HOAc (0.11 mol L ⁻¹)	7 min	20-25°C
F2. Reducible	20 mL NH ₂ OH.HCl (0.1 mol L ⁻¹ , pH = 2)	7 min	20-25°C
F3. Oxidizable	10 mL H ₂ O ₂ (30%, pH = 2) and then 25 mL NH ₄ OAc (1 mol L ⁻¹ , pH = 2)	2 and 6 min	20-25°C
F4. Residual	Aqua regia (HNO ₃ /HCl, 1:3)	120 min	100°C

3.2.5. Influence of pH on the leaching of heavy metals

3.2.5.1. pH stat leaching experiments

ZLR wastes were subjected to liquid solid partitioning as a function of pH according to the USEPA method (2012). Acid/base neutralizing capacities of the samples were initially determined by pre-titration experiments (data not shown) and the equilibration period was calculated and set at 4 h. Based on the pre-titration experiments, 8 different pH values (2.5, 3.5, 4.5, 5.5, 7.0, 8.5, 10.5 and the natural pH of the samples) were chosen. Five grams of ZLR were

taken in a 100 mL flask with 50 mL extractant solution (ultrapure water + required volume of acid/base) to maintain the solid to liquid phase ratio at 10%. To maintain the natural pH, 50 mL of ultrapure water (no acid/base addition) was added to 5 g of ZLR. The flasks were continuously agitated at 150 rpm for 48 h at room temperature. The desired pH values were maintained by adding corresponding volumes (determined by pre-titration experiments) of acid (2 M HNO₃) and base (1 M KOH). The leachates were filtered using 0.45 µm nitrocellulose filters and analyzed for cations (Al, Cd, Cu, Mn and Zn) and anions (Cl⁻, PO₄³⁻, SO₄²⁻, NO₃⁻ and alkalinity) concentrations.

3.2.5.2. Geochemical modeling of heavy metals leaching

Visual MINTEQ is a chemical equilibrium model able to predict metal speciation, solubility, adsorption and precipitation (Gustafsson, 2012; <http://vminteq.lwr.kth.se/>). It can be used to assess the chemical composition of the aqueous solutions at equilibrium. Mass distribution of the dissolved species, adsorbed species and different solid phases under different conditions in equilibrium can also be calculated using this model. All the pH dependent leaching modeling tests to predict the dissolution/precipitation (without considering surface complexation and co-precipitation) were run by using visual MINTEQ V3.1 (Gustafsson, 2012). Input molar concentrations (based on the pH 2.5 leachate composition, supplementary information Table S4) of each metal (Zn²⁺, Cu²⁺, Cd²⁺, Mn²⁺, Al³⁺, Ca²⁺, Mg²⁺, Fe³⁺, Cl⁻, PO₄³⁻, SO₄²⁻, NO₃⁻ and alkalinity) were provided based on the initial pH static leaching experiments to understand the solubility based on dissolution/precipitation mechanisms in the absence of surface complexation/adsorption reactions (van Herck et al., 2000; Zhang et al., 2008). The system pH was varied from 2.5 to 10.5 and the temperature was constantly maintained at 20 °C. Oversaturated solids were allowed to precipitate. In order to calculate the saturation indices of the solubility controlling mineral phases, a second set of visual MINTEQ models were run with the same input molar concentrations, but the oversaturated solids were not allowed to precipitate. Concentrations of the metals, saturation indices of the mineral phases and the precipitates were obtained in the output.

3.2.6. Analytical methods and statistical analysis

Unless otherwise stated, all the experiments were done in triplicates and procedural blanks were maintained at room temperature (20 ± 2 °C). Samples were collected and filtered using 0.45 μm nitrocellulose filters and the metal content (Al, Cd, Cu, Fe, Mn, Pb and Zn) of the solutions was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300 Perkin Elmer). The detection limits (metals and their corresponding wavelengths) of the ICP-OES are provided in the supplementary information (Table S1). Chloride, phosphate, carbonate (as total alkalinity) and sulfate were estimated by argentometric titrations, ammonium molybdate spectrometry, H_2SO_4 titrations and BaCl_2 turbidimetry, respectively, as prescribed in the standard methods for the examination of water and wastewater (1992). Nitrates and sulfides were determined by 2,6 dimethylphenol spectrometry (ISO 7890/1 - 1986) and mixed diamine reagent spectrometry (Cline, 1969), respectively. The means of the analyses were statistically compared using one-way analyses of variance (ANOVA) using statistical computing and graphics software R v3.1.1. The confidence limit was 95% ($P < 0.05$).

3.3. Results

3.3.1. Physico-chemical and mineralogical characterization

Table 3.2 shows various physico-chemical characteristics such as pH, total solids, fixed and volatile solids of the ZLR samples investigated.

Table 3.2. Physico-chemical characteristics of the ZLRs.

Properties	ZLR1	ZLR2	ZLR3
pH	5.7 ± 0.1	6.6 ± 0.1	6.1 ± 0.1
Moisture content (%)	9.6 ± 0.4	7.7 ± 0.3	7.3 ± 0.3
Total solids (%)	90.4 ± 1.9	92.3 ± 3.1	92.7 ± 2.3
Fixed solids (%)	91.2 ± 2.8	93.1 ± 2.4	92.4 ± 1.8
Volatile solids (%)	8.8 ± 0.5	6.9 ± 0.3	7.6 ± 0.4

The XRD analysis (supplementary information, Fig. S1a) showed that all the three leach residues investigated contain identical crystalline mineral phases. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was the only prominent mineral phase identified in all the three ZLRs investigated. It should be

noted that the XRD analysis can identify only the most abundant (> 3 wt %) crystalline mineral phases (Safarzadeh et al., 2009). Hence, in order to have more insight in the metal composition of the ZLRs, XRF analysis and bulk acid digestion were performed to determine the elemental composition of the sample (Tables 3.3 and 3.4).

Table 3.3. Elemental oxide composition (weight %) obtained from XRF analysis.

Element oxide	ZLR1	ZLR2	ZLR3
	(%)	(%)	(%)
SO ₃	32.04	27.39	28.33
SiO ₂	25.38	30.38	27.46
CaO	17.97	15.86	15.66
Fe ₂ O ₃	11.78	16.73	18.91
ZnO	6.62	4.35	3.83
PbO	2.65	2.25	3.09
Al ₂ O ₃	1.29	0.96	0.99
MnO ₂	0.72	0.27	0.03
MgO	0.56	1.28	1.03
CuO	0.18	0.11	0.24
CdO	0.12	0.06	0.04
Cr ₂ O ₃	0.007	0.01	0.013
Sum	99.31	99.65	99.62

Table 3.4. Elemental composition (by hot plate aqua regia digestion) of the ZLRs investigated.

Metals	ZLR1	ZLR2	ZLR3
Ca (g kg ⁻¹)	86.4 ± 2.1	78.9 ± 13.7	69.5 ± 3.1
Fe (g kg ⁻¹)	66.7 ± 1.1	95.8 ± 2.9	115.3 ± 2.9
Zn (g kg ⁻¹)	50.1 ± 0.5	27.3 ± 1.1	25.1 ± 0.4
Pb (g kg ⁻¹)	17.8 ± 0.2	15.3 ± 0.2	23.5 ± 1.1
Mn (g kg ⁻¹)	9.9 ± 0.4	2.90 ± 0.05	0.5 ± 0.1
Mg (g kg ⁻¹)	6.2 ± 0.2	11.7 ± 0.5	8.50 ± 0.09
Al (g kg ⁻¹)	4.0 ± 0.2	3.30 ± 0.06	3.4 ± 0.1
Cu (g kg ⁻¹)	2.0 ± 0.6	0.70 ± 0.04	1.40 ± 0.04
K (g kg ⁻¹)	1.50 ± 0.09	0.600 ± 0.001	0.700 ± 0.001
Cd (g kg ⁻¹)	0.60 ± 0.02	0.400 ± 0.005	0.200 ± 0.004

Those results confirm that other mineral phases might also be present, either at a concentration of less than 3 wt % or amorphous in nature, and could hence not be identified by XRD (Safarzadeh et al., 2009). XRF analysis (Table 3.3) reveals that the ZLR contain significant concentrations of Zn (3.8% to 6.6%), Fe (11.7% - 18.9%), and Ca (15.6% - 18%).

The ZLR further contains considerable concentrations of sulfur (27% - 32%), SiO₂ (25% - 30%), magnesium (0.5% - 1.3%) and other metals such as Mn (0.03% - 0.7%), Cu (0.1% - 0.24%), Al (0.9% - 1.3%) and Cd (< 0.1%) in detectable concentrations. Total metal analysis (hotplate aqua-regia digestion) results (Table 3.4) are well in accordance with the XRF results (Table 3.3). Generally, Cd, Mn and Zn concentrations are observed decreasing and the Fe concentration is found increasing with the decrease in the age of the ZLRs. On the other hand, Al, Cu and Pb concentrations are high in ZLR1, decrease in ZLR2 but slightly increased again in ZLR3 compared to ZLR2.

To improve the mineralogical characterization, XRD analysis on pre-concentrated ZLRs (by magnetic fractions) was performed. In ZLR1, approximately 50 mg g⁻¹ of magnetic fractions were found, but the amount of magnetic fractions (per g) in ZLR2 and ZLR3 was below the detection limit (analytical balance detection range: 1 mg - 200 g). In the magnetically pre-concentrated ZLR1, quartz (SiO₂) and magnetite (Fe₃O₄) were identified next to gypsum (supplementary information, Fig. S1b).

3.3.2. Toxicity characteristics leaching procedure

The leaching results of Cd, Cu, Pb and Zn based on the USEPA TCLP procedures are presented in Table 3.5. At the end of the TCLP leaching tests, the Pb concentrations were found 8.9 mg L⁻¹, 10.3 mg L⁻¹ and 3.9 mg L⁻¹ in ZLR1, ZLR2 and ZLR3, respectively. A concentration of 29 mg L⁻¹, 9 mg L⁻¹ and 3.2 mg L⁻¹ of Cd was released in the ZLR1, ZLR2 and ZLR3 leachates, respectively. Zn and Cu concentrations were also analyzed in the TCLP leachates. Zn was observed in higher concentrations in all the samples compared to other heavy metals such as Cd, Cu and Pb: 1052.7 mg L⁻¹, 349.3 mg L⁻¹ and 94.7 mg L⁻¹ of Zn was released from the ZLR1, ZLR2, and ZLR3, respectively. The Cu concentrations were 27.9 mg L⁻¹, 2.6 mg L⁻¹ and 13.2 mg L⁻¹ for the TCLP leachates of ZLR1, ZLR2 and ZLR3, respectively. The potential toxicity of the ZLRs is lower in the more recent ZLRs, meaning that the latest generated ZLR3 is less hazardous than the older ZLR1 (which was generated 30 years before).

Table 3.5. TCLP test results for the ZLRs investigated.

Metals	Regulatory threshold (USEPA)	Regulatory threshold (Brazil)	ZLR1 (mg L ⁻¹)	ZLR2 (mg L ⁻¹)	ZLR3 (mg L ⁻¹)
Pb	5.00	1.00	8.83 ± 0.03	10.39 ± 0.02	3.94 ± 0.01
Cu	-	-	27.87 ± 0.36	2.60 ± 0.01	13.16 ± 0.31
Cd	1.00	0.50	27.05 ± 0.09	9.05 ± 0.05	3.19 ± 0.04
Zn	-	-	1052.72 ± 52.58	349.29 ± 45.23	94.65 ± 31.05

3.3.3. Sequential extraction

Figure 1 shows the percentages of metal fractions released in each step of the BCR sequential extraction procedure. Among the studied metals, chemical fractionation of Cd, Fe and Pb follow a similar trend in all the ZLRs. As far as Zn is concerned, the fractionation is different for each ZLR. In ZLR1, the maximum Zn concentration was observed in the acid exchangeable fraction, followed by the reducible fraction and the lowest concentrations in the oxidizable and residual fractions. In ZLR2, Zn is mostly found in the acid exchangeable and residual fractions and lesser released in the other fractions. In case of ZLR3, Zn is mainly restricted to the residual fraction, then in the acid exchangeable fraction and a comparatively low concentration in the reducible and oxidizable fractions. Cd is mostly released in the acid exchangeable fraction. The Pb concentration in the acid exchangeable and reducible fraction is very low when compared to the oxidizable and residual fractions. Mn was found in abundance in all the leach residue samples in the second step of the BCR sequential extraction and Fe is mostly confined to the residual fractions.

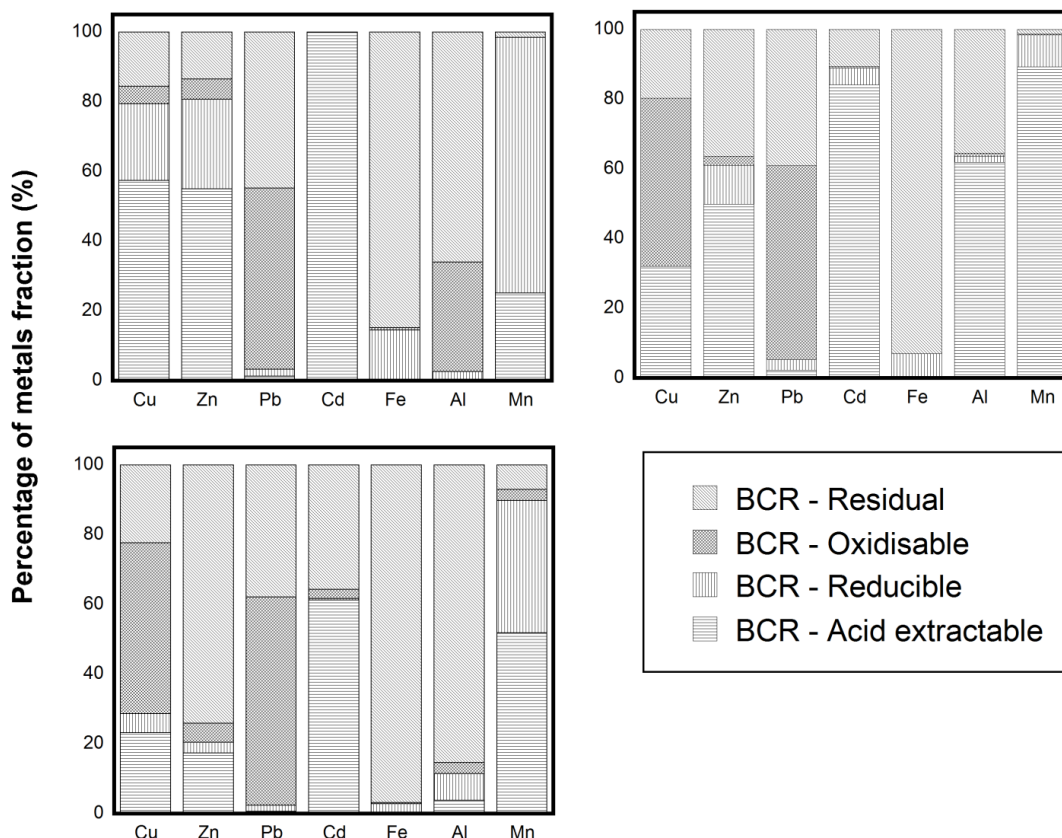


Fig. 3.1. Fractionation of heavy metals in (a) ZLR1, (b) ZLR2 and (c) ZLR3 determined by the accelerated BCR procedure.

3.3.4. Leachability of major and trace elements

The leaching behavior of the metals Al, Cd, Cu, Mn and Zn as a function of pH (Fig. 3.2a, 3.2b, 3.2c) as well as the solubility and species profile of these leached metals at a particular pH were predicted using visual MINTEQ V3.1 (Fig. 3.2d, 3.2e and 3.2f). Saturation indices of the few mineral phases that control the solubility of the studied released elements are presented in the supplementary information (Table S5 a, b and c).

The Zn leaching pattern generally follows an ‘L’ shaped curve (Fig. 3.2a, 3.2b and 3.2c), where the maximum leaching occurred at acidic pH 2.5 and then a steep decrease towards the samples at natural pH. A maximum of Zn (68%) was leached from the ZLR1 at pH 2.5. At pH 3.5, the Zn concentration in the leachate (ZLR1) was 57% and then the Zn concentration in the leachates further decreased with increase of pH. At its natural pH (pH 5.6), only 6% of Zn was leached from ZLR1. Similar trends were observed in ZLR2 and ZLR3 as well. At pH 2.5, 25%

of Zn was solubilized from ZLR2 and decreased to 0.05% at the natural pH (pH 6.6). In case of ZLR3, 6% of Zn was leached at pH 2.5 and only 0.5% was released at pH 6.1 (natural pH). The visual MINTEQ model solubility data provided for leached Zn (Fig. 3.2d, 3.2e and 3.2f) is reasonably in accordance with the experimental results (Fig. 3.2a, 3.2b and 3.2c). The solubility of leached Zn is controlled by Zn precipitating in the form of smithsonite (ZnCO_3) in the pH range 5.5 – 7.0. In the pH range 7.0 to 10.5, the visual MINTEQ model predicts the precipitation of hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) and zincite (ZnO).

The other monitored metals Al, Cd, Cu and Mn also follow the leaching pattern of Zn. Amongst the observed elements, Al experimental data and modeling curves find the best fit, while others generally follow a similar 'L' shaped trend. Al solubility is predicted to be controlled by precipitation of $\text{AlOHSO}_4(\text{s})$ at pH 3.5 and diaspore ($\text{AlO}(\text{OH})$) at pH 4.5 - 7.0. In the very alkaline condition (pH 10.5), Al could be precipitated as ettringite (hydrous calcium aluminium sulfate). In case of Cu, $\text{CuCO}_3(\text{s})$, atacamite and cupric ferrite were found as the solubility controlling phases. In contrast with other metals, Cd release was only slightly affected by the change in pH. From pH 2.5 to 6.0, the release of cadmium did not undergo any drastic changes. $\text{Cd}_4(\text{OH})_6\text{SO}_4(\text{s})$ precipitation is predicted at pH 10.5, which could be the solubility controlling mineral for Cd. Mn is found precipitating as $\text{MnHPO}_4(\text{s})$ even at low acidic pH 2.5 and is present until pH 7, but $\text{MnHPO}_4(\text{s})$ dissolves under alkaline conditions which slightly increases the Mn solubility. Pyrochroite ($\text{Mn}(\text{OH})_2$) is a possible solubility controlling precipitate of Mn (at pH 10.5). Fe also follows a similar L shaped leaching trend and the maximum dissolution was found to be 0.15% in ZLR1, 0.4% for ZLR2 and 1.6% for ZLR3 (data not shown). The Pb release in the studied pH range was low (<1% for all the ZLRs) when compared to its total concentration (data not shown).

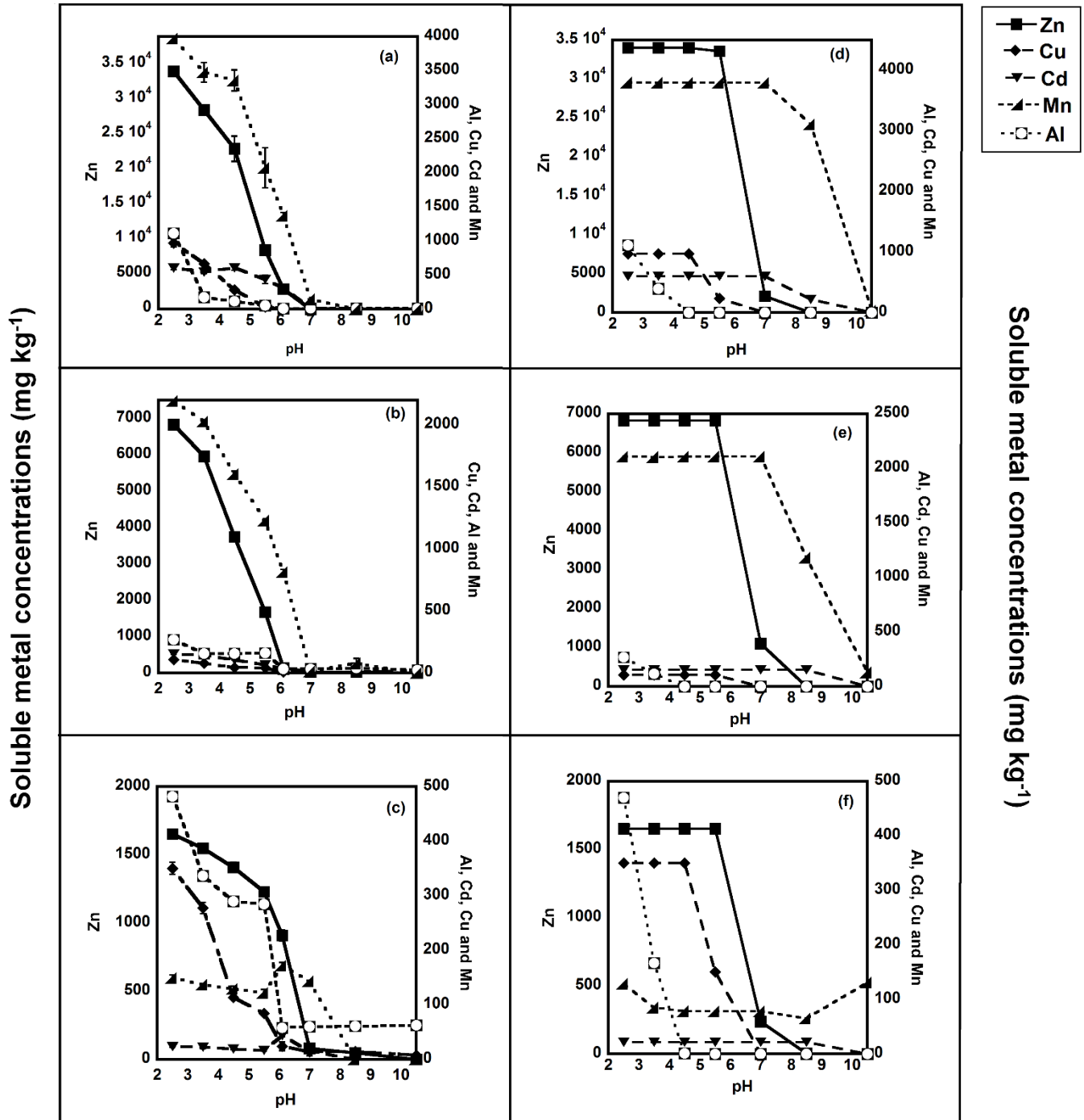


Fig. 3.2. Leaching behaviour of metals from (a) ZLR1, (b) ZLR2 and (c) ZLR3 and Visual MINTEQ model for the leach metals solubility features from (d) ZLR1, (e) ZLR2 and (f) ZLR3 as a function of pH.

3.4. Discussion

3.4.1. Physico-chemical and mineralogical characterization of the ZLR samples

This study showed that the investigated ZLRs can be a potential alternative resource for Zn, since the bulk chemical digestion and XRF analyses showed that ZLRs are rich in (weight %) Zn (2.5% to 5%), Fe (6.5% - 11.5%), and Ca (7% - 8.6%). The ZLRs also contain considerable amounts of sulfur (27% - 32%), silica (25% - 30%), magnesium (0.5% - 1.3%) and other elements such as Mn (0.03% - 0.7%), Cu (0.1% - 0.24%), and Al (0.9% - 1.3%) and Cd (0 - 0.1%). Table 3.6 summarizes previous reports on the mineralogy, metal content and potential toxicity of ZLRs from different zinc hydrometallurgical plants and compares them with the ZLRs investigated in this study. Generally higher concentrations for Ca, Fe, Pb as well as significant concentrations of Cd, Ni and Cu were reported (Safarzadeh et al., 2009; Min et al., 2013; Li et al., 2013; Ke et al., 2014). Furthermore, a significant concentration of Zn was observed in the leach residues, for example 44.3% (Safarzadeh et al., 2009), 19.5% (Min et al., 2013) and 5.4% (Li et al., 2013). As these ZLRs were generated by different zinc plants, using different primary ores and applying customized hydrometallurgical operations, the concentrations of each metal in the different ZLRs might vary. Also the ZLR1, ZLR2 and ZLR3 investigated in this study, despite originating from the same Zn plant, differ in their elemental composition. For example, the Zn content (weight %) in ZLR1 is 5%, in ZLR2 it's 2.7% and 2.5% in ZLR3. This can be explained by the fact that the Zn plant might have improved its process efficiency to extract more metals over the years, i.e. the process might be improved to extract most of the extractable Zn from the ores, leaving Zn mainly in the “stable” phases in the ZLRs. This is also supported by the results of the chemical fractionation and leaching experiments (Figures 1 and 2), discussed below in detail.

In the studied ZLRs, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was the major crystalline mineral phase identified by XRD analysis. In the magnetically pre-concentrated ZLR1, quartz and magnetite were also found. The XRD analyses suggests that the mineralogical composition of the samples was mainly influenced by the secondary minerals formed during the metallurgical processing. The Vazante deposits and Morro Agudo deposits (where the primary ores have been mined) mostly consist of Zn-ores of silicates and sulfidic composition, respectively (Sauza et al., 2007). Willemite (Zn_2SiO_4) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) mineral phases are the minerals mostly observed in the Vazante deposits and würtzite ($(\text{Zn,Fe})\text{S}$), sphalerite (ZnS), galena (PbS) and chalcopyrite (CuFeS_2) are often found in the Morro Agudo deposits. Dolomites

$((\text{Ca},\text{Mg})(\text{CO}_3)_2)$, quartz (SiO_2), CaO and magnesia (MgO) are also common mineral phases in these deposits (Ministry Of Mines and Energy, 2010).

ZnSO_4 , PbSO_4 and CdCO_3 minerals were commonly observed in many other leach residues generated in the zinc hydrometallurgical plants located in Turkey (Coruh and Ergun, 2010) and China (Min et al., 2013; Li et al., 2013; Ke et al., 2014). All the above-mentioned minerals are secondary mineral phases formed during various hydrometallurgical operations. ZnSO_4 is a typical mineral formed from the oxidized part of the sulfidic ores (superficial layer) and can often be substituted by Mn. Anglesite ($(\text{Pb},\text{Mn})\text{SO}_4$) is an oxidation product of galena in the top layer of sulfidic ore bodies with Pb-contents (Zárate-Gutiérrez and Lapidus, 2014). It can also be formed in the metallurgical process from Pb-ions with H_2SO_4 . The gypsum mineral phase (observed in the ZLRs) could be the oxidation product of CaO (during the acidic leaching stages). Apart from these minerals, ZLR contain various other forms of Zn such as $\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$ (Safarzadeh et al., 2009; Hollagh et al., 2013; Min et al., 2013), franklinite (ZnFe_2O_4) (Moradkhani et al., 2013; Li et al., 2013), ZnO (Safarzadeh et al., 2009; Li et al., 2013) and Zn_2SiO_4 (Li et al., 2013) were also reported in the literature (Table 3.6).

Table 3.6. Mineralogy, metal content and potential toxicity of ZLRs from different hydrometallurgical plants.

Source	Major mineral phases	Total metal content (%)	Potential toxicity (mg L ⁻¹)	Reference
Zinc hydrometallurgical plant in China	ZnFe ₂ O ₄	Fe - 24.02	(TCLP, USEPA 1311, pH 2.88)	Li et al. (2013)
	ZnSO ₄	Zn - 19.57		
	CaSO ₄	Ca - 1.97		
	PbS	Pb - 4.18	Zn - 4589	
	PbSO ₄	Mn - 1.41	Pb - 1.4	
	Pb ₃ SiO ₅	Cu - 0.91	Cd - 93.5	
	Zn ₂ SiO ₄	Mg - 0.37	As - 0.3	
Lead and zinc plant, located in Zhuzhou city, China	ZnS	Fe - 13.54	(*GB 5085.3 - 2007, pH 3.25)	Min et al. (2013)
	ZnSO ₃ .2.5H ₂ O	Zn - 5.35		
	PbS ₂	Ca - 3.3	Cu - 82	
	PbSO ₄	Pb - 4.66	Pb - 5.3	
	Pb ₂ O ₃	Cd - 0.15	Zn - 3500	
	Fe ₂ (SO ₄) ₂ (OH) ₅ (H ₂ O)	Cu - 0.24	Cd - 68	
		As - 0.25	Hg - 0.01	
Zinc plant located in Zanjan, Iran		Fe - 2.35	-	Moradkhani et al. (2013)
	ZnFe ₂ O ₄	Zn - 7.55		
	PbSO ₄	Ca - 7.67		
	Fe ₂ O ₃	Pb - 8.13		
	Fe ₃ O ₄	Cd - 0.09		
	CaSO ₄ .2H ₂ O	Co - 0.02		
		Ni - 0.02		
Cinkur Plant, Turkey Residue 1		Mn - 0.14	(**EPA toxicity test 1980, pH 5.0)	Altundogan et al. (1998)
		Fe - 6.25		
		Zn - 11.96		
		Ca - 2.4	<u>EP1</u>	
	PbSO ₄	Pb - 25.33	Cd - 1.61	
	CaSO ₄ .2H ₂ O	Cd - 0.06	Pb - 5.0	
		Cu - 0.04	<u>EP2</u>	
		Cd - 8.48		
		Pb - 6.57		
Cinkur Plant, Turkey Residue 2	PbSO ₄	Fe - 1.5	(**EPA toxicity test 1980, pH 5.0)	Altundogan et al. (1998)
	CaSO ₄ .2H ₂ O	Zn - 4.41		
		Ca - 1.5		

		Pb - 54.12 Cd - 0.4 Cu - 0.045	<u>EP1</u> Cd - 12.91 Pb - 5.32 <u>EP2</u> Cd - 65.4 Pb - 10.54	
Nation Iranian lead and zinc plant, Turkey	ZnSO ₄ ZnSO ₃ ·2.5H ₂ O ZnO CdO	Zn - 44.32 Cd - 15.17 Ni - 3.94 Cu - 1.44 Pb - 1.08 Fe - 0.09 Mn - 0.08 Ca - 2.27	-	Safarzadeh et al. (2009)
ZLR1 [#]	CaSO ₄ ·2H ₂ O Quartz (SiO ₂) Magnetite (Fe ₃ O ₄)	Ca - 8.64 Fe - 6.67 Zn - 5.01 Pb - 1.78 Mn - 0.99 Cu - 0.2 Cd - 0.06	(TCLP, USEPA 1311, pH 2.88) Pb - 8.83 Cu - 27.87 Cd - 27.05 Zn - 1052.72	Investigated in this study
ZLR2 [#]	CaSO ₄ ·2H ₂ O	Ca - 7.89 Fe - 9.58 Zn - 2.73 Pb - 1.53 Mn - 0.29 Cu - 0.07 Cd - 0.04	(TCLP, USEPA 1311, pH 2.88) Pb - 10.39 Cu - 2.06 Cd - 9.05 Zn - 349.29	Investigated in this study
ZLR3 [#]	CaSO ₄ ·2H ₂ O	Ca - 6.95 Fe - 11.5 Zn - 2.51 Pb - 2.35 Mn - 0.05 Cu - 0.14 Cd - 0.02	(TCLP, USEPA 1311, pH 2.88) Pb - 3.94 Cu - 13.16 Cd - 3.19 Zn - 94.65	Investigated in this study

“-” - Not applicable/available

*GB 5085.3 - 2007 - Identification standards for hazardous wastes-Identification for extraction toxicity, China

**EPA - Methods for Chemical Analysis of Water and Wastes, Environmental Monitoring and Support Laboratory, EPA-600/4-79-020, Cincinnati, USA

ZLR1, 2 & 3 investigated in this study (ZLR1 > 30 years, 2 years < ZLR2 > 30 years, ZLR3 < 2 years).

3.4.2. Fractionation and mechanisms controlling the leaching and solubility of trace and major elements from ZLRs

This study revealed that the respective releases of metals in the acid exchangeable fractions of the BCR were comparable (Table 3.7) with the metal concentrations in the TCLP leachates and HNO₃ leachates in the acidic pH range (pH 2.5 – 4.5). To assess a waste's potential toxicological risk, metals released in the BCR acid exchangeable fractions alone are often taken into consideration instead of the total metal content (Perin et al., 1985; Singh et al., 2005; Sundaray et al., 2011; Zhu et al., 2012; Zhou et al., 2013; Min et al., 2013). By considering the higher mobility of metals like Cd, Cu and Zn in these leachates (acetic and nitric acid) of ZLR1 and ZLR2, it can be concluded that these metallurgical wastes are hazardous, whereas in ZLR3, the release of Cd, Cu and Zn is comparatively lower (Table 3.7).

Mobility and fractionation of heavy metals in the environment can be assessed by analyzing each fraction of the sequential extraction (Dang et al., 2002). The Zn fractionation data in the more recent samples (ZLR2 and ZLR3) are comparable with the results obtained by Li et al. (2013) and Min et al. (2013). They also observed that the major fractions of Zn from zinc metallurgical residues are more associated with the acid exchangeable fractions and the residual fractions than with the oxidizable and reducible ones. The Zn concentration in the acetic acid leachates was slightly higher than the nitric acid leaching. Under alkaline conditions, the Zn concentration was low and sometimes below the detection limit of the ICP-OES. The water soluble fractions might be attributed to the Zn-sulfates and the rest of the acid leachable fractions might be from carbonates and oxides associated phases (Dold, 2003). Under acidic pH conditions (2.5 – 4.5), Zn (approximately) 22 g kg⁻¹ – 34 g kg⁻¹ of ZLR1, 3.5 g kg⁻¹ – 7 g kg⁻¹ of ZLR2 and 1.4 g kg⁻¹ – 1.6 g kg⁻¹ of ZLR3 were released (Table 3.7). The ZLR1, ZLR2 and ZLR3 contain 3 g kg⁻¹, 0.4 g kg⁻¹ and 0.9 g kg⁻¹ of water soluble Zn – fraction, respectively (Fig. 3.2). Based on the comparison of the geochemically modeled Zn solubility and the actual Zn leached (supplementary information, Fig. S2), it can be concluded that the Zn solubility (calculated from the total Zn fraction leached at pH 2.5) is controlled by the smithsonite, zincite and hydrozincite mineral phases. Also the gap between the actual concentration of the leached Zn and the calculated Zn soluble concentration might be partly explained by the dissolution of the smithsonite, zincite and hydrozincite mineral phases, but also by the dissolution of adsorbed or co-precipitated Zn from ZLRs. This latter dissolution process is likely responsible for the

lower concentration of leached Zn compared to the predicted values. We can indeed assume that Zn is adsorbed onto or co-precipitated with Fe/Al – oxides.

Table 3.7. Fractionation of metals (Cd, Cu, Pb and Zn) from ZLRs under different acidic conditions.

Samples	Metals	TCLP (g kg ⁻¹)	BCR acid exchangeable fractions (g kg ⁻¹)	pH _{stat} 2.5 (g kg ⁻¹)	pH _{stat} 3.5 (g kg ⁻¹)	pH _{stat} 4.5 (g kg ⁻¹)
ZLR1	Pb	0.18 ± 0.007	0.14 ± 0.01	-	-	-
	Cu	0.56 ± 0.074	0.73 ± 0.26	0.97 ± 0.06	0.67 ± 0.03	0.29 ± 0.04
	Cd	0.54 ± 0.02	0.57 ± 0.11	0.60 ± 0.02	0.55 ± 0.02	0.61 ± 0.04
	Zn	21.05 ± 1.05	20.81 ± 1.28	34.01 ± 0.26	28.50 ± 0.27	22.95 ± 1.81
ZLR2	Pb	0.21 ± 0.004	0.19 ± 0.07	-	-	-
	Cu	0.05 ± 0.001	0.06 ± 0.01	0.11 ± 0.01	0.08 ± 0.01	0.04 ± 0.01
	Cd	0.18 ± 0.01	0.23 ± 0.02	0.15 ± 0.01	0.14 ± 0.01	0.11 ± 0.01
	Zn	6.99 ± 0.91	7.88 ± 0.27	6.83 ± 0.15	5.95 ± 0.05	3.74 ± 0.04
ZLR3	Pb	0.08 ± 0.01	0.10 ± 0.01	-	-	-
	Cu	0.26 ± 0.061	0.17 ± 0.04	0.35 ± 0.01	0.28 ± 0.01	0.11 ± 0.01
	Cd	0.06 ± 0.01	0.06 ± 0.01	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.01
	Zn	1.89 ± 0.62	1.72 ± 0.10	1.65 ± 0.03	1.55 ± 0.02	1.41 ± 0.04

Copper followed a similar leaching curve as Zn, while Cd and Mn underwent a similar trend, which is slightly different from Cu and Zn (Fig. 3.2). For Cu, even though acetic acid leaching and nitric acid leaching were comparable in the acidic conditions, the Cu concentration in the acetic acid leachates was slightly higher. The Cu concentration in the water leachate was very low (<0.003 g kg⁻¹) in all the ZLRs investigated. In the acidic pH range 2.5 - 5.5, the predicted curve (for Cu and Zn) is flat and slightly overestimated, still it can be explained by the fact that at equilibrium, the model predicts the concentration based on the maximum amount that can be leached (van Herck et al., 2000; Quina et al., 2009; Vitkova et al., 2013). Furthermore, it can also be speculated that the lower Cu and Zn solubility in the acidic region (especially in mild acidic conditions) is affected by the possibility of co-precipitation of these metals with Fe/Al - oxides.

Cadmium release was 27 times, 9 times and 3 times higher than the permissible limits by U.S. EPA in the ZLR 1, 2 and 3 respectively. The concentration of Cd in the TCLP leachates,

BCR acid exchangeable and also nitric acid leaching were comparable (Table 3.7). Approximately 0.04 g kg^{-1} (ZLR2 & ZLR3) and 0.4 g kg^{-1} (ZLR1) of exchangeable/water-soluble Cd minerals were present in the ZLRs. The simulated leaching model for Cd is overestimated in the pH range 5.5 to 8.5 and suggests that it can be also dependent on adsorption/surface complexation mechanisms, meaning that the Cd solubility might also depend on its sorption towards opposite charged surfaces. The pH dependent curves of Cd and Mn follow closely similar patterns. It hints that Cd solubility can be also controlled by the co-precipitation with Mn-oxides. Cadmium release was 27 times, 9 times and 3 times higher than the permissible limits of the U.S. EPA in the ZLR 1, 2 and 3, respectively.

The Pb concentration in the studied pH range (pH 2.5 – 4.5) is very low and sometimes below the detection limit of ICP-OES and is not comparable with the TCLP or BCR acid exchangeable fractions (Table 3.7). This could be due to the high stability of the Pb-acetate complexes compared to the nitric acid leaching products (Cappuyns and Swennen, 2008). The Pb concentrations in the TCLP leachates of ZLR1 and ZLR2 were at-least twice higher than the acceptable levels as per the U.S. standards and the release of lead from ZLR3 was under the regulatory limit (3.9 mg L^{-1}), denoting that Pb release is controlled and not a threat to the environment. The general solubility phenomena for pure Pb minerals in decreasing order of solubility is $\text{PbO} = \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 > \text{PbSO}_4$ (Bataillard et al., 2003). The presence of PbSO_4 (due to the sulfuric acid leaching of primary ores, lead sulfate accumulates) was often observed in similar zinc hydrometallurgical residues in the past (Turan et al., 2004; Li et al., 2013; Min et al., 2013)

A study (data not shown) performed to understand leaching kinetics of metals released in the presence of nitric acid (at pH 2.5) showed that within 6 h, 4 g Fe kg^{-1} to 10 g Fe kg^{-1} ZLR was found soluble. But after 48 h the soluble Fe concentration decreased several folds, indicating the precipitation of secondary Fe-minerals (concomitant decrease of Pb and Al in all ZLRs and Cu, Mn and Zn in ZLR3 was observed). In Fe and sulfate rich solutions (acidic pH), precipitation of jarosite, schwertmannite, ferrihydrite most likely occurred and in the mild acidic region the possibility of Al-hydroxysulfate precipitation is also high (Lottermoser, 2010). These minerals were shown to co-precipitate Al with divalent metal ions such as Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} . Also, Fe and Al solubility curves (data not shown) show a great similarity in the case of ZLR2 and ZLR3 hinting the formation of colloids. However, the model does not predict the formation of any schwertmannite precipitates, instead it predicts the precipitation of

$\text{Fe}(\text{OH})_2 \cdot 7\text{Cl}_3$ only. This may be due to the lower input Fe concentration (based on the leachate composition at 48 h) used for the modelling.

3.5. Conclusions

- The ZLRs are polymetallic in nature, rich in Pb (1.5% – 2.5%) and Zn (2.5% - 5%) and also contain Al, Cd, Cu, Fe and Mn. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was the main crystalline mineral phase in all the investigated ZLRs.
- According to the USEPA TCLP test, the three zinc leach residues investigated can be classified as hazardous waste. But the potential toxicity of the most recently produced residue ZLR3 is much less than the decades old ZLR 1 and 2. A higher bioavailable heavy metal (Cd, Cu, Pb and Zn) concentration in the acid extractable fractions of accelerated BCR experiments endorses this.
- The pH stat leaching test showed that maximum leaching of Zn and other metals was found at acidic pH (2.5). The experimental data and the geochemical modeling show that the Zn leaching is controlled by Zn sulfate and carbonate and likely by the dissolution of Zn co-precipitated with Al/Fe oxides. Zn solubility is thus controlled by the precipitation of smithsonite, zincite and hydrozincite minerals under alkaline conditions.

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Chapter 4

Leaching and selective zinc recovery from acidic leachates of zinc metallurgical leach residues

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Abstract:

Zinc (Zn) leaching yields and kinetics from three different zinc plant leach residues (ZLR) generated in different periods (ZLR1 > 30 years, ZLR2 5 - 30 years and ZLR3 < 2 years) were investigated. The factors affecting the Zn leaching rate such as solid to liquid ratio, temperature, acid concentration and agitation were optimized. Under optimum conditions, 46.2 (± 4.3), 23.3 (± 2.7) and 17.6 (± 1.2) mg of Zn can be extracted from per g of ZLR1, ZLR2 and ZLR3, respectively. The Zn leaching kinetics of ZLRs follow the shrinking core diffusion model. The activation energy required to leach Zn from ZLR1, ZLR2 and ZLR3 were estimated to be 2.24 kcal/mol, 6.63 kcal/mol and 11.7 kcal/mol, respectively, by the Arrhenius equation. Order of the reaction with respect to the sulfuric acid concentration was also determined as 0.20, 0.56, and 0.87 for ZLR1, ZLR2 and ZLR3, respectively. Zn was selectively recovered from the leachates by adjusting the initial pH and by the addition of sodium hydroxide and sodium sulfide. More than 90% of Zn was selectively recovered as sphalerite from the ZLR polymetallic leachates by chemical sulfide precipitation.

Key words: Leaching kinetics, Metallurgical wastes, Shrinking core model, Selective recovery, Metal sulfide precipitation

4.1.Introduction:

Zinc (Zn) is one of the most widely used metals that finds application in cosmetics, constructions, automobiles, electronics and healthcare (Lew, 2008; Xin et al., 2013). As per the International Lead and Zinc Study Group (ILZSG), Zn demand and usage have increased many folds in the recent years, e.g. in 2015 the demand & usage for Zn exceeds the supply by 151000 tons (ILZSG, 2015). Consequently, there is a depletion of high grade Zn sulfide ores, which are the common source of Zn metal production (Han et al., 2014). Hence in recent years, extraction of Zn from non-sulfidic ores such as carbonate ores, silicate ores and secondary resources is explored (Jha et al., 2001; Abkhoshk et al., 2014). Roasting-leaching-electrowinning hydrometallurgical processes contribute 85% of the Zn production and the remaining are pyrometallurgical processes. During the pyro/hydro-metallurgical production of Zn from primary ores, various mineral processing wastes are generated such as Zn leach residues (Chapter 2).

Zn-plant leaching residues (ZLR) are usually rich in Zn and other metals. Leaching of Zn from ZLRs is challenging because most of the Zn is usually associated to stable spinel zinc ferrites (Raghavan et al., 1998; Peng et al., 2012). Leaching of Zn from ZLRs by sonoleaching (Wang et al., 2013; Xin et al., 2013) or by a combination of pyro and hydrometallurgical processes (Yan et al., 2014) has been proposed. Leaching and recovery of metals such as Cd, Ni, Pb and Ag from ZLRs have also been reported. Lead is the most often found and extracted metal from the ZLRs (Turan et al., 2004; Ruşen et al., 2008; Şahin and Erdem, 2015), sometimes cadmium (Safarzadeh et al., 2009; Gharabaghi et al., 2012), nickel (Gharabaghi et al., 2013) and precious metals like silver have also been observed in association with ZLRs (Ju et al., 2011; Xianjin et al., 2011).

In metallurgy, kinetic analysis of solid-fluid heterogeneous reactions is of great importance at the industrial level as this is the basis for scale-up and reactor designs (Dhawan et al., 2011). The change of solid size is an important aspect in the solid-fluid heterogeneous reaction kinetics. The model in which the size of the solid changes significantly, is more suitable for a hydrometallurgy process and termed as shrinking core model (SCM) (Levenspiel, 1999). As per the SCM, the reaction rate can be controlled by three processes either individually or in combination. These three processes are diffusion through the liquid film (Uchenna et al., 2015), chemical reaction at the solid surface ((Dhawan et al., 2011) and solid product diffusion through the ash layer (Xin et al., 2013).

Few researchers (Filippou et al., 1992; Turan et al., 2004; Ruşen et al., 2008; Hollagh et al., 2013) have reported on the Zn leaching and kinetics from different Zn containing waste materials using sulfuric acid medium. However, based on the phase composition of the wastes, leaching kinetics and extraction efficiency of the desired metals will vary. For instance, Zn leaching and recovery from an Iran based Zn plant purification residue and Zn ferrite rich hydrometallurgical residue by sulfuric acid follows the shrinking core model and grain pore chemical reaction model, respectively. The activation energy in both the cases also differs greatly: the Iran based Zn plant hydrometallurgical residue reported an activation energy of 0.24 kcal/mol, while zinc ferrite rich hydrometallurgical residue has an apparent activation energy of 15.5 kcal/mol (Filippou et al., 1992; Hollagh et al., 2013). Therefore, it can be concluded that the leaching efficiency and kinetic models are strongly dependent of the phase composition of the particular wastes. Zn recovery from the leachate is indeed the final and important process in the metallurgy. However, the leachate is always polymetallic and thus, a selective recovery process is needed. Recovery of Zn from the leachate has been studied using solvent extraction, electrolysis and precipitation (Radzymińska-Lenarcik et al., 2015). Sulfide precipitation processes are attractive as they are relatively simple to operate and offer lower solubility and potential selective recovery (Lewis, 2010).

The main objective of this study was to assess the technical viability of using ZLR as a secondary resource. The study also addresses several specific objectives such as (i) elucidation of optimum conditions for the extraction of Zn and the leaching kinetics of Zn dissolution, (ii) investigation of the effects of sulfuric acid concentration, temperature, solid to liquid phase ratio and agitation rates on Zn leachability from these ZLR, (iii) estimation of the reaction kinetics were studied using different kinetic models and the required activation energy and the reaction order and (iv) study of the selective recovery of zinc from the iron-rich acid leachates by the combination of chemical hydroxide/sulfide precipitation.

4.2. Materials and Methods

4.2.1. Zinc plant leaching residues

The ZLRs used in this study were collected from a currently operating Zn metallurgical plant located in Três Marias (Minas Gerais, Brazil). Three different ZLRs based on their age of production and landfilling of this plant (ZLR1 > 30 years, ZLR2 5- 30 years and ZLR3 < 2 years) were collected. The elemental composition studies reveal that these samples are rich in Zn (5% in ZLR1, 2.7% ZLR2 & 2.5% in ZLR3). ZLRs are also found to contain iron (6.5% -

11.5%), calcium (7% - 9%) and trace amounts of few other heavy metals (Cu, Cd, and Pb). The pH of the samples was mild acidic (pH 5.6 – 6.6) and also the samples contain SiO₂ (25% - 30%) and sulfur (27% - 32%). The mineralogical characterization of the studied ZLRs were described elsewhere (Chapter 3).

4.2.2. Phase composition of Zn in ZLRs

4.2.2.1. Chemical extraction procedure

A sequential extraction procedure (Zhang, 1992; Li et al., 2013) was used to understand the chemical forms of Zn present in the ZLRs. 1 gram of ZLRs was placed in a 250 mL Erlenmeyer flask and particular chemical phases of Zn were dissolved by different solvents/temperature combinations. The detailed stepwise procedure, solvents used and the reaction conditions such as temperature and agitation are provided in Table 4.1. After each step, the leachate was centrifuged at 4000 g for 10 minutes (Hettich Rotina 420) to separate the supernatant and the residue. The supernatant was filtered (0.45 µm, nitrocellulose filters), acidified (0.5% HNO₃) and analyzed for its Zn concentration by atomic absorption spectroscopy (Perkin Elmer AAnalyst 200). The residue was then subjected to the next step.

Table 4.1 – Extracting agent and reaction conditions of the sequential chemical phase extraction of zinc from the ZLRs (Zhang, 1992; Li et al., 2013).

Chemical phases of Zn	Extraction agent	Agitation / time	Temperature
F1. Zinc sulfates	100 mL of ultrapure water	150 rpm / 60 minutes	20 ± 2 °C
F2. Zinc oxides	100 mL of ammonium acetate (150 g/L)	150 rpm / 120 minutes	20 ± 2 °C
F3. Zinc silicates	100 mL of 20% ethanoic acid	150 rpm / 60 minutes	100 ± 2 °C
F4. Zinc ferrites	100 mL of 9% HCl + 7% H ₃ PO ₄	150 rpm / 90 minutes	100 ± 2 °C
F5. Other forms of Zn	Aqua regia*	- / 120 minutes	100 ± 2 °C

* - Hot plate aqua regia described elsewhere (Chapter 3)

4.2.2.2. X-ray absorption near edge spectroscopy

ZLR samples prior and after acidic leaching (at pH 2.5) were prepared for Zn speciation studies at Zn K-edge using X-ray absorption near edge spectroscopy (XANES). The spectra were collected on the DUBBLE (Dutch-Belgian beamline) BM26A of the European Synchrotron Radiation Facility (Grenoble, France) (Borsboom et al., 1998). Spectra were also collected for Zn reference compounds, including ZnSO₄ (goslarite), ZnO (zincite), Zn₅(CO₃)₂(OH)₆ (hydrozincite), Zn₂SiO₄ (willemite), Zn₄Si₂O₇(OH)₂.H₂O (hemimorphite) and ZnFe₂O₄ (franklinite). Spectra for ZnS (sphalerite) were taken from previous experiments of Villa-Gomez et al. (2014). The detailed procedure of data acquisition and the analysis is described in the supporting information of Villa-Gomez et al. (2014).

4.2.3. Leaching experiments

ZLRs (1, 2 and 3) were investigated for the maximum leaching of Zn by using sulfuric acid (Merck, 95% - 98%, density 1.84 g/mL). The leaching experiments were carried out in 250 mL Erlenmeyer flasks with a working volume of 100 mL. To maintain the desired temperature and agitation rate, the experiments were carried out in a temperature controlled incubator shaker (IKA KS 4000i control). The effects of temperature (20 - 80, ± 2 °C), acid concentration (0.1 - 1.5 M sulfuric acid), solid to liquid phase ratio (1 - 20%) and agitation speed (50 - 450 rpm) on Zn leaching from ZLRs were determined. The experiments were carried out in triplicates and the average and standard deviations were reported. Samples (leachates) were collected at regular intervals and filtered using 0.45 µm (nitrocellulose) syringe filters. The filtered leachates were acidified using 0.5% HNO₃ and stored for analyses of the metal concentrations by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300 Perkin Elmer).

4.2.4. Kinetic model

The kinetic analysis of the Zn leaching from the ZLRs by H₂SO₄ was investigated by the SCM (Fig. 4.1). If the heterogeneous Zn dissolution from the ZLR by sulfuric acid was controlled by the chemical reaction at the mineral surface, then the dissolution kinetics can be

expressed as 1 (assuming that the Zn containing minerals have a spherical size) (Levenspiel, 2008):

$$1 - (1 - \alpha)^{1/3} = K_c \cdot t \quad (1)$$

Where:

α - fraction of Zn reacted

t – leaching time (mins)

K_c (chemical reaction rate constant, dimensionless)

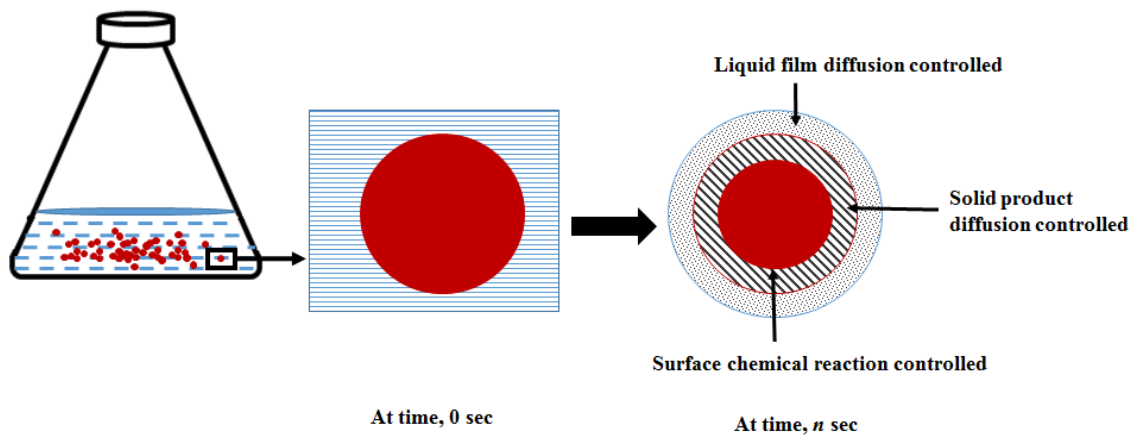


Fig. 4.1. A schematic diagram depicting the various shrinking core kinetics phenomena.

Likewise if diffusion of the leaching agent through the solid product layer around the unreacted core is the rate-limiting step, then the kinetics were determined by Equation 2:

$$1 - 3(1 - \alpha)^{2/3} - 2(1 - \alpha) = K_s \cdot t \quad (2)$$

Where: K_s (solid product layer diffusion rate constant, dimensionless)

Similarly, if the reaction rate is controlled by diffusion of the leaching agent through the liquid film formed, then Equation 3 is applied to determine the kinetics:

$$1 - (1 - \alpha)^{2/3} = K_L \cdot t \quad (3)$$

Where: K_L (liquid film diffusion rate constant, dimensionless)

The activation energy required for the sulfuric acid leaching of Zn from the ZLRs was determined by using the Arrhenius plot. Determination of the activation energy is important to understand more about the kinetics of the leaching process. The Arrhenius equation for the activation energy is given in Equation 4.

$$K_D = K_0 \cdot \exp(-E_a/RT) \quad (4)$$

Where:

K_D , is the diffusion rate constant as a function of temperature

K_0 , is the frequency factor

E_a , is the apparent activation energy

R , is the universal gas constant (8.314 KJ) and T , is the temperature

Integration of equation 4, equation 5

$$\ln K_D = \ln K_0 - \frac{E_a}{RT} \quad (5)$$

Please note that α is fraction of Zn reacted and 't' is leaching time in all the above reactions.

4.2.5. Selective precipitation of Zn from ZLR leachates

4.2.5.1. Prediction of selective sulfide precipitation

Prediction of the selective precipitation of Zn from the acid leachates was carried out by using visual MINTEQ V3.1. Visual MINTEQ is a chemical equilibrium model that can predict the speciation, solubility, adsorption and precipitation of metals at equilibrium (2). Input molar concentrations of each metal (Zn^{2+} , Cu^{2+} , Cd^{2+} , Mn^{2+} , Al^{3+} , Ca^{2+} , Mg^{2+} , Fe^{2+} , K^+ , Na^+ , Cl^- , PO_4^{3-} , SO_4^{2-} and NO_3^-) were provided based on the leachate composition obtained at the optimized leaching conditions. Different dissolved sulfide concentrations were provided and the pH was varied from 0.5 to 7.5 at 0.5 intervals. The temperature was constantly maintained at 20 °C and oversaturated solids were allowed to precipitate. Concentrations of the dissolved metals and the amount of sulfide precipitates were obtained in the output.

4.2.5.2. Sulfide precipitation experiments

25 mL ZLR leachates were transferred to 100 mL glass bottles and the pH of the leachates were adjusted to 0.5, 1.5, 3.0, 4.0, 6.5 and 7.5. The dissolved sulfide (100 mg L^{-1}) solution was freshly prepared by dissolving 0.75 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in 0.1 M NaOH. 25 mL of dissolved sulfide (100 mg L^{-1}) solution was added to the pH adjusted leachates. The glass bottles were closed with an air tight septum and agitated (150 rpm) for 1 hour at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$). Then, the solutions were centrifuged (Hermle Z200A) (6000 rpm for 10 minutes) and the supernatant was analyzed for its dissolved metal concentrations.

4.2.6. Characterization of the ZnS precipitates

The metal sulfide precipitates were separated by centrifugation (6000 rpm for 10 minutes). The precipitates were air dried at room temperature. Aquaregia digestion, X-ray diffraction (XRD) and scanning electron microscope – energy dispersive X-ray spectroscopy (SEM-EDS) analyses were also done for the dried metal-sulfide. X-ray diffraction (XRD) studies were carried out on a Bruker D8 Advance diffractometer equipped with an energy dispersion Sol-X detector with copper radiation ($\text{Cu K}\alpha$, $\lambda = 0.15406 \text{ nm}$). The acquisition was recorded between 2° and 80° , with a 0.02° scan step and 1 s step time. Prior to XRD analysis, the precipitates were ground to powder using a pestle and mortar and dried at $25 \text{ }^\circ\text{C}$. Scanning electron microscope – Energy dispersive X-Ray spectroscopy analyses (SEM-EDS, Jeol JSM 6010LA) at 10-20 KeV and high vacuum conditions were also done for the dried metal-sulfide precipitates. Total metal content of the precipitates was determined by modified hotplate aqua-regia digestion (Chen and Ma, 2001). A volume of 9 mL of HCl (37%) and 3 mL of HNO_3 (65%) was added to 1.0 g of solid sample taken in a digestion flask. The flasks were placed in a digester (DigiBlock ED16S, Lab Tech) heated to a temperature of 100°C for 2 h, covered with a watch glass and left to cool at room temperature for 2 h. Then, 20 mL of HNO_3 (2%) was added on the sides of the flask to recover metals and the solid residues were separated by filtration through Whatman grade 5 filter paper (mesh size $2.5 \text{ }\mu\text{m}$). The filtrate was then made up to 100 mL with ultrapure water. The final solution was analyzed for its metal concentrations

4.3. Results

4.3.1. Chemical phase composition of Zn in ZLRs

The phase compositions of Zn in ZLRs were investigated using chemical extraction procedure (CEP) and XANES analysis. Table 4.2 shows that the Zn is mainly associated with sulfates, oxides, silicates and ferrites. Generally, zinc sulfate concentrations in the studied ZLRs were lower than the other phases. Zinc associated with Fe-minerals (Zn-ferrites or ZnO co-precipitated or Zn sorbed onto Fe-oxides) is found increasing in ZLR1 (1.15 ± 0.02 wt % per g) < ZLR2 (1.46 ± 0.06 wt % per g) < ZLR3 (1.79 ± 0.08 wt % per g) while Zn associated with silicate phases are found decreasing i.e. the Zn-silicate fractions are higher in the decades old ZLR1 and lower in the most recent ZLR3.

Table 4.2. Zn - Chemical phase composition of the ZLRs investigated.

Fraction	ZLR1 (Wt % per gram)	ZLR2 (Wt % per gram)	ZLR3 (Wt % per gram)
Zinc sulfates	0.37 ± 0.05	0.05 ± 0.01	0.14 ± 0.01
Zinc oxides	0.49 ± 0.02	0.22 ± 0.02	0.04 ± 0.01
Zinc silicates	2.80 ± 0.08	0.80 ± 0.11	0.13 ± 0.02
Zinc ferrites	1.15 ± 0.02	1.46 ± 0.06	1.79 ± 0.08
Other Zn forms	0.20 ± 0.04	0.21 ± 0.06	0.42 ± 0.04

Zn K-edge XANES spectra for the raw ZLRs, acid leached ZLRs (at pH 2.5) and selected Zn (II) reference compounds are shown in Fig. 4.2. From the XANES spectra, Zn speciation in ZLR1 is very different than the Zn speciation in ZLR2 and ZLR3. Two well-defined edge peaks were identified at 9665.3 eV and 9669 eV for both ZLR2 and ZLR3 while a strong peak at 9668.7 eV was identified for ZLR1. The energy position of the ZLR1 and second feature of ZLR2 and ZLR3 is similar to the peaks of ZnSO₄, ZnO and Zn₅(CO₃)₂(OH)₆ compounds. A small shoulder of ZLR1 at 9665 eV may be due to zinc silicate and zinc ferrite. However, the white line intensity registered, which depends on matrix elements, is quite different from zinc

silicate and zinc ferrite, particularly the steep drop in the intensity in ZLR1, ZLR2 and ZLR3 samples after the peak. This drop, however, was completely missing in zinc silicate and zinc ferrite further validating that all the ZLR samples are mixture of various Zn compounds as indicated by sequential extraction.

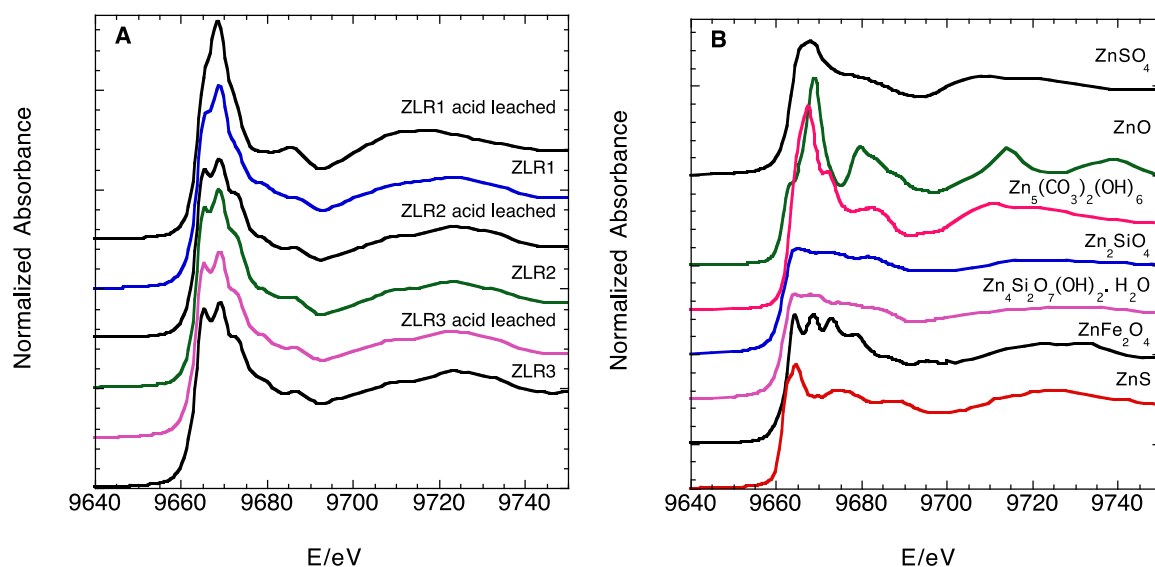


Fig. 4.2. Zn K-edge XANES spectra for selected samples of (a) the Zn(II) ZLR harboring samples; (b) Zn(II) reference compounds.

4.3.2. Factors influencing Zn leaching from ZLRs

Different leaching agents such as sulfuric, nitric, hydrochloric and citric acid were tested for their Zn leaching efficiency from ZLRs. Based on the preliminary results (data not shown), sulfuric acid was selected for further leaching experiments and 6 hours was selected as the optimal leaching time. The influence of the agitation rates on the Zn leaching yield from ZLRs was studied by increasing the agitation rate from 50 rpm, 150 rpm, 250 rpm and 350 rpm at 80 °C containing a solid/liquid ratio 1:50 g mL⁻¹ with 1 M sulfuric acid for 6 hours (Fig. 4.3).

Increasing the agitation speed (150 – 450 rpm) was not significantly affecting (< 5% difference) the leaching yield of Zn from the ZLRs (except for the very low agitation, 50 rpm, Fig. 4.3). The percentage of the leaching efficiency of Zn increased only by 3% (for ZLR 1), 5% (for ZLR2) and 5% (for ZLR3), when the agitation rate was increased from 150 rpm to 450 rpm. Based on the results, 150 rpm was found to be optimum, and subsequently used in all further experiments. Fig. 4.4 shows the effect of temperature on the leaching of Zn from the

ZLRs as a function of time. The results show that the temperature has a negligible effect on the leaching of Zn from ZLR1, but significantly impacts Zn leached from ZLR 2 and 3.

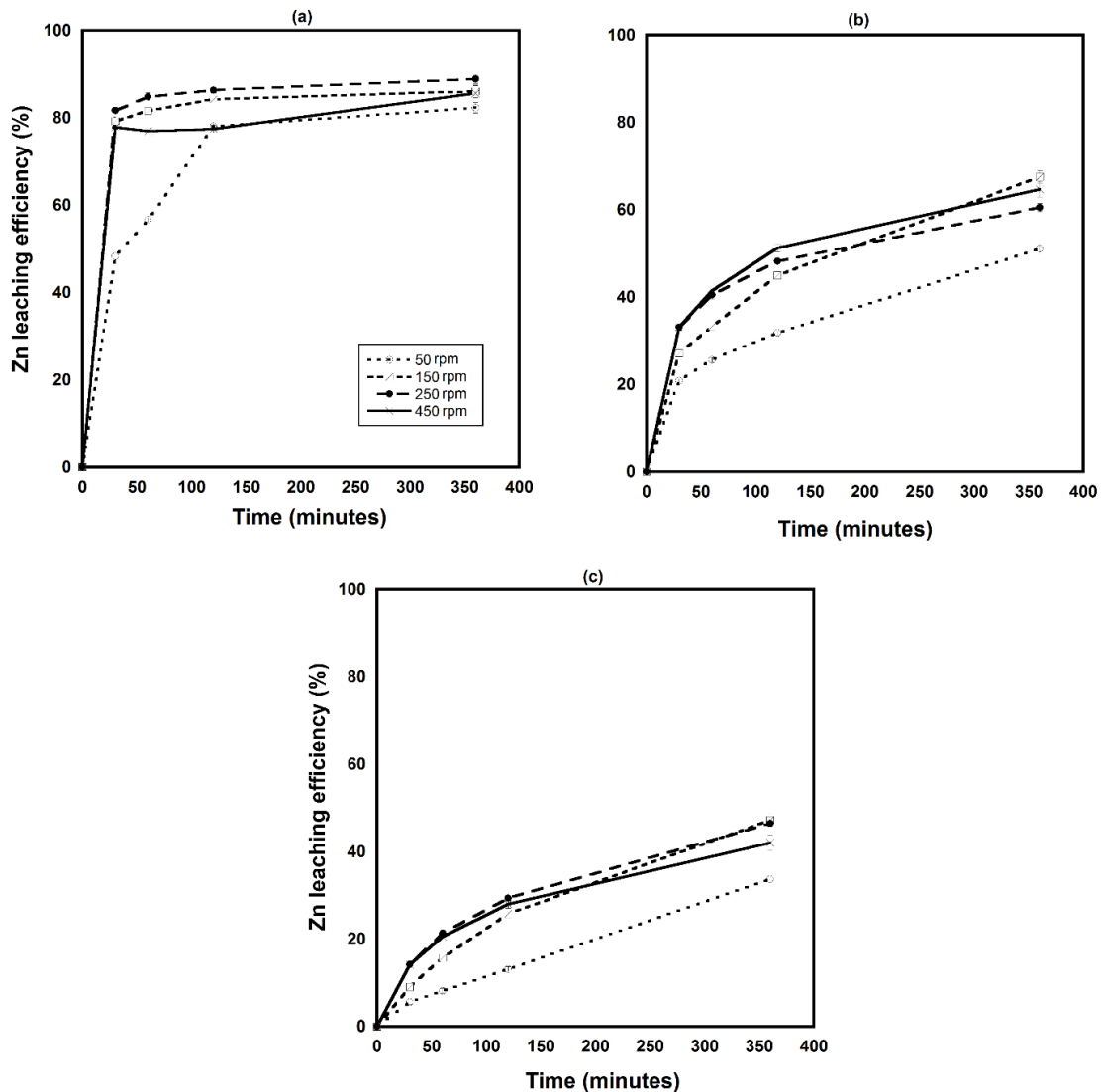


Fig. 4.3. Effect of agitation rates on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (Pulp density – 2%, Temperature – 80 °C, 1 M Sulfuric acid) (Legends shown inside panel (a)).

When the temperature increased from 20 to 80 °C, the leaching rate of Zn from ZLR1 was increased only by 2 % (84% ($\pm 1\%$) - 86% ($\pm 2\%$)). But in the case of ZLR2 and ZLR3, the temperature variation shows a significant increase in the leaching efficiency of 27 % (from 39% ($\pm 1\%$) to 67% ($\pm 1\%$)) for ZLR2 and 34% (from 13% ($\pm 3\%$) to 47% ($\pm 2\%$)) for ZLR3.

Fig. 4.5 illustrates the effect of the sulfuric acid concentration on Zn leaching. The sulfuric acid concentration was increased from 0.1 M to 1.5 M and the leaching efficiency was

generally directly proportional to the acid concentration, especially for ZLR2 and ZLR3. However, the increase of sulfuric acid concentration does not significantly affect the leaching rate in the case of ZLR1. The Zn leaching yield from ZLR1 was increased only from 84% ($\pm 1\%$) to 86% ($\pm 2\%$) when the acid concentration was increased from 0.1 M to 1.5 M. But the increase in the acid concentration shows a considerable effect on the Zn leaching yield from ZLR2 (increased from 41% ($\pm 1\%$) to 69% ($\pm 2\%$)) and ZLR3 (increased from 19% ($\pm 2\%$) to 50% ($\pm 1\%$)) after 6 hours of leaching.

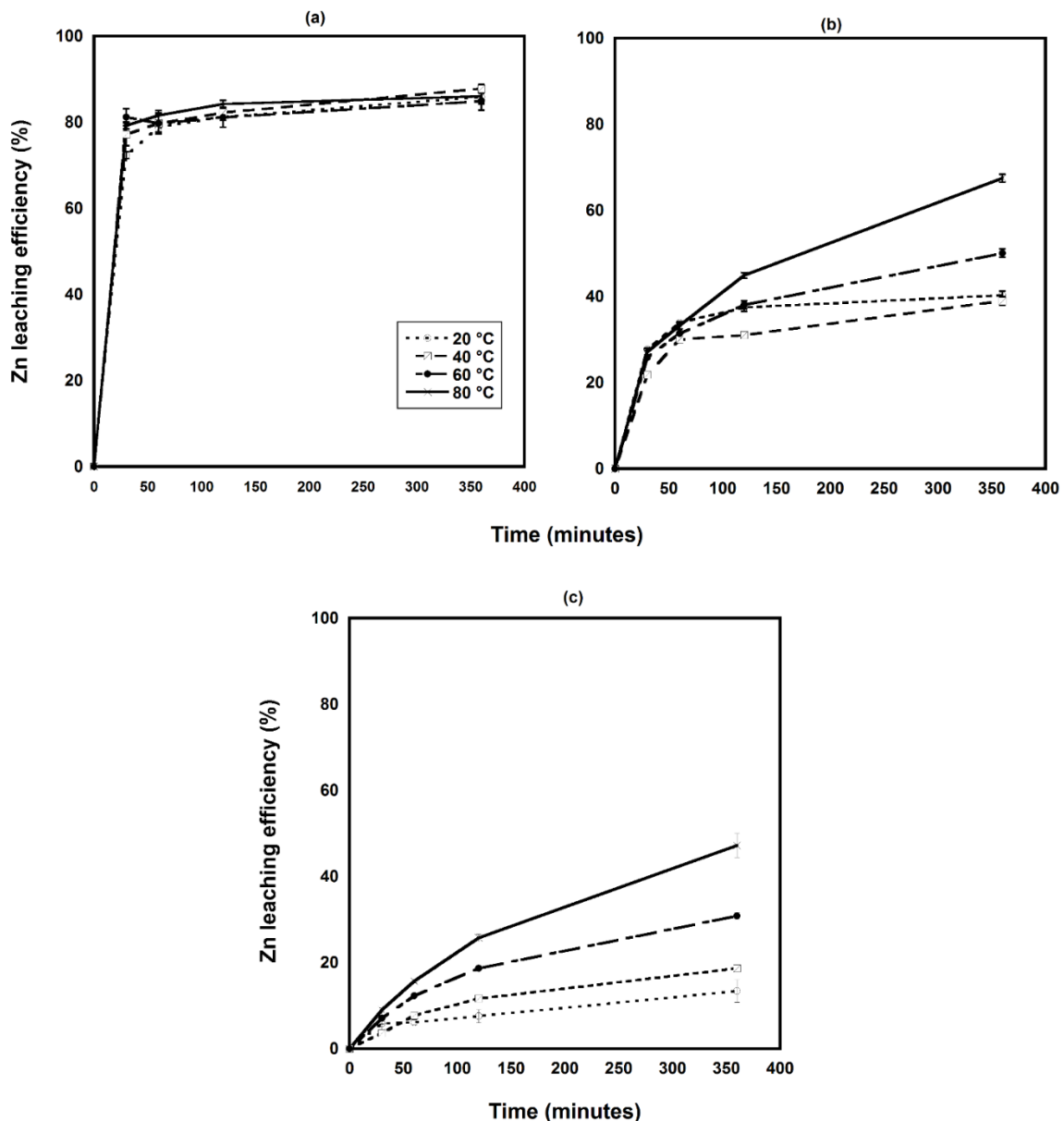


Fig. 4.4. Effect of temperature on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (Pulp density – 2%, Agitation – 150 rpm, 1 M Sulfuric acid) (Legends shown inside panel (a)).

The effect of solid to liquid ratio was investigated on the dissolution of Zn from ZLRs by varying the ratio to 1:100, 1:50, 1:20, 1:10 and 1:5 g mL⁻¹. Fig. 4.6 shows the effect of varying the solid to liquid ratio (80 °C, 150 rpm with 1M sulfuric acid concentration for 6 hours). Fig. 4.6 shows that the increase in the pulp density generally decreases the dissolution yield of Zn from ZLRs. However the decrease in the leaching efficiency is not significant (< 5%) for all the ZLRs investigated. Based on the experimental results (Figures 4.3, 4.4, 4.5 and 4.6), 80 °C, 250 rpm, 1.5 M sulfuric acid and 2% solid to liquid phase ratio were selected as optimum conditions for the maximum leaching of Zn from ZLRs and the leaching time was extended to 24 hours. The results disclose that more than 90%, 85% and 70% of Zn can be leached under these conditions.

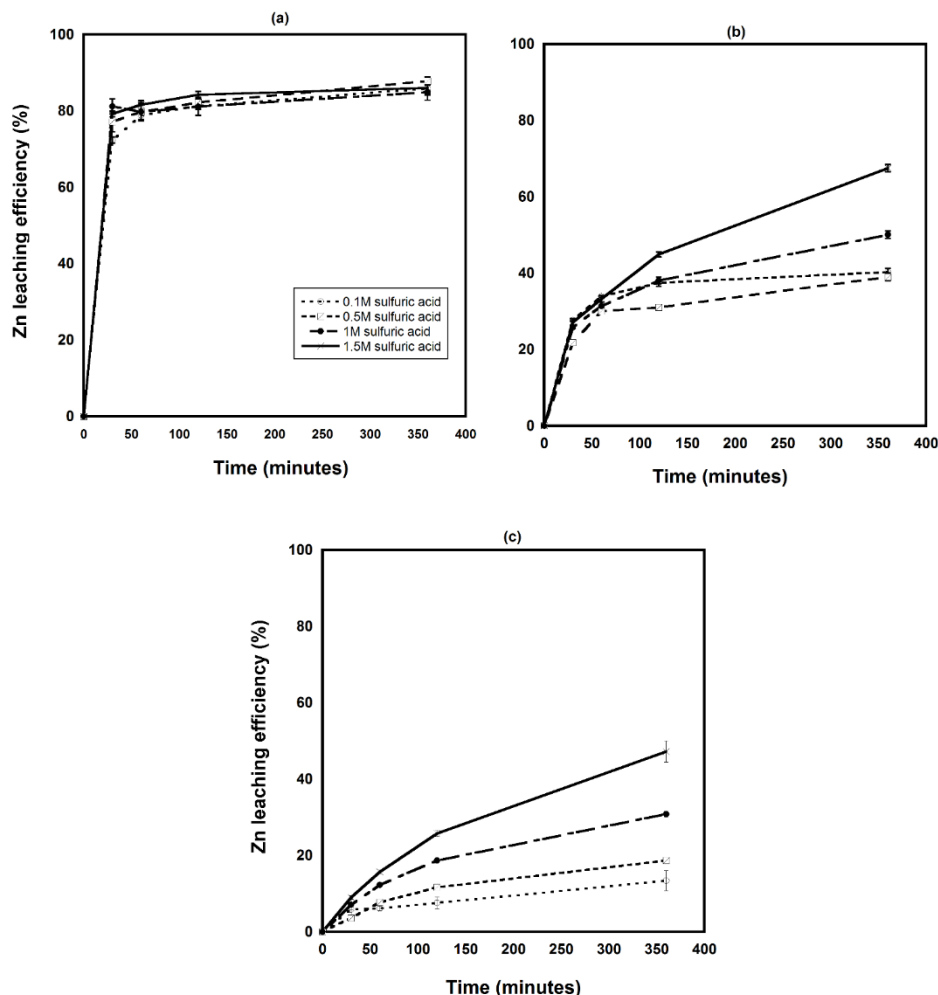


Fig. 4.5. Effect of sulfuric acid concentration on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (Pulp density – 2%, Temperature – 80 °C, Agitation 150 rpm) (Legends shown inside panel (a)).

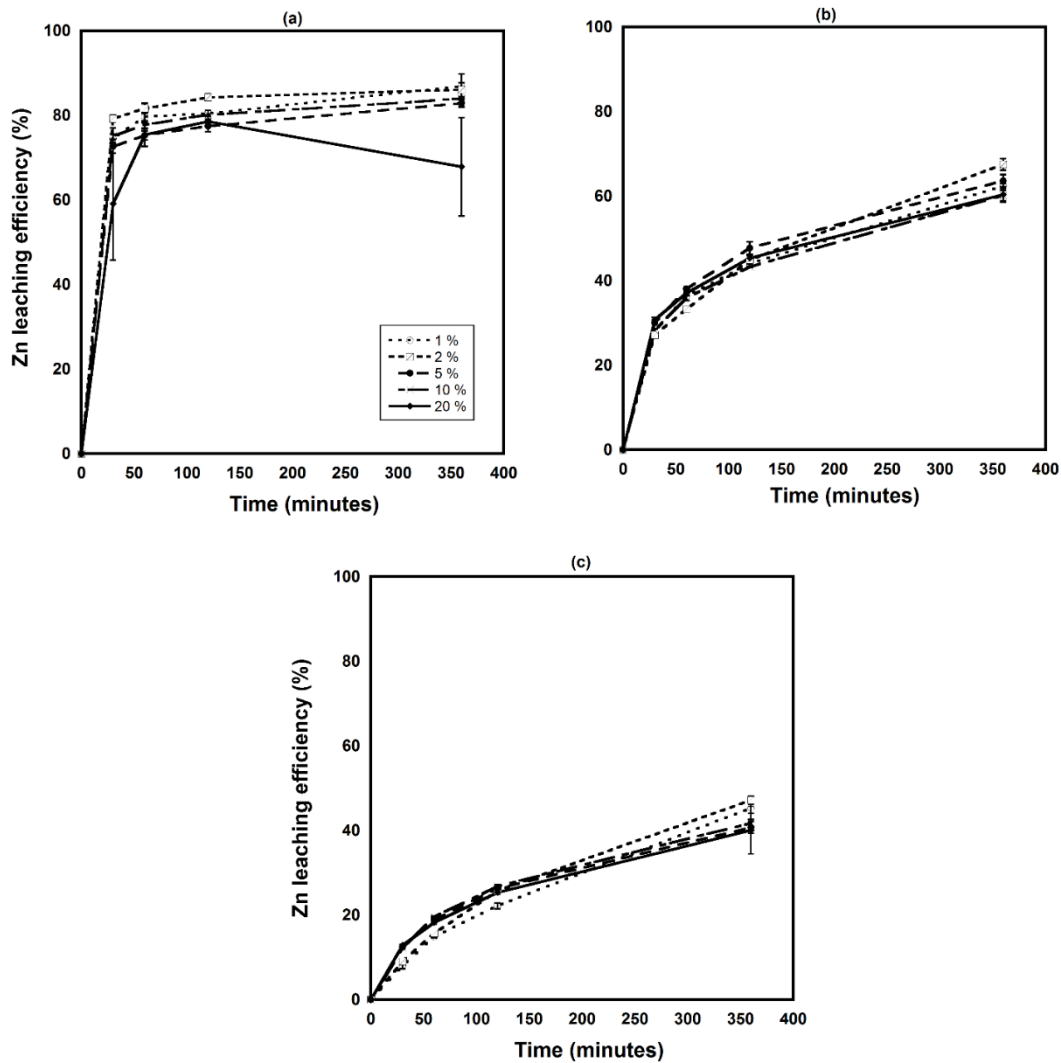


Fig. 4.6. Effect of solid to liquid phase ratio on the leaching of Zn from ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) (1 M sulfuric acid, Temperature – 80 °C, Agitation 150 rpm) (Legends shown inside panel (a)).

4.3.3. Kinetic analysis of Zn leaching from the ZLRs investigated.

The kinetic analyses for the Zn leaching from the ZLRs were investigated using the SCM. The relationship between, $1-(1-x)^{2/3}$ (liquid film diffusion) and $1-(1-x)^{1/3}$ (chemical reaction model), $1-3(1-x)^{2/3}+2(1-x)$ (solid product diffusion model) and experimental values against time were plotted and is given in Fig. 4.7. The fraction of Zn leached (α) at optimum conditions were also provided in Fig. 4.7. The results show that solid product diffusion was found to be the best fitting model with high regression coefficient. The Zn leaching from ZLRs

follows the solid product diffusion with a good regression coefficient (ZLR1 R^2 0.98; ZLR2 R^2 0.98 and ZLR3 R^2 0.99) (Fig. 4.7).

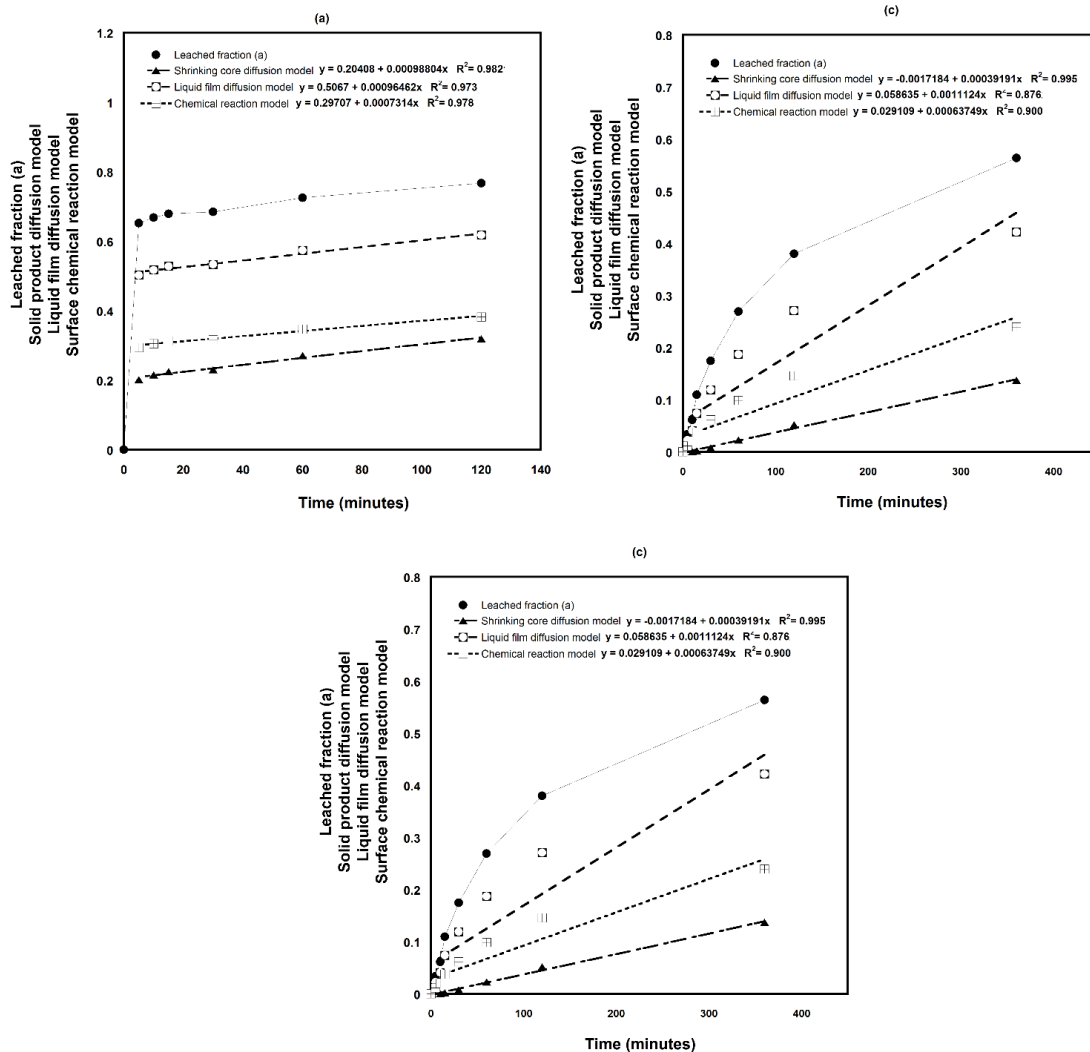


Fig. 4.7. Kinetic model fits of ZLRs ((a) ZLR1, (b) ZLR2 and (c) ZLR3) to experimental results of Zn leaching at temperature – 80 °C, agitation speed – 250 rpm, acid concentration – 1.5 M H₂SO₄ and pulp density – 2 %).

Based on the experimental values on the effect of temperature, the liquid film diffusion (data not shown), the chemical reaction model (data not shown) and the solid product diffusion model (Fig. 4.8a) against time were plotted. The apparent activation energy values of Zn dissolution were calculated as 2.24 kcal/mol, 6.63 kcal/mol and 11.7 kcal/mol for ZLR1, ZLR2, and ZLR3, respectively. Similar to the activation energy plot, the order of the acid concentration was calculated based on the leached fractions of Zn. Fig. 4.8b shows the fractions of Zn leached at various sulfuric acid concentrations were plotted for shrinking core solid product diffusion

(surface chemical reaction and liquid film diffusion models, data not shown). The kinetics analysis showed that the sulfuric acid concentration does not have a significant effect on the Zn leaching from ZLR1, but it does play an important role in the leaching of Zn from ZLR2 and ZLR3. The order of the reactions with respect to the sulfuric acid concentration was calculated as 0.2, 0.56 and 0.87 for ZLR1, ZLR2 and ZLR3, respectively.

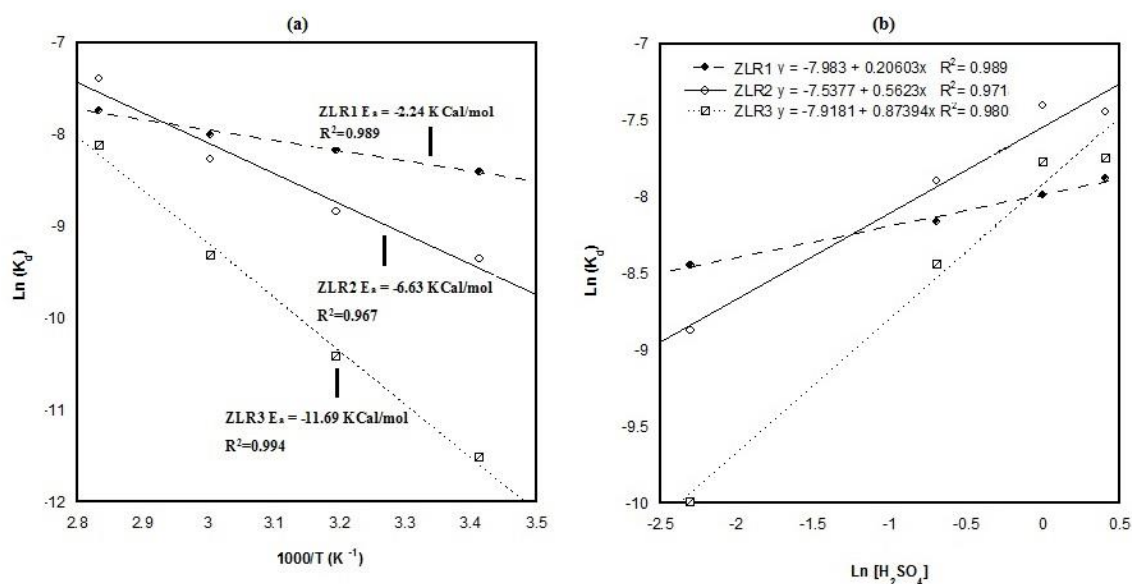


Fig. 4.8. (a) Arrhenius plot for the determination of activation energy and (b) plot for the order of sulfuric acid concentration.

4.3.4. Selective recovery of Zn from ZLR leachates

The effects of the initial pH on the metal hydroxides removal and metal sulfide precipitation were examined at different initial pH values (0.5, 1.5, 3.0, 4.0, 6.5 & 7.5) (Fig. 4.9). It was observed that there were no detectable Zn losses until the pH is adjusted to 6.5, but significant amounts of cadmium, copper and iron can be removed by this step. Table 4.3 shows more than 95% of Cd and Fe and 60% of Cu were removed by sodium sulfide/hydroxide addition (with no detectable Zn loss) until pH 4.

Table 4.3. Composition of leachate (ZLR1) and amounts of metals precipitated (%) at each step

		Zn	Cu	Cd	Fe
Leachate composition (mg L⁻¹)		904	27	11	1103
		Metal precipitation (%)			
Leachate (pH units)	Sulfide (mg L⁻¹)	Zn	Cu	Cd	Fe
Adjusted pH 1.5	-	-	10	-	-
Adjusted pH 1.5	100 (0.1 M NaOH)	-	51	98	75
Adjusted pH 4.0	-	-	-	-	19
Adjusted pH 4.0	100 (H ₂ O)	92	37	1	2

Table 4.3 shows selective recovery of Zn from the ZLR leachate is possible by the combination of pH adjustment and sulfide precipitation and a customized hydrometallurgical process for the selective recovery of Zn from the ZLRs is proposed (Fig. 4.10). The ZLRs leachate pH is first adjusted to pH 1.5 and 100 mg L⁻¹ of dissolved sulfide precipitates 51% of Cu. After the Cu-precipitate is removed (by centrifugation), the supernatant pH is again adjusted to pH 4 to remove other remaining impurities (Cd, Cu and Fe). Addition of 100 mg L⁻¹ of dissolved sulfide will precipitate >90% dissolved of the Zn from the leachate. Fig. 4.11 shows the ZnS precipitation kinetics of the Cu, Cd, and Fe depleted ZLRs. The ZnS precipitation starts just after the addition of the sulfide and it can be observed that most of the Zn is precipitated within 5 minutes of the sulfide dosage.

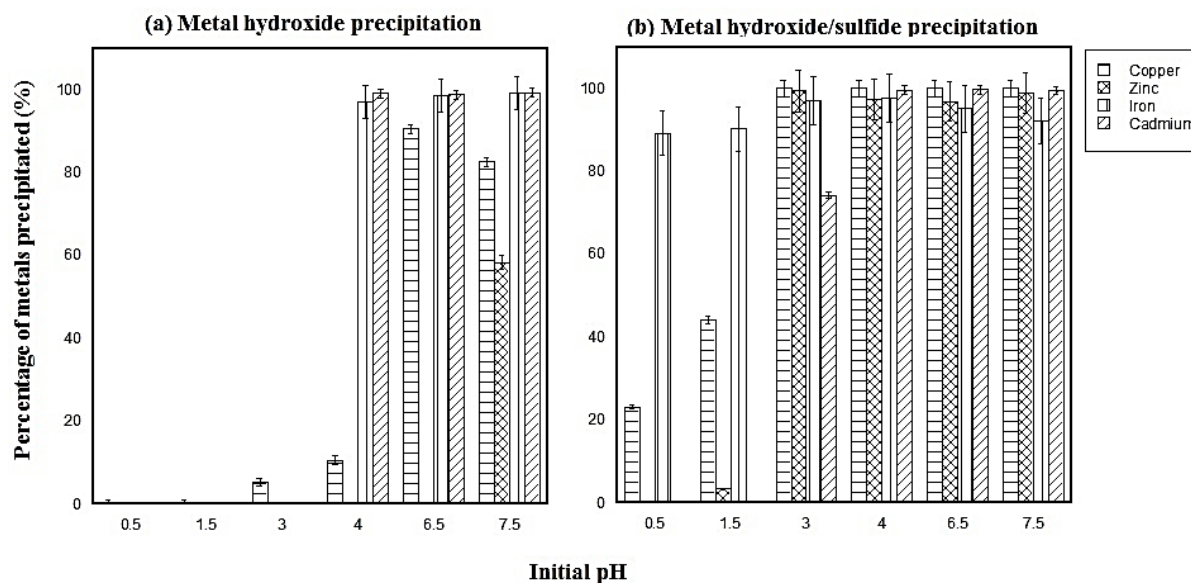


Fig. 4.9. Metal precipitation versus initial pH, from ZLR1 leachate, a – percentage of metal hydroxide precipitated after initial pH adjusted with 10 M NaOH, b – percentage of metals precipitated after the addition of 100 mg/L of dissolved sulfide.

The constituents of the precipitates were examined by the SEM-EDS analysis (Fig. 4.12) and mineral nature of the ZnS precipitates was investigated using XRD (Fig. 4.13). The precipitates were light brown to black in color. SEM – EDS analysis showed that the precipitates contain Zn and S with impurities of sodium. Fig. 4.12 reveals that the precipitates contain poorly crystallized sphalerite and impurities of sodium sulfate minerals. The precipitates mainly contain 34 – 43 % of Zn, 7 – 8 % of Na and 0.5 – 2.5 % of Fe and minor concentrations of Al, Cd, Cu and Mn (Table 4.4).

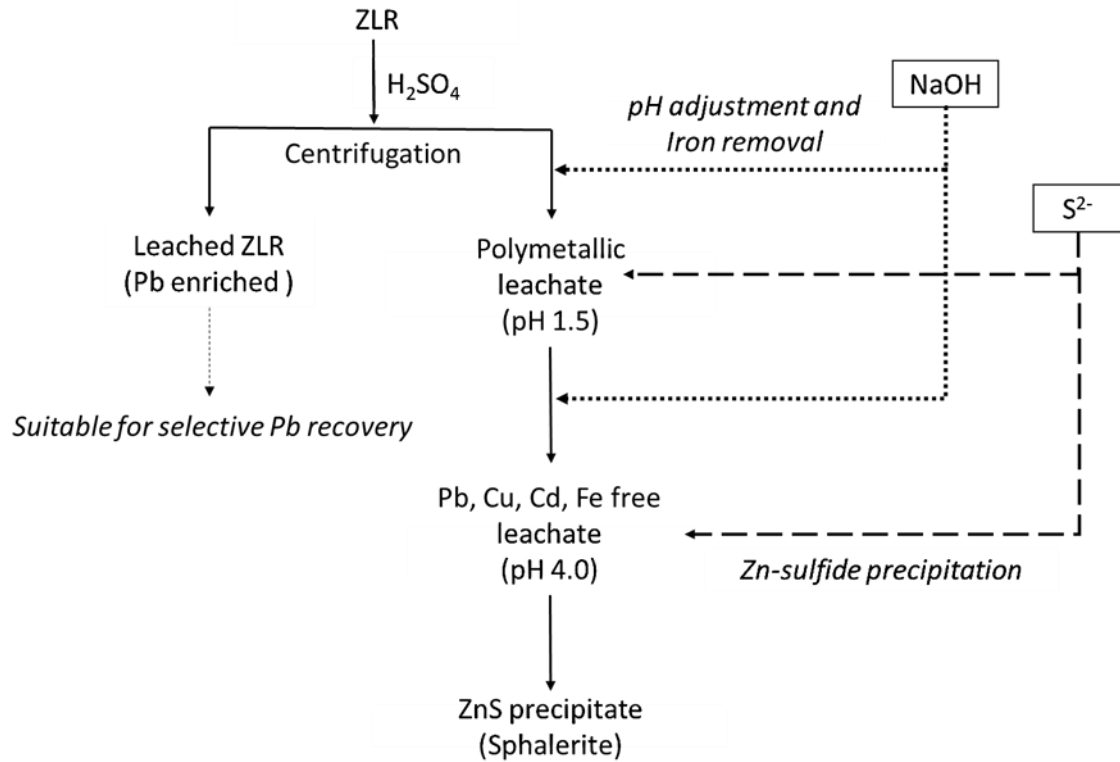


Fig. 4.10. Schematic hydrometallurgical flow chart for the selective recovery of Zn from the Zn-plant leach residues.

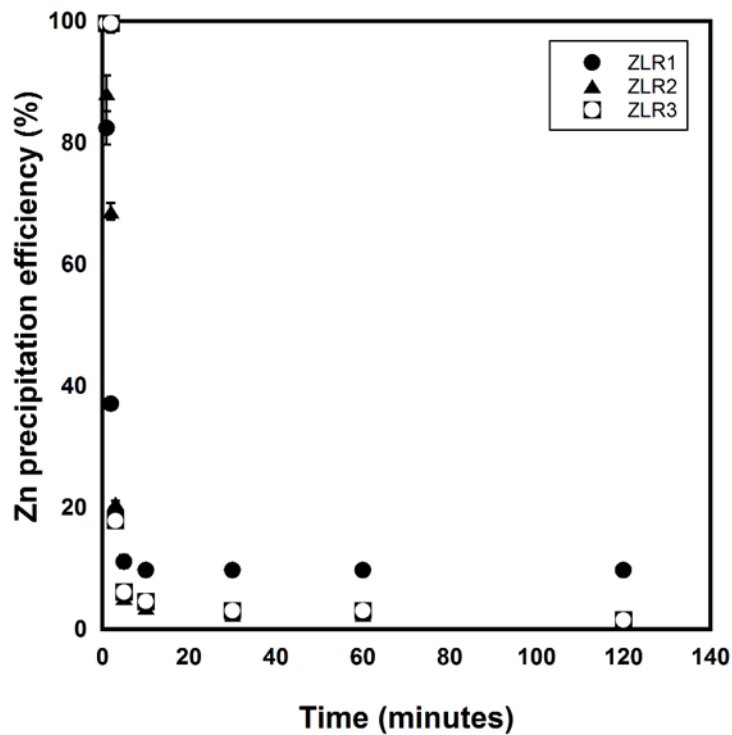


Fig. 4.11. Zn-sulfide precipitation Vs Time in the ZLR (Cd, Cu, Fe, Pb free) leachates at pH 4 (100 mg L⁻¹ of dissolved sulfide).

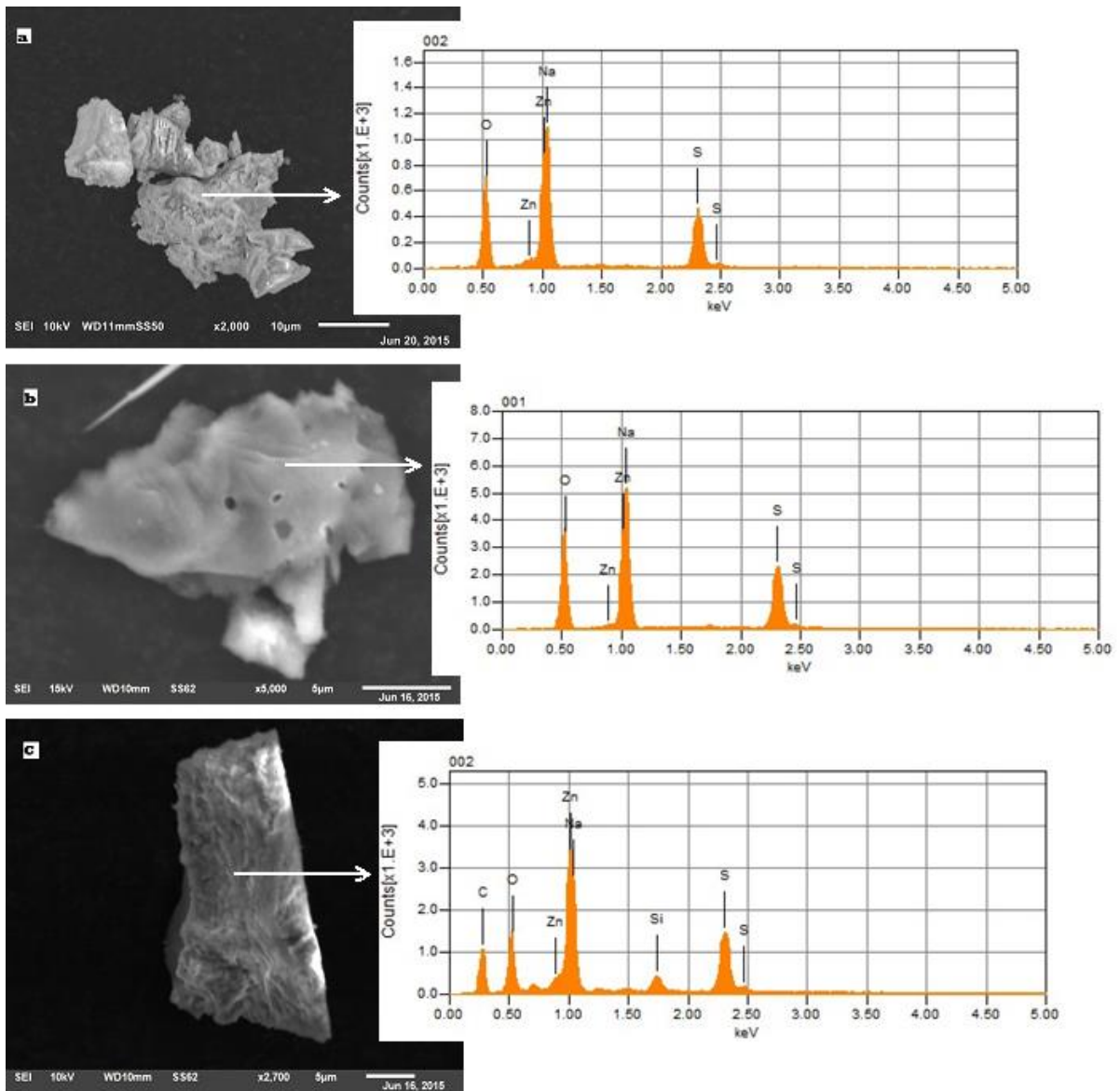


Fig. 4.12. SEM-EDS micrographs of the Zn-sulfide precipitates of (a) ZLR1, (b) ZLR2 and (c) ZLR3.

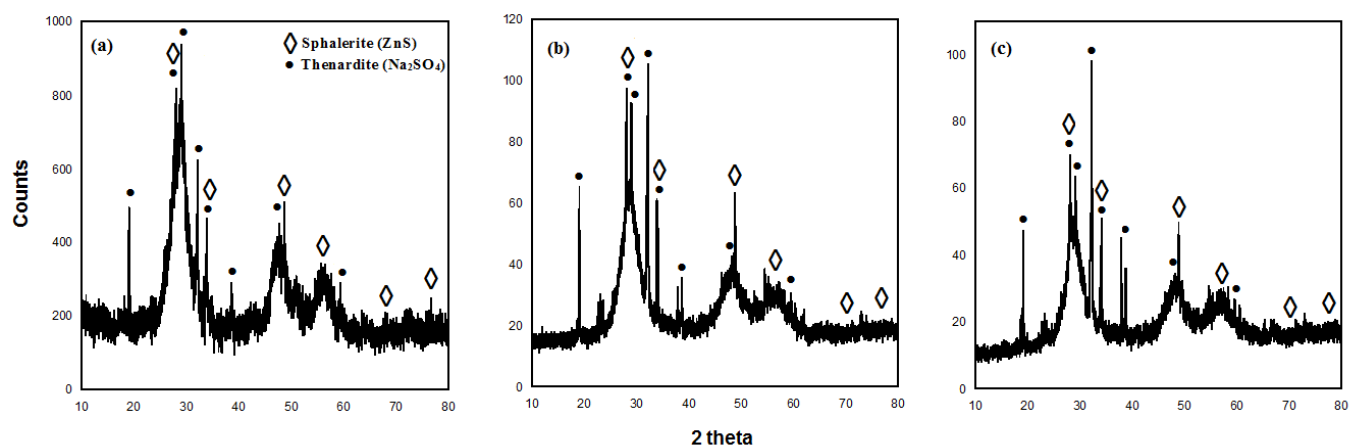


Fig. 4.13. XRD spectrum of Zn-sulfide precipitate from (a) ZLR1, (b) ZLR2 and (c) ZLR3 leachate.

Table 4.4. Elemental composition of the ZLR precipitates by hot-plate aqua-regia digestion.

Element	ZLR1	ZLR2	ZLR3
Zn	43.33 ± 2.52	34.87 ± 0.42	34.05 ± 0.96
Na	7.13 ± 0.33	8.10 ± 0.15	8.00 ± 0.22
Fe	0.67 ± 0.11	0.56 ± 0.01	2.47 ± 0.02
Cu	0.68 ± 0.13	0.82 ± 0.01	2.13 ± 0.29
Cd	1.43 ± 0.14	0.82 ± 0.01	0.39 ± 0.04
Mg	0.22 ± 0.01	0.34 ± 0.01	0.38 ± 0.02
Al	0.10 ± 0.02	0.61 ± 0.03	0.98 ± 0.14
Mn	0.25 ± 0.01	0.24 ± 0.01	0.18 ± 0.01
Ca	0.11 ± 0.01	0.12 ± 0.01	0.11 ± 0.02

4.4. Discussion

4.4.1. ZLRs as secondary Zn resource and its environmental significance

This study demonstrated that the ZLRs can be used as a secondary source of Zn (recovered as sphalerite) by using sulfuric acid leaching followed by selective sulfide precipitation (Fig. 4.10). The maximum leaching achieved (under optimum conditions) for ZLR1, ZLR2 and ZLR3 was 46.2 (± 4.3), 23.3 (± 2.7) and 17.6 (± 1.2) mg of Zn per g of ZLR (Fig. 4.7). The maximum selective precipitation achieved from the leachates of ZLR1, ZLR2 and ZLR3 was 90.3 (± 0.9), 97.7 (± 0.4), and (96.9 ± 0.3) %, respectively. Thus, the recovery of zinc from ZLR1, ZLR2 and ZLR3 was 41.7 (± 0.4), 22.8 (± 0.1) and 17.1 (± 0.1), mg per g respectively. The amount of Zn present in precipitates after the selective precipitation (Table

4.4) (34 – 43 %) is higher than the Zn present in the primary Zn ores deposits such as Morro Agudo (5.1 %), Vazante deposit (10 %) (Ministry of mines and energy (Brazil), 2010) submarine sediment volcanic (3-20%) and sandstone hydrothermal (0.5-0.75%) and comparable with veins deposit (40-60%) (Gordan et al., 2003).

If not disposed properly, ZLRs are hazardous wastes which can pollute the environment because of the presence of toxic heavy metals (Li et al., 2013; Min et al., 2013). The ZLRs investigated in this study are also potentially toxic to the environment as they contain exchangeable fractions of Cd and Pb (Chapter 3). On the other hand, high grade Zn-sulfide ores are being depleted in the recent decades. The present study addresses both these issues by leaching and removal of heavy of toxic metals such as Cd & Cu and recovery of zinc (as sphalerite) (Fig. 4.13).

4.4.2. Zinc leaching mechanisms from ZLR

From the agitation results (Fig. 4.3), it can be concluded that the Zn leaching does not depend on the mass transfer through the liquid boundary layer, when the agitation exceeds 150 rpm. Similar results were observed with sulfuric acid leaching of zinc silicate calcine and ferric sulfate leaching zinc sulfides by Souza et al. (2007a, 2007b). The decrease in the Zn leaching rate with the solid to liquid ratio (Fig. 4.6) can be explained by the decrease in the solid ZLRs particles per amount of leachant in the reaction mixture. But the decrease in leaching yield due to the increase in pulp density is not significant. This could be due to the low buffering capacity of the residues against strong (1 M) sulfuric acid.

The increase in Zn leaching for ZLR2 and ZLR3 (Fig. 4.4 and 4.5) with the increase in temperature and acid concentration finds a good agreement with previous investigations conducted on silicate rich Zn-calcine (Abdel-Aal et al., 2000; He et al., 2010), Zn-silicate ores (Abdel-Aal et al., 2000), high silica Zn-Pb oxide ores (He et al., 2010) and synthetic Zn silicate (He et al., 2011). However, the Zn leaching from ZLR1 did not increase with increase in temperature and acid concentration. The temperature and acid independency in the leaching kinetics of ZLR1 could be mainly due to the difference in the ratio of Zn-phases for e.g. the percentage of franklinite minerals in the ZLR2 and ZLR3 comparatively higher than ZLR1, for which a hot acid leaching (HAL) is required. Indeed, the Table 4.2 shows that the ZLRs contain significant concentration of Zn (2.5% - 5.0%) associated with different mineral phases, but XRD analysis did not identify crystalline Zn or any other metal mineral phase except gypsum

(Chapter 3). Accelerated sequential fractionation studies also did not give much insights on the mineral forms of Zn, except that the ZLR1 composition is very much different compared to ZLR2 and ZLR3 (Chapter 3). A chemical phase extraction procedure (CEP) revealed that the Zn is mainly associated with sulfates, oxides, silicates and ferrites where there was significant differences zinc silicate, zinc sulfate and zinc oxide concentration in ZLR1 when compared to ZLR2 and ZLR3 (Table 4.2).

The XANES data analysis also confirms the differences in the zinc phases between ZLR1 and ZLR2 and 3 (Fig. 4.2). The association of Zn with sulfates and oxides was also confirmed by the XANES analyses. The energy peak at 9669 eV (Fig. 4.2) is similar to that of the goslarite (ZnSO_4), zincite (ZnO) and hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) minerals. The differences in zinc local chemistry might be attributed by the ability of secondary minerals (like jarosite, schwertmannite, ferrihydrite etc) to co-precipitate/sorb Zn and ZnO (Waychunas et al., 2002; Waychunas et al., 2003; Cismasu et al., 2013). The presence of ZnSO_4 in the ZLR is due to the acid leaching of primary ores (secondary oxidation product). Zinc oxide is another secondary phase formed during the calcination/roasting stages of ZnS primary ores. In the later acid leaching metallurgical processes, ZnO will also be converted to ZnSO_4 . Zinc ferrites are the most often observed secondary mineral phase in the zinc hydrometallurgical residues (Li et al., 2013; Min et al., 2013). These minerals are formed due to the desulfurization of iron containing sulfide ores. For determining the Zn coordination chemistry in the ZLRs, Extended X-Ray Absorption Fine Structure (EXAFS) data analysis needs to be carried out, however, such analysis was out of scope for this study.

The kinetic analysis (Fig. 4.7) revealed that the sulfuric acid leaching of Zn from ZLRs follows shrinking core diffusion. Chemical reaction at the mineral surface does not have a significant impact. The results were very well in accordance with the Zn dissolution from zinc silicate calcine ores (Souza et al., 2007a), smithsonite (Dhawan et al., 2011) and iron bearing calcine (Han et al., 2014). The activation energies obtained from the Arrhenius plot (Fig. 4.8a) are also close to other reports for the extraction of Zn from the samples with similar mineralogy (Espiriari et al., 2006; Souza et al., 2007a; Smith et al., 2008; Qian et al., 2013). The effect of temperature in a leaching process can also be understood by determining the activation energy. A higher activation energy states that the temperature has a significant role in the leaching, while a lower activation energy reveal that temperature does not affect the particular reaction. The activation energies for ZLR1 and ZLR2 are again endorsing that leaching of Zn from those samples follows a diffusion controlled process, but the apparent activation energy determined

for ZLR3 is slightly high for a diffusion process. This might be because the leaching kinetics of Zn from ZLR3 was controlled in parallel by a surface chemical reaction mechanism and solid product diffusion mechanism. Similar findings have been reported for zinc silicate calcine minerals by Souza et al. (2007a). Thus, based on the CEP of the ZLRs and the previous reports on Zn bearing materials (Xianjin et al., 2011; Souza et al., 2007a; Souza et al., 2007b), the zinc dissolution in the sulfuric medium can be possibly explained by Equations 6 - 10:



4.4.3. Selective Zn precipitation from the ZLR leachates

Addition of sodium hydroxide (in order to adjust the initial pH) causes metal removal in the form of metal hydroxides (Lewis, 2010). The presence of iron in the leachate is a serious challenge for the selective recovery of zinc using processes such as roast-leach-electrowinning process wastes (Radzymińska-Lenarcik et al., 2015). In the present study, iron was mainly removed as Fe-hydroxide precipitates by addition of sodium hydroxide to change the pH to 4.0 (Table 4.3). The mineral nature of the Fe-precipitates was not investigated in this study. Cadmium removal at this stage cannot be attributed to hydroxide precipitates formation, instead Cd might have co-precipitated with Fe-hydroxides (Lottermoser, 2010). Cu removal in this study was mainly achieved by Cu-sulfide precipitates (Table 4.3).

The addition of sulfide to the leachates depleted from the impurities (Cd, Cu and Fe) led to 90.3 (± 0.9), 97.7 (± 0.4), and 96.9 (± 0.3) %, of Zn recovery from the ZLR1, ZLR2 and ZLR3 leachates. The obtained results were similar to the previous investigations using polymetallic synthetic solutions by different sulfide sources such as hydrogen sulfide gas (Al-Tarazi et al., 2005), thioacetamide (Gharabaghi et al., 2012), sodium sulfide (Esposito et al., 2006), biogenic hydrogen sulfide (Esposito et al., 2006; Alvarez et al., 2007). The final pH of the solution was found in the mild acidic range (6.4 ± 0.3). Sahinkaya et al. (2009) selectively precipitated Zn (pH 6.8 – 7.4) from acid mine drainage using biogenic sulfide. Gharabaghi et al. (2012) selectively precipitated Cu (pH < 2.5), Cd (pH 4) and Zn (pH 5.5) using thioacetamide. Figure 4.11 clearly show that the maximum of Zn is precipitated in less than 5 minutes, and no dissolution of the Zn-sulfide precipitates occurred. Under some circumstances

such as high ionic strength, high salinity or high sulfide/Zn ratio, Zn and sulfide can also form a soluble complex (Esposito et al., 2006), which consequently decreases the precipitation efficiency. The Zn to sulfide ratio in this study was not optimized.

As Zn has only one redox state Zn (II), the Zn-sulfide precipitate can form only ZnS minerals. Sphalerite and wurtzite are the two polymorphs of Zn-sulfide precipitates reported and the XRD analysis revealed the presence of the poorly crystallized sphalerite mineral phase. The sphalerite precipitation results were well in accordance with the Visual MINTEQ theoretical prediction (data not shown). SEM - EDS and the XRD analyses detect the presence of sodium impurities (as thenardite) along with the sphalerite precipitates. These impurities are influenced by the usage of sodium hydroxide and sodium sulfide for the pH adjustment and precipitation purposes, respectively. The efficiency of selective precipitation can be further confirmed by the absence of the peaks for Cd, Cu and Fe in the EDS spectra of Zn-Sulfides precipitation. It is worth to mention that the leachates are rich in sulfates, because 1.5 M H₂SO₄ was used as the leaching agent. So, consequently lead to the formation of thenardite minerals.

4.5. Conclusions and perspectives

The study showed the zinc leach residues can be used as a secondary resource for Zn extraction. The major fractions of Zn are associated with sulfates, oxides and ferrite minerals. Hot acid leaching is required to leach maximum Zn from the ZLRs. The difference in phases of ZLR1 and ZLR2 and 3 possibly lead to different leaching characteristics at higher temperature and acid concentration. Sulfuric acid leaching of Zn from the ZLRs follows shrinking core kinetics. The activation energy required was determined as 2 - 12 kcal/mol and the order acid concentration 0.2 – 0.9 for the ZLRs investigated. Sodium hydroxide/sulfide addition helps to remove the impurities such as Cd, Cu and Fe from the ZLRs leachates. Zinc could be selectively precipitated as sphalerite from the impurities depleted ZLR leachates. This study can be further extended to investigate the various characteristics like settleability and particle size distribution of the precipitates to further improve its candidature as a secondary resource. The H₂SO₄ leached ZLRs are enriched in Pb, these leached ZLRs can be further investigated for selective recovery of Pb.

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Chapter 5

Bioleaching and selective biorecovery of zinc from zinc metallurgical leach residues from the Três Marias zinc plant (Minas Gerais, Brazil)

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Abstract

Gradual depletion of high-grade ores for supply of heavy metals encourages industries to search for alternative resources. Waste generated from metallurgical industries can be used as a secondary resource as it still contains high concentrations of metals which can be recovered. The bioleaching kinetics and bio-recovery of zinc from Zn-plant leach residues (ZLR), collected from a currently operating Zn-plant in Três Marias (Minas Gerais, Brazil) using sulfuric acid producing *Acidithiobacillus thiooxidans* (*A. thiooxidans*) were investigated. Response surface methodology (RSM) with full factorial central composite design (CCD) was applied to optimize Zn bioleaching by *A. thiooxidans*. The experiments were performed by varying the initial elemental sulfur concentration ($0.5 - 3 \text{ g L}^{-1}$), pulp density ($5 - 50 \text{ g L}^{-1}$) and initial pH (pH 3.0 - 4.0). More than 75% of Zn could be released from the ZLR by *A. thiooxidans* under optimized conditions. The Zn leaching kinetics from ZLR followed the shrinking core diffusion model. Zn was selectively recovered from the Fe rich acidic bioleachate by biogenic sulfide precipitation. Fe was first removed (more than 85% of total Fe in the leachate) by adjusting the initial pH to 5.0, followed by selective Zn biorecovery using sulfidic precipitation. Zn (>95%) was selectively recovered from the Fe depleted ZLR leachate by biogenic sulfide (with 1:1, Zn:biogenic sulfide mass ratio). Biohydrometallurgy coupling bioleaching using *A. thiooxidans* with selective precipitation of Zn using biogenic sulfide is an alternative base metal recovery strategy, allowing the selective recovery of Zn from ZLR.

Keywords:

Biohydrometallurgy; bioleaching; biogenic sulfide precipitation; secondary resources; zinc recovery

5.1. Introduction

Rapid progression of metallurgical industries has led to the generation of large quantities of metal containing solid wastes. These wastes, when released into the environment, have shown to cause adverse environmental and health impacts (Clemente et al., 2003; Hilson and Monhemius, 2006). Therefore, it is important to design a sustainable recovery strategy of metals from metallurgical residues and other wastes which is economic and eco-friendly. Biohydrometallurgy is an eco-friendly and cost-effective technique compared to conventional pyrometallurgical processes for the extraction of precious metals from mineral ores (Olson et al., 2003; Watling, 2006; Johnson et al., 2013). Although biomining has been well constituted for processing reduced ores and mining wastes, research pertaining to biohydrometallurgy of oxidized resources is still in its initial stages. The bioleaching process (by oxidative dissolution mechanisms) requires reduced mineral phases which are actually absent in oxide ores (Johnson, 2009).

Two approaches have been proposed in the literature for the bioleaching of oxidized minerals: (i) anaerobic reductive bioleaching (Hallberg et al., 2011; Nancucheo et al., 2014; Schippers et al., 2014) and (ii) aerobic bioleaching by biogenic acid producing microorganisms. Aerobic bioleaching (by complexolysis or acidolysis) is the most investigated technique for the extraction of metals from oxidized ores/resources (Castro et al., 2000; Mulligan and Galvez-Cloutier, 2000; Mulligan et al., 2004, Biswas et al., 2014). Organic acid producing heterotrophic bacteria (*Pseudomonas aeruginosa*; Shabani et al., 2013) and fungi (*Aspergillus niger*; Castro et al., 2000; Mulligan et al., 2004,) have been applied for the extraction of Cu from Cu-oxide ores. Organic acids (e.g. citric, oxalic and maleic acids) produced by the fungi/bacteria have the inherent capacity to leach out metals from the resources by forming soluble metal-organic ligand complexes. Only few studies reported on the use of acidolysis by sulfuric acid produced by bacteria such as *Acidithiobacillus thiooxidans* (*A. thiooxidans*) or *A. caldus* (de Oliveira et al., 2014; Hocheng et al., 2014; Pangayao et al., 2015). A maximum of 88% of Cu from low grade Cu-oxide ores was extracted by the biogenic sulfuric acid produced by *A. thiooxidans* (de Oliveira et al., 2014). Hocheng et al. (2014) investigated the biogenic acids containing supernatants of *A. thiooxidans*, *Acidithiobacillus ferrooxidans* and *Aspergillus niger* cultures and reported that the *A. thiooxidans* supernatant was a better bioleachant in terms of the extraction of metals from an oxidized steel waste.

Optimization of the bioleaching parameters such as substrate concentration, pH and pulp density is important to enhance the bioleachability of a desired metal from primary ores or secondary resources. Optimizing one factor at a time has been widely used for bioleaching

optimization studies (Soliso et al., 2002, Deveci et al., 2004; Mousavi et al., 2006). The major disadvantage of this approach is that it does not provide any information on the relationship between the process variables (Haghshenas et al., 2012). Full factorial design of experiments such as response surface methodology (RSM) can optimize various process variables at different levels. RSM also provides high quality predictions of the relationship between the parameters and their linear and interaction effects (Montgomery, 2008; Mullai et al., 2010). The kinetics of any bioleaching process is important as it forms the basis for scale-up, reactor design and process intensification for real applications (Levenspiel, 2008). Hydrometallurgy follows the shrinking core kinetic model (SCM), in which the size of the solid changes significantly throughout the course of the reaction (Levenspiel, 2006).

Recovery of the leached metals from the leachate is the final and critical step in biohydrometallurgy which can be achieved by chemical (precipitation and solvent extraction), physical (adsorption), electrolytic (electrowinning) or biological (biosorption and biogenic sulfide precipitation) processes (Chapter 2). Each process has its own advantages and limitations. Among the available techniques, biorecovery methods such as biosorption and biogenic sulfide precipitation are more eco-friendly and economic (Chapter 2).

In the present study, Zn biohydrometallurgy from an oxidized Zn-metallurgical waste was investigated. The main objective of this study was to study Zn bioleaching characteristics and the biological recovery of soluble Zn from the bioleachate from Zn-plant leach residues (ZLR) collected from a Zn metallurgical plant located in Três Marias (Minas Gerais, Brazil). The bioleaching process parameters such as (i) elemental sulfur supplementation, (ii) pulp density and (iii) culture pH were optimized for the maximum Zn bioleaching, by performing experiments designed by central composite design (CCD). The kinetics of the Zn leaching by biogenic sulfuric acid and chemical sulfuric acid were compared and the shrinking core model was applied to interpret the bioleaching data. This study also examined biogenic metal sulfide precipitation to selectively recover Zn from the bioleachate.

5.2. Materials and methods

5.2.1. Zinc metallurgical leach residues

The ZLR used in this study were collected from an operational Zn metallurgical plant located in Três Marias (Minas Gerais, Brazil). The most recently produced ZLR (<5 years) was investigated in this study (Chapter 3). The major elemental composition of ZLR comprised of (in wt %) (Chapter 3): Zn - 2.5%, Pb - 2.3%, Fe - 11.5% and Ca - 7%. The ZLR also contained minor concentrations of Al, Cd, Cu, Mg and Mn. Zn is mainly associated to Zn-ferrites and Zn-

silicates (Chapter 4). The particle size of the ZLR was less than 2 mm in diameter for all the experiments.

5.2.2. Microorganisms

A commercial strain of *A. thiooxidans* (DSM 9463) was obtained from the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ, Germany), and investigated for its ability to leach Zn from the ZLR studied. The bacteria were grown in a mineral salt (MS) medium containing (g L^{-1}): $(\text{NH}_4)_2\text{SO}_4$ - 2.0, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - 0.25, K_2HPO_4 - 0.1, KCl - 0.1. The most probable number technique (MPN) was performed to determine the number of viable bacteria (Starosvetsky et al., 2013). The *Thiobacillus* medium (ATCC medium #125) (Anonymous, 2011) was used to carry out the MPN technique (g L^{-1}): $(\text{NH}_4)_2\text{SO}_4$ - 0.2, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ - 0.5, CaCl_2 - 0.25, KH_2PO_4 - 3.0, FeSO_4 - 0.005, sulfur - 10, in 1 L of tap water. The MPN setup consisted of duplicates and up to 8 dilutions per sample analyzed. Sulfur was added after sterilization (autoclaved at 121 °C for 20 min) in order to allow the sulfur to float. pH changes were recorded at time intervals of 0, 7, 14, 21, 29 and 45 days.

5.2.3. Bioleaching experiments

5.2.3.1. Process optimization - Response surface methodology CCD approach

Preliminary bioleaching experiments were carried out to ascertain the important parameters that can influence Zn bioleaching from ZLR by *A. thiooxidans*. The bioleaching experiments were carried out using the same medium composition as mentioned in section 2.2, with 5 g L^{-1} pulp density. The effect of sulfur addition was studied by adding 10 g L^{-1} to the MS medium. Samples were withdrawn at regular intervals, filtered and analyzed for their Zn concentration using atomic absorption spectroscopy (Perkin Elmer, AAnalyst 200). The pH of the bioleaching cultures was also monitored.

Based on preliminary experiments, the pH, sulfur concentration and pulp density were chosen as the parameters to be optimized. Minitab v16.0 (United States of America) was used to design the RSM experiments. A full factorial CCD (face centered, unblocked) was used. The process variables such as sulfur supplementation (5 - 30 g L^{-1}), pulp density (5 to 50 g L^{-1}) (Liu et al., 2004) and initial pH (3.0 - 4.0) were selected as the factors to be optimized, while the Zn leaching efficiency (%) was selected as the response variable. The design matrix in non-coded and coded units is presented in Table 5.1.

Table 5.1. Bioleaching process parameters and experimental runs based on a 2³ - central composite design

Run no	Non-coded units			Coded values		
	Sulfur concentration	Pulp density	Initial pH	Sulfur concentration (g L ⁻¹)	Pulp density (g L ⁻¹)	Initial pH
1	-1	-1	-1	5	5	3
2	1	-1	-1	30	5	3
3	-1	1	-1	5	50	3
4	1	1	-1	30	50	3
5	-1	-1	1	5	5	4
6	1	-1	1	30	5	4
7	-1	1	1	5	50	4
8	1	1	1	30	50	4
9	-1	0	0	5	27.5	3.5
10	1	0	0	30	27.5	3.5
11	0	-1	0	17.5	5	3.5
12	0	1	0	17.5	50	3.5
13	0	0	-1	17.5	27.5	3
14	0	0	1	17.5	27.5	4
15	0	0	0	17.5	27.5	3.5
16	0	0	0	17.5	27.5	3.5
17	0	0	0	17.5	27.5	3.5
18	0	0	0	17.5	27.5	3.5
19	0	0	0	17.5	27.5	3.5
20	0	0	0	17.5	27.5	3.5

Temperature (30 °C) and agitation speed (150 rpm) were kept constant as per DSMZ specifications. Particle size (2 mm) was also kept constant. An initial inoculum size of 2% (v/v) containing 10⁸ cells mL⁻¹ was used in all the experiments. RSM experiments were performed in duplicates and the center point experiments were performed in 6 batches for statistical reproducibility. All the leached samples were analyzed after 30 days of batch incubations. The statistical analysis, in the form of analysis of variance (ANOVA), of the bioleaching efficiencies was performed by the Minitab v16.0 software. A quadratic equation (Equation 1) was derived to determine the optimum leaching conditions based on the responses (Zn bioleaching) after 30 days:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (1)$$

where

Y - Zn bioleaching efficiency (%), A - sulfur concentration (g L^{-1}), B - pulp density (g L^{-1}), C - initial pH, β_0 - intercept coefficient, $\beta_{1,2,3}$ - linear coefficients, $\beta_{11,22,33}$ - square effect coefficients, $\beta_{11,12,13}$ - interaction coefficients

5.2.3.2. Bioleaching under optimum conditions

The bioleaching experiments were also carried out with the same media composition as mentioned in section 2.2. These experiments were run in triplicates. Samples were withdrawn at regular intervals (1, 2, 4, 7, 15, 22, 29, 37 and 45 days) and analyzed for residual Zn and Fe concentrations by atomic absorption spectroscopy (PerkinElmer AAnalyst 200).

5.2.3.3. Biogenic sulfuric acid vs chemical sulfuric acid leaching

In order to understand the leaching kinetics, a comparative study on the leaching behavior of Zn by biogenic sulfuric acid (culture supernatant) and chemical sulfuric acid (0.2 M) was performed. The sulfuric acid production by the pure culture was estimated periodically by acid/base titrations. The culture supernatant with a biogenic sulfuric acid concentration of 0.2 M was collected by centrifugation and used in this study. The experiments were run in triplicates under the following conditions: temperature 30 °C, agitation 150 rpm and pulp density 20 g L^{-1} . Samples were withdrawn at regular intervals (0, 0.5, 1, 2, 4, 7, 24, 72, 120 and 192 h) and analyzed for Zn and Fe concentrations by atomic absorption spectroscopy (PerkinElmer AAnalyst 200). One-way analysis of variance (ANOVA) (confidence limit of 95%, $P < 0.05$) was performed using KaleidaGraph v4.0 to ascertain if there were significant differences in the Zn leaching behavior between biogenic and chemical sulfuric acid.

5.2.3.4. Bioleaching kinetic analysis

The kinetic analysis of the Zn bioleaching from the ZLR by *A. thiooxidans* was investigated by SCM. According to the dissolution kinetics, if the heterogeneous Zn dissolution from the ZLR by sulfuric acid was controlled by a chemical reaction occurring at the mineral surface, then the kinetics can be expressed by Equation 2 (Levenspiel, 2006):

$$1 - (1 - \alpha)^{1/3} = K_c \cdot t \quad (2)$$

Where:

α - fraction of Zn reacted, t - leaching time (min), K_c - chemical reaction rate constant (dimensionless)

Likewise, if diffusion of the leaching agent through the solid product layer around the unreacted core is the rate-limiting step, then the kinetics can be explained according to Equation 3²⁴:

$$1 - 3(1 - \alpha)^{2/3} - 2(1 - \alpha) = K_s \cdot t \quad (3)$$

where, K_s - solid product layer diffusion rate constant (dimensionless).

Similarly, if the reaction rate is controlled by diffusion of the leaching agent through the liquid film formed, then Equation 4 can be applied to determine the kinetics²⁴:

$$1 - (1 - \alpha)^{2/3} = K_L \cdot t \quad (4)$$

where, K_L - liquid film diffusion rate constant (dimensionless). All the above kinetic equations were derived based on the assumption that the Zn containing minerals have a spherical size.

5.2.4. Fe and Zn biorecovery experiments

5.2.4.1. Sulfate reducing bacteria enrichment and biogenic sulfide production

Sulfate reducing bacteria (SRB) were enriched in a slightly modified Postgate medium (initial pH 7.0 - 7.5) containing (in g L⁻¹): K₂HPO₄ - 0.5, NH₄Cl - 1.0, CaSO₄ - 1.0, FeSO₄·7H₂O - 0.5, sodium lactate - 3.5, MgSO₄·7H₂O - 2.0, yeast extract - 1.0 and ascorbic acid - 0.1. All experiments were run anaerobically for 15 days, in triplicates. The biogenic sulfide production in the culture bottles was determined by mixed diamine reagent spectrometry (Cline, 1969).

5.2.4.2. Biogenic metal sulfide precipitation

Visual MINTEQ is a chemical equilibrium model that can predict the metal speciation, solubility, adsorption and precipitation (Gustafsson, 2012). Input molar concentrations of each metal (Zn²⁺, Cu²⁺, Cd²⁺, Fe³⁺, Ca²⁺, Na⁺, Cl⁻, PO₄³⁻ and SO₄²⁻) were provided based on the leachate composition at the optimized bioleaching conditions. To predict metal precipitation as a function of increasing pH, the pH was varied from 0.5 to 7.5 at an interval of pH 0.5. Zn-sulfide precipitation was also theoretically predicted by Visual MINTEQ with the Fe depleted leachate composition and a 1:1 mass ratio of Zn:sulfide was provided as the input. The temperature was constantly maintained at 20°C and oversaturated solids were allowed to precipitate. Concentrations of the dissolved metals and the amount of precipitates were obtained as the outputs.

The bioleachate was collected in a 250 mL glass beaker and the pH's of the bioleachates were adjusted to pH values of 2, 3, 4, 5, 5.5, 6 and 6.5 by using 10 M NaOH. The pH adjusted leachates were filtered through 0.45 μm nitrocellulose filters and analyzed for residual metal (Fe and Zn) concentrations. 25 mL of the leachate was transferred to an airtight bottle and biogenic sulfides (0.4 g L⁻¹, supernatant from the SRB culture) were added. The solution was agitated at 150 rpm in an orbital shaker for 1 h. Later, the solution was filtered and analyzed for its metal concentration. The metal sulfide precipitates were separated by centrifugation (centrifuge Hermle Z200A) (4185 g for 10 min). The precipitates were air dried at room temperature and investigated for elemental analysis by scanning electron microscope - energy dispersive X-ray spectroscopy (SEM-EDS) and mineralogy by X-ray diffraction (XRD).

5.2.5. Analytical methods and statistical analysis

Unless otherwise stated, all experiments were done in triplicates and procedural blanks were maintained at room temperature (20 \pm 2 °C). Unless otherwise specified, samples were collected and filtered using 0.45 μm nitrocellulose filters and the metal content (Cd, Cu, Fe, Mn, Pb and Zn) of the solutions was determined by atomic absorption spectroscopy (PerkinElmer AAnalyst 200). SEM-EDS analysis were also done for the dried metal sulfide precipitates using a Jeol JSM 6010LA at 10-20 KeV and high vacuum conditions. XRD (Bruker D8 advance diffractometer) studies were carried out on a diffractometer equipped with an energy dispersion Sol-X detector with copper radiation (Cu K α , λ = 0.15406 nm). The acquisition was recorded between 2° and 80°, with a 0.02° scan step and 1 s step time. The means of the analysis were statistically compared using one-way ANOVA (Minitab v16.0) at a confidence limit of 95% (P<0.05).

5.3. Results

5.3.1. Bioleachability of Zn from ZLR by *A. thiooxidans* and optimization of bioleaching parameters by response surface methodology

Preliminary bioleaching studies were carried out in 2 different conditions: (i) with external elemental sulfur addition (10 g L⁻¹) and (ii) no external sulfur supply. Procedural abiotic blanks (no bacterial inoculation) were run in parallel as well. The results of the preliminary bioleaching studies carried out on the ZLR are provided in Fig 1a. From Fig. 5.1a, shows that the flasks containing *A. thiooxidans* showed higher Zn concentration than the abiotic

control, especially the ones containing 10 g L^{-1} sulfur showed a better leaching capacities (9610 mg kg^{-1} , 38%) than the samples where sulfur was absent (3140 mg kg^{-1} , 13%). *A. thiooxidans* was able to produce sulfuric acid and decrease the system pH by utilizing the elemental sulfur. The pH profile of the cultures is provided in Fig. 5.1b. *A. thiooxidans* supplied with the elemental sulfur showed a steep decrease in the pH from 3.5 to 1.9 (after 7 days) and further to 1.5 (after 14 days of incubation). In the control flasks, the pH increased from 3.5 to 4.5 (with no bacteria, no sulfur) and 4.8 (no bacteria, 1% sulfur).

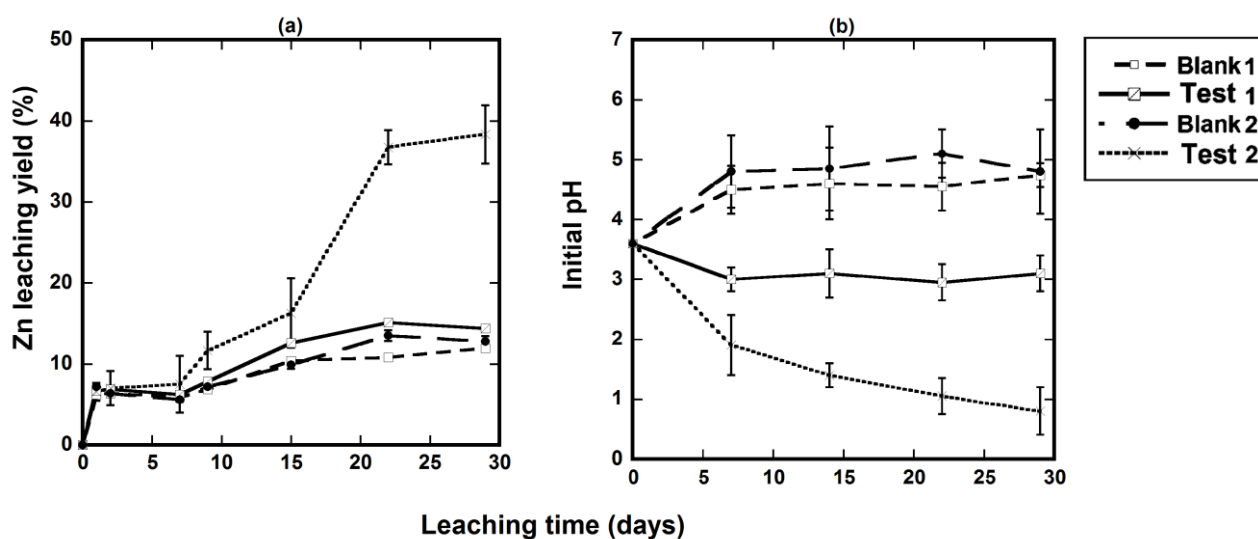


Fig. 5.1. (a) Bioleaching of Zn from ZLR by *A. thiooxidans* and (b) pH profile of the preliminary bioleaching studies on ZLR by *A. thiooxidans* (legends, blank 1 = MS medium + 50 g L^{-1} ZLR, Test 1 = MS medium + *A. thiooxidans* + 50 g L^{-1} ZLR, blank 2 = MS medium + 50 g L^{-1} ZLR + 10 g L^{-1} elemental sulfur, test 2 = MS medium + *A. thiooxidans* + 50 g L^{-1} ZLR + 10 g L^{-1} elemental sulfur).

The bioleaching process variables (sulfur supplementation, pulp density and initial pH) were optimized using the RSM-CCD approach and the results are shown in Fig. S5.1. The main effects of the individual process variables are shown in Fig. 5.2. From Fig. 5.2 shows that, except the sulfur concentration, variables such as pulp density and pH do not have a significant effect. As evidenced, when the sulfur concentration was increased from 5 to 27.5 g L^{-1} the Zn bioleaching increased from 45 to 55%. Regression results from the statistical analysis (ANOVA) of the optimization studies are provided in Table 5.2. The *T* values and *P*-values were used as a tool to check the significance of the parameter. From a statistical view point, when a particular variable has higher *T* and lower *P* values; this implies that the variable is

highly significant. It can be observed that the sulfur supplementation has a significant linear effect on the bioleaching of Zn. Besides, squared and interaction effects also played a significant role in the case of sulfur (Table 5.2). This observation fits with the main effects plot (Fig. 5.2) and experimental data (Fig. 5.1). Other than sulfur supplementation, the interactions between pulp density and the initial pH also contributed to the bioleaching of Zn. Based on the regression analysis, a full quadratic equation (Equation 5) was derived to estimate the optimum values of the process parameters:

$$Y_{\text{Zn bioleaching}} = 76.116 + 6.779A - 8.775B + 0.142C - 2.673A^2 - 0.251B^2 - 1.895C^2 + 0.719AB + 1.415AC + 2.310BC \quad (5)$$

Where $Y_{\text{Zn leaching}}$ is Zn bioleaching efficiency (estimation), A - sulfur supplementation, B - pulp density and C - initial pH.

Table 5.2. Regression analysis from the data of the central composite designed experiments

Term	Regression estimate coefficient	Standard error coefficient	Computed <i>T</i> value	<i>P</i> -value	Note
A	1.186	0.595	8.963	< 0.001	*
B	-0.732	0.595	-0.148	0.885	-
C	55.480	0.595	-1.981	0.076	-
A×A	-0.026	1.135	-3.521	0.006	*
B×B	0.001	1.135	0.457	0.658	-
C×C	-8.871	1.135	-1.955	0.079	-
A×B	0.006	0.665	2.601	0.026	*
A×C	-0.010	0.665	-0.092	0.929	-
B×C	0.161	0.665	2.724	0.021	*

Note: A - Sulfur concentration (g L⁻¹), B - Pulp density (g L⁻¹), C - Initial pH, * - significant, and '-' - insignificant.

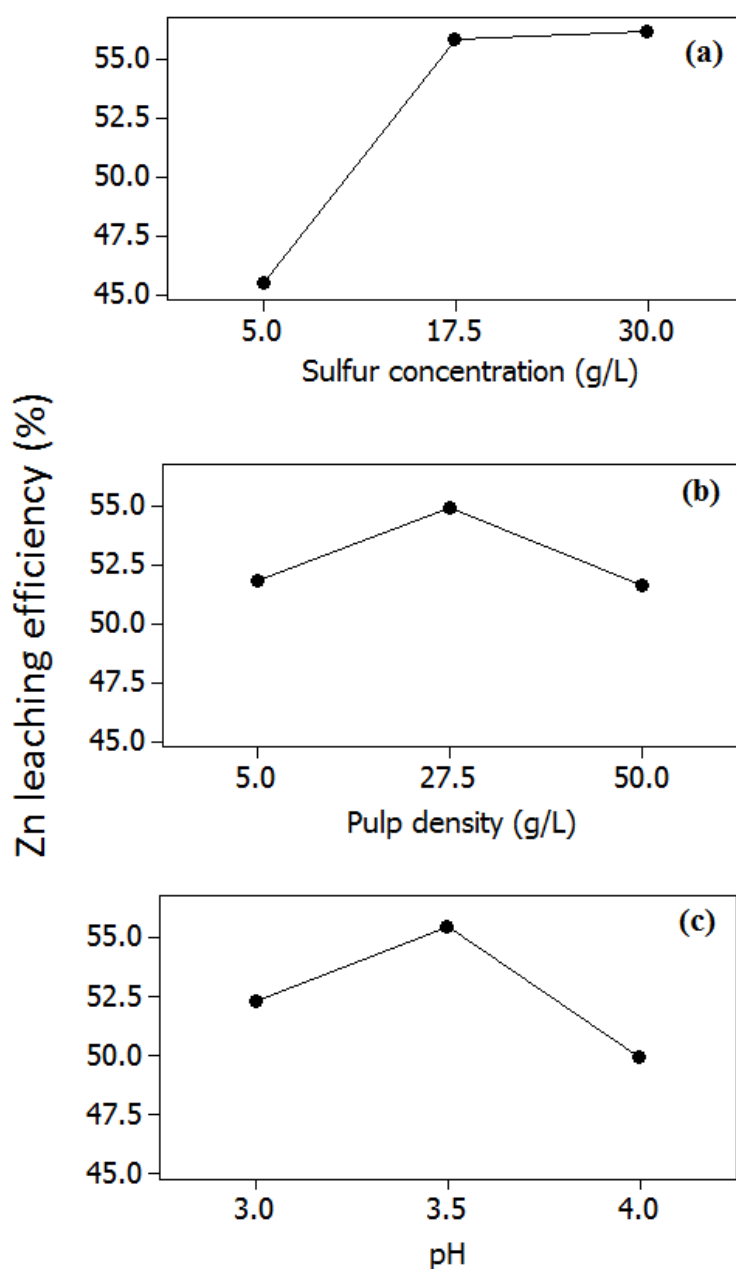


Fig. 5.2. Bioleaching efficiency of Zn from ZLR as a function of (a) sulfur concentration, (b) pulp density and (c) pH using *A. thiooxidans*.

5.3.2 Interaction between process variables during Zn bioleaching from ZLR

Table 5.2 shows that the interactions between the sulfur concentration and pulp density as well as pulp density and pH are statistically significant. Surface and contour plots showing the interaction between the process variables are provided in Fig. 5.3. Interaction plots between the process variables and the contour plots are provided in the supplementary information Fig. S5.2 and Fig. S5.3, respectively. Fig. S5.2 shows that when the sulfur concentration decreases,

then the pulp density should also be low (5 g L^{-1}) to increase the Zn leaching from the ZLR and vice versa. Response surface plots (Fig. 5.3b) and interaction plots between the variables (Fig. S5.3) shows that the Zn bioleaching is high ($\sim 55\%$) when the sulfur concentration is high ($17.5 - 30 \text{ g L}^{-1}$), irrespective of the pulp density. When the sulfur concentration is low, the Zn bioleaching efficiency is also low ($\sim 45\%$). The interaction between the sulfur concentration and the pH also followed a similar trend (Fig. 5.3a and S5.2). Concerning the interaction between pulp density and pH, a saddle type response surface was observed wherein the Zn leaching efficiency profiles curved upward in one direction and downward in another direction, especially with increasing pH values (Fig. 5.3c and S5.2). The estimated surface showed a definite optimum for pH well within the range of experimentation, and for the case of pulp density, lower values favored Zn leaching from the ZLR.

The quadratic equation was solved by the matrix method to obtain the values for sulfur (A), pulp density (B) and initial pH (C). 25.1 g L^{-1} of sulfur, 21.5 g L^{-1} pulp density and 3.31 initial pH were the optimized outputs of this quadratic equation. The bioleaching experiments were again performed under the optimized conditions (Fig. 5.4). Figure 4 shows the bioleaching efficiency (Zn and Fe) increased steadily until 30 days and approached a near plateau region after 30 days. A maximum of $78 (\pm 0.9) \%$ of Zn can be bioleached under the optimum conditions within 45 days.

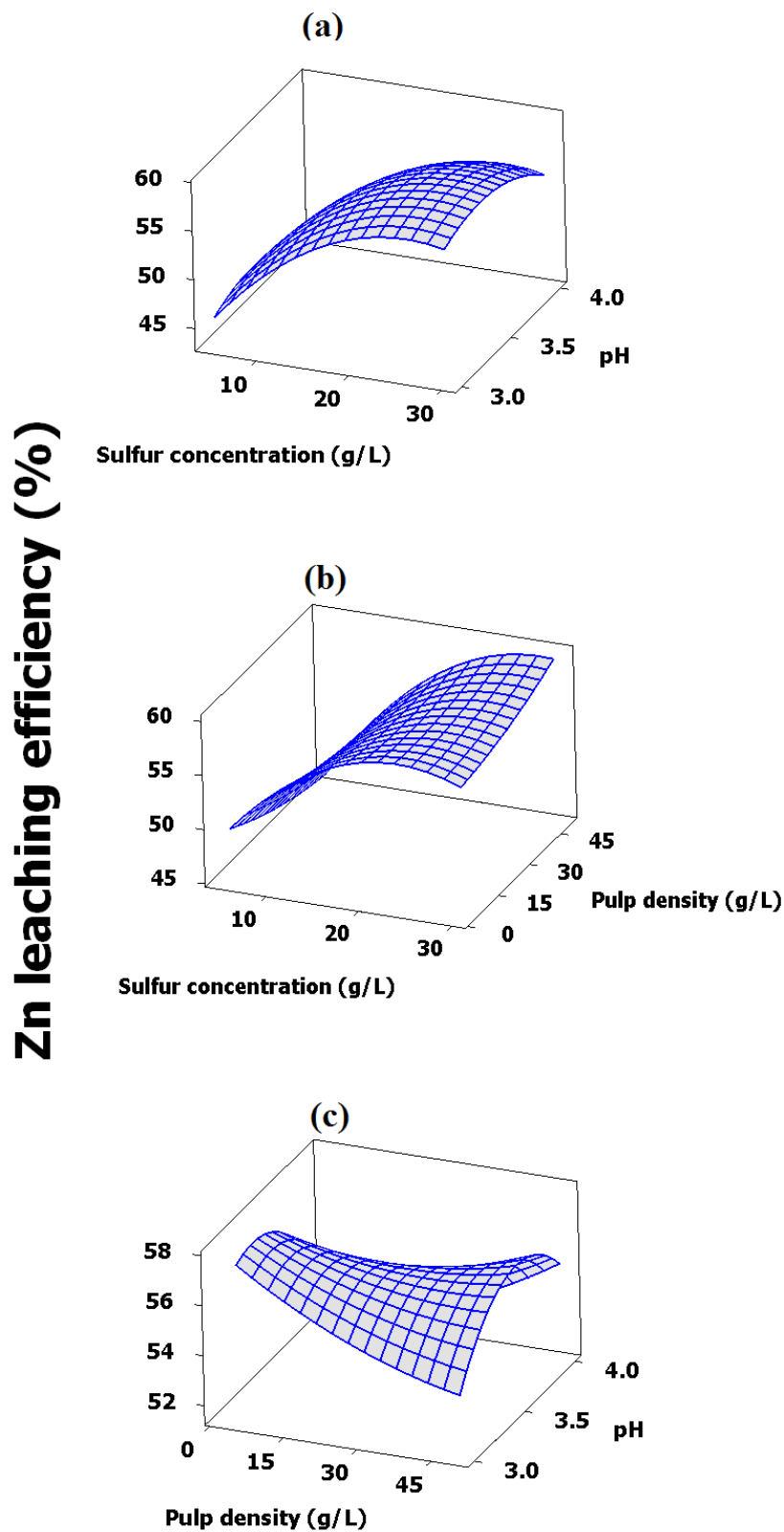


Fig. 5.3. 3-D surface plots for the optimization of Zn bioleaching from ZLR (a) sulfur concentration vs pH, (b) sulfur concentration vs pulp density and (c) pulp density vs pH.

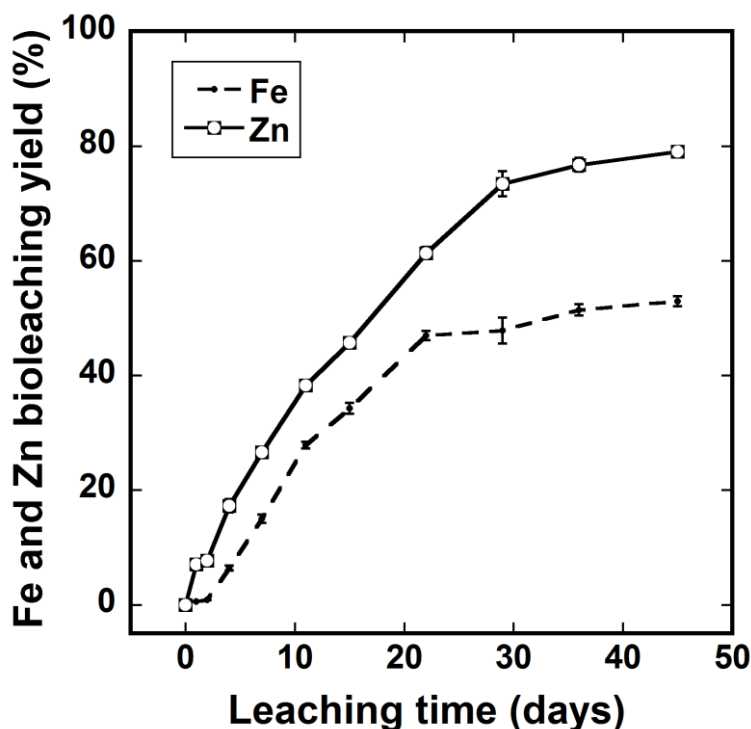


Fig. 5.4. Bioleaching yield of Zn and Fe (from ZLR) by *A. thiooxidans* under optimized conditions (sulfur concentration 25.1 g L⁻¹, pulp density 21.5 g L⁻¹, initial pH 3.3, temperature 30 °C and agitation at 150 rpm).

5.3.3. Bioleaching kinetics

The leaching efficiency of chemical (0.2 M) and biogenic (0.2 M) sulfuric acid was compared (Fig. 5.5). The differences in the leaching efficiencies were statistically insignificant, as ascertained by one-way ANOVA (data not shown). The kinetics of the Zn bioleaching was investigated using the SCM kinetics with experimental data obtained under optimum conditions (Fig. 5.4). The solid-product diffusion model, liquid film boundary diffusion model and the surface chemical reaction model were fitted with the experimental data (Fig. 5.6). Fig. 5.6 shows that the Zn bioleaching follows shrinking core kinetics, wherein the leaching is controlled by the solid product layer diffusion ($R^2 = 0.97$).

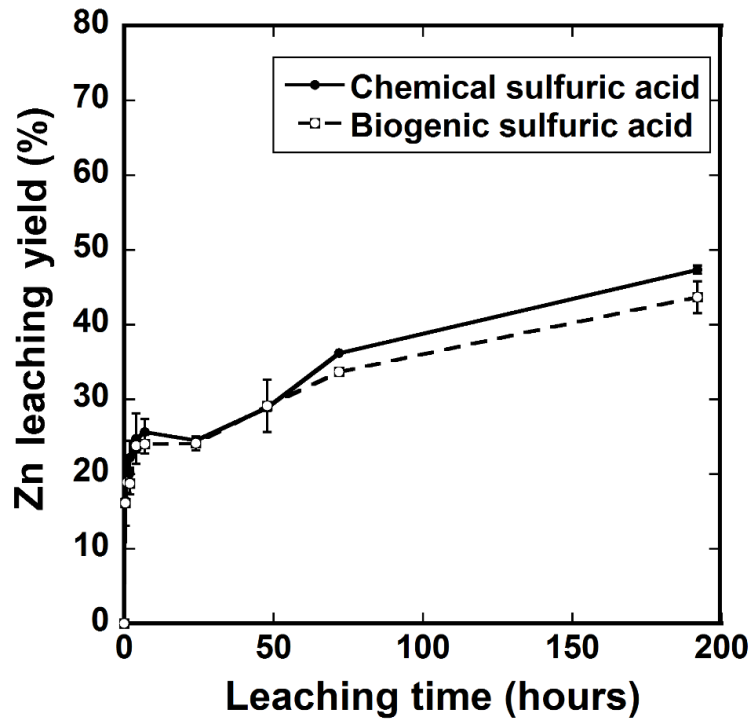


Fig. 5.5. Zn leaching efficiency of chemical sulfuric acid vs biogenic sulfuric acid (pulp density 2%, acid concentration 0.2 M, temperature 30 °C and agitation at 150 rpm).

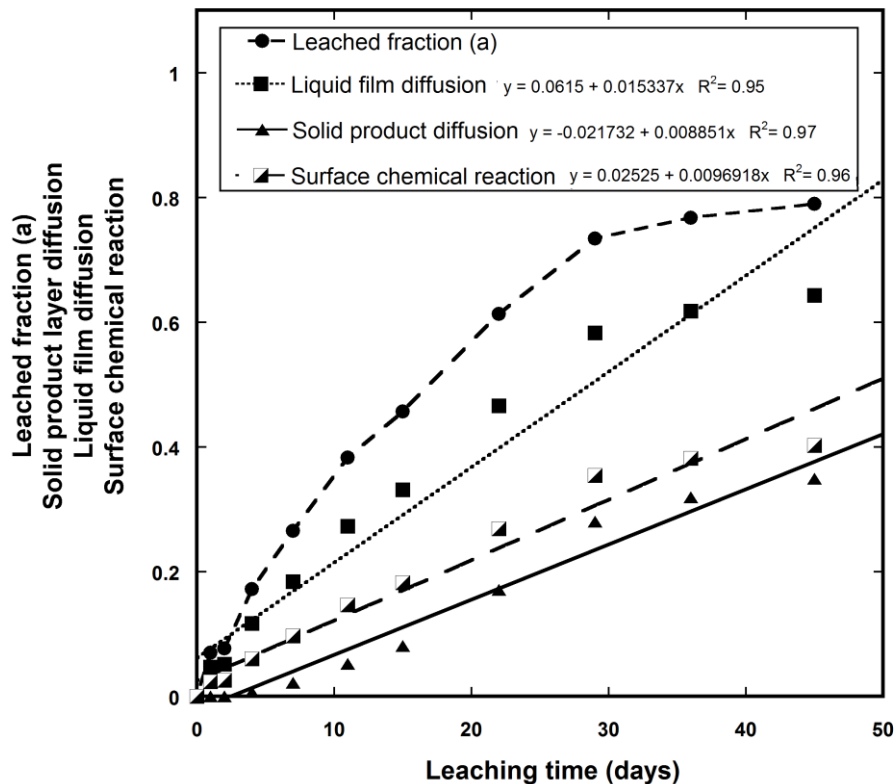


Fig. 5.6. Kinetic model fits of ZLR to experimental results of Zn bioleaching (sulfur - 2.51 g L⁻¹, pulp density 2.15%, initial pH 3.3, temperature 30 °C and agitation at 150 rpm).

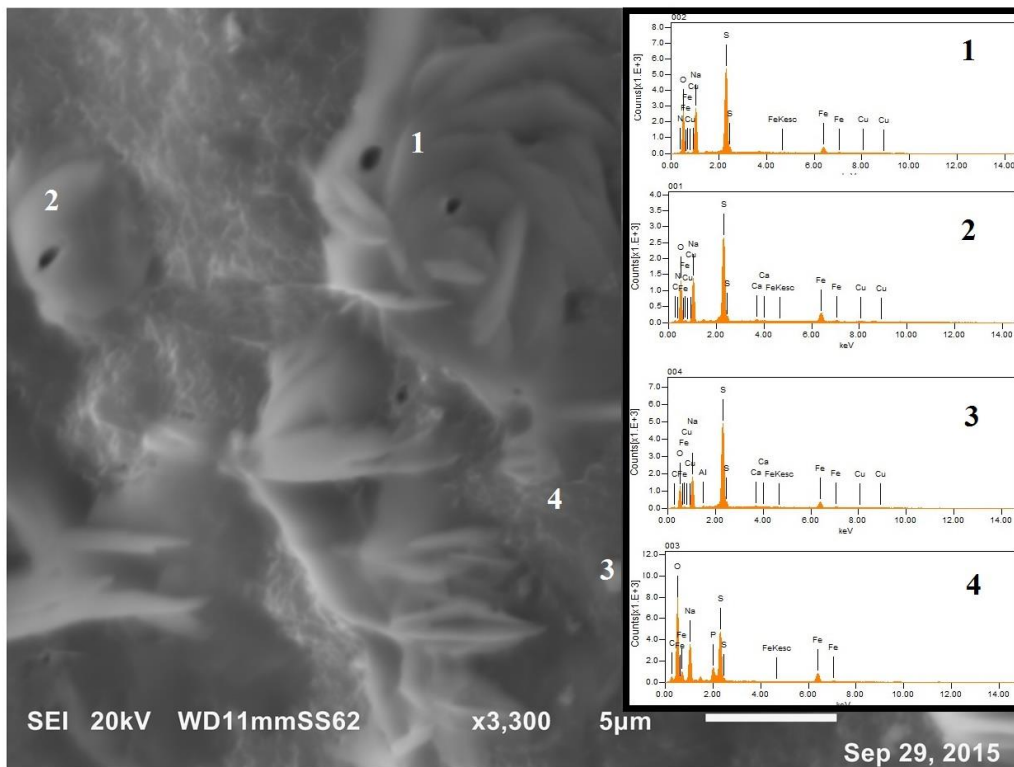
5.3.4. Selective Zn biorecovery from the acidic bioleachate

5.3.4.1. Fe removal from the acidic bioleachate

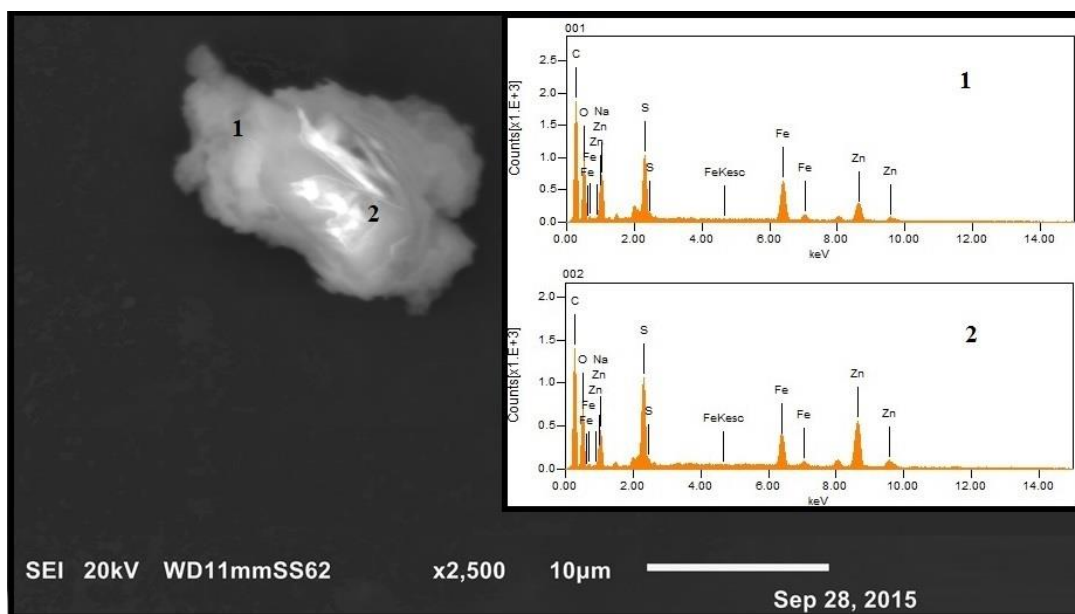
The first step in the selective Zn recovery was the removal of Fe from the bioleachate (pH 0.8). Fe was precipitated from the bioleachate by the addition of NaOH and the Fe removal efficiency is shown in Fig. S5.4. A significant amount (20 - 40%) of Fe can be removed even at acidic pH (pH 1.5 to 3.5). Theoretical prediction (data not shown) of Fe removal from the leachate indicated that more than 90 - 99 % of Fe can be precipitated (by adjusting the pH 1.0 to 6.5), in the form of $\text{Fe}(\text{OH})_2 \cdot 7\text{Cl}_3$. The experimental data showed that until pH 5.0, a maximum of 85 (± 2) % of Fe can be removed from the leachate. No detectable loss of Zn was observed until the pH was adjusted to 5.0. Besides, the theoretical prediction also showed no precipitation of Zn until pH 6.5 (data not shown). When the pH was increased to values >5.0 , Zn was also found to be depleted in the leachate.

5.3.4.2. Zn biorecovery from Fe depleted bioleachate

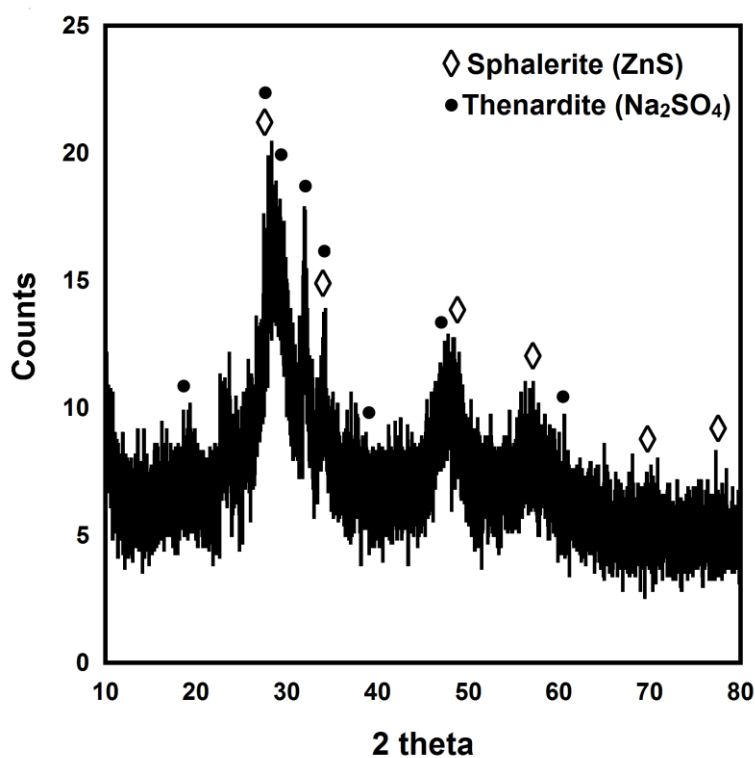
The selective Zn biorecovery trials were carried out in the Fe depleted leachate at a Zn:biogenic sulfide mass ratio of 1:1. After 15 days of growth, the supernatant of the sulfate reducing bacteria (SRB) culture was found to contain 405 (± 18) mg L^{-1} biogenic sulfide and used to biorecover Zn. The black colored precipitates settled at the bottom of the precipitation bottle. The solutions were analyzed for soluble metal concentrations and more than 97% of Zn was precipitated as Zn-sulfide. The composition of the precipitates was examined by SEM-EDS and XRD analysis (Fig. 5.7). The precipitates were light brown to black in color. SEM-EDS (Fig. 5.7b) analysis detected the presence of sodium impurities along with the Zn-sulfide precipitates. XRD spectra (Fig. 5.7c) confirmed that poorly crystalline sphalerite (ZnS) and thenardite (Na_2SO_4) were present in the precipitates.



(a)



(b)



(c)

Fig. 5.7. (a) SEM-EDS analysis of the Fe-precipitates, (b) SEM-EDS analysis of the Zn-sulfide precipitates and (c) XRD spectrum of Zn-sulfide precipitate from ZLR bioleachate.

5.4. Discussion

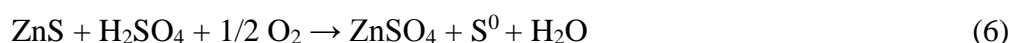
5.4.1. Biohydrometallurgy for selective Zn recovery from ZLR

This study showed that the biohydrometallurgical selective recovery of Zn from ZLR is a potential alternative strategy to chemical Zn leaching and recovery. Zn can be selectively recovered as sphalerite by bioleaching using *A. thiooxidans*, followed by biogenic sulfide precipitation: $19.9 (\pm 2.3)$ mg g⁻¹ of Zn can be leached from the ZLR within 45 days (Fig. 5.4) and $19.4 (\pm 0.3)$ mg g⁻¹ can be recovered from the acidic polymetallic bioleachate by dosing biologically produced sulfides (Fig. 5.7c). These results are comparable to results achieved by chemical sulfuric acid (1.5 M) leaching and chemical sulfide (100 mg L⁻¹) was used to leach $17.6 (\pm 1.2)$ mg g⁻¹ of Zn and precipitate $17.1 (\pm 0.1)$ mg g⁻¹ of Zn from the leachate (Chapter 4). The biohydrometallurgy is, however, much more time consuming: ~45 days were required to recover $19.4 (\pm 0.3)$ mg g⁻¹ of Zn, while its chemical counterpart recovered (17.1 ± 0.1 mg g⁻¹) in 6 h. On the other hand, chemical hydrometallurgy involves highly concentrated sulfuric acid (1.5 M), high temperature (80 °C) and a slightly higher agitation speed (250 rpm) (Chapter

4). In contrast, biohydrometallurgy can be performed at ambient temperature (30 °C) under the following conditions: agitation speed - 150 rpm, sulfur concentration - 3 g L⁻¹ and using bacteria (*A. thiooxidans*). The results obtained from this study show a proof-of-concept that biohydrometallurgy is an alternative strategy for Zn recovery from ZLR that is as efficient as chemical hydrometallurgy. This study should be explored further in continuous lab-scale bioreactors to optimize the Zn to biogenic sulfide ratio. Also various characteristics like settleability and particle size distribution of the precipitates need to be done in further studies.

5.4.2. Bioleaching of Zn from ZLR and its kinetics

This study showed that sulfur supplementation and pulp density are the key parameters in the bioleaching of Zn from ZLR and the Zn bioleaching followed the solid product diffusion kinetic model. Abiotic controls showed that ~10 to 12% of Zn was leached from the ZLR, which might be due to the sulfuric acid added to adjust the initial pH of the culture to 3.5 and also because of the presence of water soluble ZnSO₄ (Fig. 5.1). In the sulfur deficient *A. thiooxidans* culture, a slight decrease in the pH from 3.5 to 3.0 and slightly more Zn was leached than in the abiotic controls. This might be due to that bacteria were able to utilize trace amounts of reduced “S” compounds present in the ZLR to produce sulfuric acid, which lower the pH and leach out Zn. Based on the results obtained from the bioleaching studies (Fig. 5.1a), statistical analysis of the optimization experiments (Table 5.2) and comparative leaching studies (Fig. 5.5), leaching of Zn is mainly due to the biological sulfuric acid produced. Zn present in the studied ZLR was associated with sulfates, silicates, oxides and ferrites (Chapter 4). Thus the Zn bio-dissolution from the ZLR can be explained by Equations 5 to 8:



The optimization studies of the bioleaching parameters showed that the Zn leaching yield increased significantly with increased sulfur supplementation (Fig. 5.2). This was attributed to the high sulfur concentration which ensured a high production of sulfuric acid, thereby contributing to the Zn leaching. It is also noteworthy to mention that the Zn dissolution from ZLR is sulfuric acid concentration dependent. The order of this dissolution reaction with

respect to sulfuric acid concentration is 0.87 (Chapter 4). Liu et al. (2004) stated that only sulfur supplementation has a substantial impact on the biological sulfuric acid production by *A. thiooxidans* and reported 24 g L⁻¹ of sulfur as the optimum concentration. Based on the optimization studies performed in this study, 25.1 g L⁻¹ was found to be the optimum supplementation, which is comparable to the results of Liu et al. (2004). Besides, the pulp density also affected the Zn bioleaching characteristics, but the initial pH does not appear to have a significant effect on the Zn bioleaching (Table. 2). The decrease in the leaching of Zn with an increase in pulp density was presumably due to the buffering capacity of ZLR against diluted acids (Chapter 3). This is supported by the observation that strong (1 M) sulfuric acid leaching of Zn from this ZLR was not affected by the pulp density (Chapter 4).

The bioleaching of Zn from the ZLR followed a solid-product diffusion model. Statistical analysis in the form of 1-way ANOVA (data not shown) showed that the difference in the leaching efficiency of Zn (from the ZLR) by chemical or biogenic sulfuric acid was insignificant ($P > 0.95$). Hence, it can be concluded that the biogenic sulfuric acid is the sole leachant in the system. Kinetic analysis of the Zn bioleaching (Fig. 5.6) shows that the leaching is solid-product diffusion controlled, i.e. diffusion of the biogenic sulfuric acid through the solid-product layer and not on the liquid film boundary layer. The Zn bioleaching kinetics from ZLR by biogenic sulfuric acid are comparable with previous studies carried out with chemical sulfuric acid leaching of Zn from ZLR (Chapter 4; Safarzadeh et al, 2009; Hollagh et al., 2013).

5.4.3. Selective biorecovery of Zn from the bioleachate

Biogenic sulfide could selectively precipitate Zn-sulfides from the Fe depleted bioleachate. The presence of Fe in the leachate can interfere with the selective recovery of Zn (Chapter 4; Radzymińska-Lenarcik et al., 2015). Goethite, paragoethite, and jarosite precipitation processes have been used for Fe removal from the acidic polymetallic leachates (Buban et al., 1999; Hu et al., 2012; Yazici et al., 2014). Jarosite can also co-precipitate divalent metals like Cu and Zn in sulfate rich solutions (Dutrizac and Dinardo, 1983). Most of the Fe can also be removed by the acidic leachate by adjusting the initial pH with NaOH (Chapter 4). In this study, Fe was removed, without any detectable loss/precipitation of Zn by adjusting the initial pH to 5.0 (Fig. S5.4). Visual MINTEQ (data not shown) predicted that most of the Fe in the leachate can be removed, even at highly acidic pH (1.0 - 1.5) in the form of $\text{Fe}(\text{OH})_2 \cdot 7\text{Cl}_3$, but SEM-EDS analysis did not reveal the presence of any chloride species. When the theoretical prediction was again performed by excluding the $\text{Fe}(\text{OH})_2 \cdot 7\text{Cl}_3$ phase, hematite (Fe_2O_3) formation was predicted (data not shown). Fig 7a shows that Cu can also be removed in this

step by co-precipitation or sorption with Fe-oxides. There were many instances where Cu was shown to sorb onto hematite (Chakravarty et al., 1998; Peacock and Sherman, 2004; Bekényiová et al., 2015). Zn depletion in the leachate at $\text{pH} > 5.0$ might also be due to the sorption of Zn to Fe-oxides (Bekényiová et al., 2015). Cd and Pb removal was not optimized in this study, as their total concentrations in the leachate were negligible when compared to Fe and Zn (Fe - 1.7 g L^{-1} , Zn - 0.415 g L^{-1} , Cd and Pb $< 0.01 \text{ g L}^{-1}$).

The Fe depleted leachate ($\text{pH} 5.0$) was subjected to the selective recovery of Zn. Approximately 1:1 mass ratio of Zn:biogenic sulfide could precipitate $97 (\pm 2.1) \%$ of the dissolved Zn in the Fe depleted bioleachate. The Zn precipitation from acidic solutions by biogenic sulfides has been reported in the literature (Esposito et al., 2006; Alvarez et al., 2007; Sahinkaya et al., 2009). The result of selective Zn bioprecipitation, at an initial pH of 5.0, is comparable to chemical precipitation carried out by Gharabaghi et al. (2012). Gharabaghi et al. (2012) selectively precipitated 94% of Zn at an initial pH of 5.5 using thioacetamide from synthetic solutions within 45 min. In this study, the final pH was increased to $6.9 (\pm 0.3)$ in the Zn-sulfide precipitated solution. Sahinkaya et al. (2009) reported the selective Zn precipitation from acidic mine drainage in the pH range of 6.8 to 7.4. Chemical sulfide (100 mg L^{-1}) showed a recovery efficiency exceeding 90% from acidic ZLR leachate (Chapter 4). In contrast, Esposito et al. (2006) reported that biogenic sulfide precipitation was not as effective as chemical sulfide (Na_2S) because of the interferences caused by SRB metabolites such as acetate or media components such as ethylene diamine tetra-acetic acid (EDTA). The interferences with such chelating agents were not investigated in this study.

Sphalerite or würtzite are the two possible polymorphs of ZnS . XRD analysis (Fig. 5.7c) confirmed the presence of poorly crystalline sphalerite and thenardite minerals in the precipitates which is in strong agreement with the Visual MINTEQ predictions (data not shown). SEM-EDS analysis (Fig. 5.7b) also showed that other than Zn and S, the precipitates also contain Fe and Na. These impurities can be attributed by the use of sodium hydroxide for pH adjustment and residual Fe concentration (after pH adjustment).

5.5. Conclusions

This study demonstrated a proof-of-concept that biohydrometallurgy can be a potential alternative strategy for the recovery of metals (e.g. Zn) from oxidized secondary resources like ZLR. The sulfur concentration plays a significant role in the bioleaching of Zn. A maximum of 79% of Zn can be bioleached from ZLR within 45 days under optimum conditions. The leaching

efficiency of biogenic sulfuric acid and chemical sulfuric acid were comparable. The bioleaching of Zn from ZLRs followed solid-product shrinking core kinetics. Biorecovery of Zn of the soluble Zn from the bioleachate is comparable with the chemical recovery. More than 85% of Fe can be removed from the bioleachate by adjusting the initial pH by the addition of NaOH. 97% of soluble Zn can be recovered from the acidic bioleachate at a Zn:biogenic sulfide mass ratio of 1:1.

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Chapter 6

Leaching and selective copper recovery from acidic leachates of Três Marias zinc plant (MG, Brazil) metallurgical purification residues

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Abstract

Zinc plant purification residue (ZPR), a typical Zn-hydrometallurgical waste, was collected from the Três Marias Zn plant (MG, Brazil). ZPR was characterized for its metal content and fractionation, mineralogy, toxicity and leachability. Toxicity characteristics leaching procedure (TCLP) and BCR sequential extraction results revealed that this ZPR displays high percentages of metals (Cd, Cu, Zn and Pb) in the highly mobilizable fractions, increasing its hazardous potential. Bulk chemical analysis, pH dependent leaching and acid (H_2SO_4) leaching studies confirm that the ZPR is polymetallic, rich in Cd, Cu and Zn. The sulfuric acid concentration (1 M), agitation speed (450 rpm), temperature (40 °C) and pulp density (20 g L⁻¹) were optimized to leach the maximum amount of heavy metals (Cd, Cu and Zn). Under optimum conditions, more than 50%, 70% and 60% of the total Cd, Cu and Zn present in the ZPR can be leached, respectively. The metals in the acid leachates were investigated for metal sulfide precipitation with an emphasis on selective Cu recovery. The optimized process variables for metal sulfide precipitation for initial pH and Cu to sulfide mass ratio were pH 1.5 and 1:0.5 (Cu:sulfide) ratio: more than 95% of Cu can be selectively recovered from the polymetallic ZPR leachates. The Cu precipitates characterization studies reveal that they are approximately 0.1 µm in diameter and mainly consist of Cu and S. XRD analysis showed covellite (CuS), chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and natrochalcite ($\text{NaCu}_2(\text{SO}_4)_2(\text{OH}) \cdot \text{H}_2\text{O}$) as the mineral phases. ZPRs can thus be considered as an alternative resource for copper production.

Key words: Fractionation, pH dependent leaching, Selective recovery, Sulfide precipitation, Zn metallurgical residue.

6.1. Introduction

Copper is one of the important non-ferrous metals that has a lot of commercial applications in a wide range of industries such as medicine, construction, machineries, electrical and electronics and telecommunication (Dollwet et al., 1985; Camarillo et al., 2010; Lambert et al., 2014). Chalcopyrite (CuFeS_2) is the most commonly used ore in copper metallurgy. Usually Cu is extracted from these ores by pyrometallurgical operations as they are not easily soluble by hydrometallurgy (Schlesinger et al., 2011). Other sulfidic ores such as chalcocite (Cu_2S) and covellite (CuS) can be used for hydrometallurgical processes (Monteiro et al., 1999). While the demand for copper is growing rapidly, metallurgists have to address the depletion of high-grade ores with the utilization of low-grade ores and metallurgical wastes (Walting, 2006; Künkül et al., 2013). Low-grade oxidized ores (such as oxides, carbonates and sulfates) are also used for copper production. Worldwide, Cu production (10-15%) is based on secondary Cu resources such as alloys and scraps (Schlesinger et al., 2011). In recent decades, many Cu-bearing waste materials (like copper slags, furnace sludges, dusts and electronic wastes) are used for Cu recovery (Jandova and Niemczyková, 2000; Banza et al., 2002; Bakhtiari et al., 2008; Carranza et al., 2009; Kim et al., 2011; Karwowska et al., 2014; Lambert et al., 2015).

Zinc plant purification residues (ZPR) are typical metallurgical wastes produced during the hydrometallurgical processing of primary zinc ores (Chapter 2). These purification residues are generated as by-products during the separation of the desired metal (zinc) from the impurities present, based on the mineralogy and tap location of the primary ores (Lottermoser, 2010; Chapters 2 and 3). Cadmium, cobalt (Haghshenas et al., 2007; Safarzadeh et al., 2011; Li et al., 2013), copper (Hodjaoglu and Ivanov, 2014), manganese (Haghshenas et al., 2007), lead and zinc (Haghshenas et al., 2007; Li et al., 2013) are often found in elevated concentrations in these ZPR. Cu is usually present in copper oxide or copper carbonate phases in the ZPR (Kul and Topkaya, 2008; Hodjaoglu and Ivanov, 2014).

Copper leaching kinetics from synthetic or low grade Cu-oxides and Cu-carbonates have been well documented (Bingöl and Canbazoglu, 2004; Habbache et al., 2009; Ata et al., 2011). Usually Cu is recovered from the leachates by solvent extraction and electrowinning techniques (Sole and Hiskey, 1995; Fornari and Abbruzzese, 1999; Panda and Das, 2001; Lan et al., 2005; Reddy et al., 2007). Though electrowinning is an established recovery technology, recovery of pure metals from multi-metallic solutions is difficult as impurities can greatly influence the selective metal recovery (Youcai and Stanforth, 2001; Steyn and Sandenbergh, 2004). Metal precipitation by chemicals (such as sulfides and hydroxides) offers selective

recovery and faster recovery in relatively simple operating conditions (Lewis, 2010). The major demerit of the hydroxide precipitation is the higher solubility of metal hydroxides compared to metal sulfides (Lewis, 2010). There were few investigations on Cu sulfide precipitation (MSP), but mostly as effluent or acid mine drainage treatment technique (Al-Tarazi et al., 2005; Alvarez et al., 2007; Sahinkaya et al., 2009; Gharabaghi et al., 2012; Hu et al., 2012).

In this study, ZPR was collected from an operating Zn - metallurgical industry (Três Marias, Brazil) and investigated for the selective recovery of copper by sulfide precipitation. The ZPR was studied to understand its characteristics in detail, including mineralogy, metal fractionation and potential toxicity. The major objectives of the study were to examine the leaching yield and kinetics of Cu from ZPR. The factors affecting the leaching rate of Cu such as pulp density, agitation speed, temperature and leachant concentration were optimized. Finally, selective recovery of Cu from the polymetallic acidic ZPR leachates by chemical sulfide precipitation was achieved and the mineralogy, purity and particle size of the precipitates were characterized. The effect of initial pH and Cu to sulfide mass ratio on Cu-sulfide precipitation was also optimized.

6.2. Materials and Methods

6.2.1. Samples

ZPR samples were collected from the Zn-hydrometallurgical plant located in Três Marias (MG, Brazil), which processes Zn-sulfide and Zn-silicate primary ores to produce Zn. During acidic leaching of the primary ores, several impurities (such as Cd, Co, Cu, Ni and Pb) are also leached alongside zinc. These acid leachates are then purified to remove the impurities prior to further downstream processing. A Zn dust cementation strategy is applied to purify these acidic leachates as illustrated in equation 1 (Feijo, 2007):



As shown in Equation 1, Zn powder is added to the acidic leachate at 55 °C with constant stirring. A residue is generated as a by-product at this stage. These zinc plant residues are called zinc purification residues and contain impurities (Cd, Co, Cu and Ni) associated with the natural ores as well as secondary zinc mineral phases. The purified solution is then subjected to further

Zn recovery processes. Detailed mineral processes and unit operations employed by the Três Marias Zn - plant to produce Zn were described elsewhere (Souza, 2000; Souza et al., 2007).

6.2.2. Characterization of the ZPR

6.2.2.1. pH, total, volatile and fixed solids

The ZPR samples were dried at room temperature and ground to a particle size below 1 mm in diameter. The pH of the ZPR was estimated by the protocol suggested by Pansu and Gautheyrou (2007). Ten grams of the dried samples were taken in a polyethylene flask and 25 mL of boiled water were added to the flask. The flask was agitated in an orbital shaker (IKA Labortechnik K550 Digital) for 1 hour. The solution was filtered (0.45 μ m, nitro cellulose membrane) and the pH of the filtrate was measured using a Horizon pH-meter. Total, volatile and fixed solids as well as moisture content of the samples were determined according to the USEPA 1684 (2001) procedure.

6.2.2.2. X – Ray Diffraction

Dried and powdered ZPR samples were examined for crystalline mineral phases by a X-Ray diffractometer. X-ray diffraction (XRD) analyses were carried out on a Bruker D8 Advance diffractometer equipped with an energy dispersion Sol-X detector with copper radiation ($\text{CuK}\alpha$, $\lambda = 0.15406$ nm). The acquisition was recorded between 2° and 80° , with a 0.02° scan step and 1 s step time.

6.2.2.3. X-Ray Fluorescence

X-ray fluorescence (XRF) analyses was carried out using a Panalytical X-fluorescence spectrometer equipped with an Energy Dispersive Minipal 4 (Rh X Ray tube-30 kV-9W) at a resolution of 150 eV (MnKa).

6.2.2.4. Total metal content

The bulk metal content of the samples was investigated by modified hotplate aqua-regia digestion (Chen and Ma, 2001; Chapter 3). Aqua regia (9 mL of HCl (37%): 3 mL of HNO₃ (65%)) was added to 1.0 g of sample taken in a custom digestion flask. The solutions in the flasks were then digested for 2 hours (100°C) using DigiBlock ED16S, Lab Tech. During digestion, the flasks were covered with watch glass and after digestion they were cooled at room

temperature for 2 hours. Twenty milliliters of 2% nitric acid were added on the sides of the flasks to recover the metals. The solution was filtered at 2.5 μm on Whatman grade 5 filter paper. The filtrate was made up to 100 mL by ultrapure water and the final solution was analyzed for metal concentrations (Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb and Zn).

6.2.3. Fractionation and potential toxicity of the ZPR

6.2.3.1. Toxicity characteristics leaching procedure (USEPA 1311)

The potential toxicity of the ZPR was investigated by the USEPA 1311 (1992) protocol. As for the laboratory convenience the protocol was slightly modified without changing the pulp density. The pH of the extractant (acetic acid) was chosen as pH 4.93 (± 0.1), according to the USEPA 1311 protocol. A volume of 10 mL of extractant was taken in a poly-ethylene extraction bottles and 0.5 g of the ZPR was added to the extraction bottle. The solution containing extraction bottles were rotated for 18 hours at room temperature (20 ± 2 °C). The leachates were filtered at 0.45 μm on nitro cellulose filters. The filtrate was analyzed for final pH and the metals release (Cd, Cu, Pb and Zn).

6.2.3.2. Sequential extraction (Perez-Cid et al., 1998)

The ultrasound assisted community bureau of reference (BCR) sequential extraction procedure was used to study the fractionation of metals at natural environmental conditions (Perez-Cid et al., 1998). Detailed information regarding the extraction solutions, ultrasound accelerated extraction time and the metals associated phases were provided in supplementary information Table 6.1. The reducing agent (hydroxyl ammonium chloride) was always freshly prepared at the start of the experiments. The leachates were analyzed for their Cd, Cu, Pb and Zn concentration.

Table 6.1. Ultrasound assisted BCR sequential extraction procedure (Perez-Cid et al., 1998).

Fraction	Extracting agent	Extraction conditions	
		Ultrasound time	Temperature
F1. Acid soluble	20 mL HOAc (0.11 mol L ⁻¹)	7 min	20-25°C
F2. Reducible	20 mL NH ₂ OH.HCl (0.1 mol L ⁻¹ , pH = 2)	7 min	20-25°C
F3. Oxidizable	10 mL H ₂ O ₂ (30%, pH = 2) and then 25 mL NH ₄ OAc (1 mol L ⁻¹ , pH = 2)	2 and 6 min	20-25°C
F4. Residual	Aqua regia (HNO ₃ /HCl, 1:3)	120 min	100°C

6.2.3.3. pH stat leaching experiments (USEPA 1313)

The pH effect on the liquid solid partitioning of ZPR samples was investigated according to USEPA 1313 (2012). Acid/base neutralizing capacities of the samples were initially determined by pre-titration experiments (data not shown). Ten different pH values (2.5, 3.5, 4.5, 5.5, 8.0, 9.0, 10.5, 11.5, 13.0 and natural pH (pH 6.9) of the samples) were selected based on the pre-titration experiments. All the experiments were carried out at a pulp density of 100 g L⁻¹. The flasks were continuously agitated at 150 rpm for 48 hours at room temperature. The desired pH values were maintained by the addition of acid (5 M HNO₃ and 14 M HNO₃) and base (1 M KOH). A flask with only ultrapure water was used (without any acid/base addition) to study the release of metals under natural pH. The leachates were filtered, acidified (if necessary) and analyzed for metal concentrations.

6.2.4. Leaching experiments

Leaching experiments were carried out in 250 mL Erlenmeyer flasks, with a working volume of 100 mL. Sulfuric acid (Merck, 95% - 98%, density 1.84 g mL⁻¹) was used as the leaching agent. The factors affecting the leaching rate such as (i) agitation (50 rpm, 150 rpm, 250 rpm, 350 rpm and 450 rpm), (ii) temperature (20 °C, 40 °C, 60 °C and 80 °C, ± 2 °C), (iii) sulfuric acid concentration (0.1 M, 0.5 M, 1 M, 1.5 M and 2 M) and (iv) pulp density (20 g L⁻¹, 50 g L⁻¹, 100 g L⁻¹ and 200 g L⁻¹) were investigated. All the leaching experiments were performed in an incubator shaker (IKA KS 4000i control). The samples were withdrawn at

regular time intervals (15, 30, 60, 120 and 240 minutes) and analyzed for their metal concentrations (Cd, Cu, Pb, Fe and Zn).

6.2.5. Metal sulfide precipitation

Theoretical prediction of the selective precipitation of Cu from the acidic leachates was carried out using visual MINTEQ V3.1 (Gustafsson, 2012; <http://vminteq.lwr.kth.se/>). Visual MINTEQ is a chemical equilibrium model that can predict the speciation, solubility, adsorption and precipitation of metals at equilibrium. Input molar concentrations of each metal (Zn^{2+} , Cu^{2+} , Cd^{2+} , Fe^{2+} , Pb^{2+} , Na^+ , SO_4^{2-} and S^{2-}) were provided based on the leachate composition obtained at the optimized leaching conditions. Different dissolved sulfide concentrations were provided and the pH was varied from 0.5 to 8.0 at 0.5 intervals. The temperature was constantly maintained at 20 °C and oversaturated solids were allowed to precipitate. Concentrations of the dissolved metals and the amount of sulfide precipitates were obtained in the output.

The ZPR leachates were collected in a glass beakers and the pH was adjusted to pH 0.5 – pH 8.0 using 10 M NaOH. The total metal concentrations (Cd, Cu, Fe, Pb and Zn) in the pH adjusted leachates were analyzed to understand the hydroxide precipitation or co-precipitation with iron oxides. Metal sulfide precipitation studies were carried out in airtight glass bottles. 10 mL of the pH adjusted leachates were taken in a glass bottle and N_2 gas was purged (into the solution and filled up the head space) to ensure anoxic conditions. 10 mL of a $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ($0.75 - 69 \text{ g L}^{-1}$) solution was added using 20 mL syringes. The glass bottles were agitated at 150 rpm and room temperature ($20 \pm 2 \text{ }^\circ\text{C}$) for 1 h. In the precipitation kinetic studies, samples were collected at regular time intervals (1, 2, 3, 5, 10, 20, 30, 60 and 90 minutes).

The effect of the Cu-sulfide mass ratio was studied by varying the sulfide concentration against constant Cu concentration, i.e. Cu:sulfide mass ratios of 1:0.25, 1, 0.5, 1:1 and 1:2. After precipitation, the solution was filtered at $0.45 \text{ }\mu\text{m}$ on nitrocellulose filters and the filtrate was analyzed for their metal (Cd, Cu, Fe, Pb and Zn) concentration by atomic absorption spectroscopy (PerkinElmer, AAnalyst 200). These Cu-sulfide mineral precipitates were characterized for constituents, mineralogy and particle size distribution. Mineralogy of the precipitates was studied by XRD as mentioned in section 2.2.2. The constituents and morphology of the precipitates were examined by Scanning Electron Microscope – Energy Dispersive X-Ray spectroscopy analyses (SEM-EDS, Jeol JSM 6010LA) at 10-20 KeV and high vacuum conditions. The particle size distribution of the precipitates was studied using a Malvern Zetasizer (Nano ZS).

6.2.6. Analytical methods and statistical analysis

Unless specified otherwise, all experiments were performed in triplicates and procedural blanks were performed. Samples were filtered on 0.45 μm nitrocellulose filters and the metal content of the solutions was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300 Perkin Elmer). The detection limits (metals and their corresponding wavelengths) of the ICP-OES are provided in the supplementary information (Table S2). The means of the analyses were statistically compared using one-way analyses of variance (ANOVA) using statistical computing and graphics software, R v3.1.1. The confidence limit was 95% ($P < 0.05$).

6.3. Results

6.3.1. Total metal contents of ZPR

The ZPR had a pH of 6.9 (± 0.2), a moisture content of 7%, and a total, volatile and fixed solids content of 93%, 89% and 11%, respectively. Fig. 6.1 shows the XRD spectra of raw ZPR and ZPR leached at pH 2.5 (2 M HNO_3). XRD analysis (Fig. 6.1a) indicated the presence of copper oxide (cuprite, Cu_2O) and copper carbonate (azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) in the raw ZPR and anglesite (PbSO_4) was observed in the nitric acid leached (pH 2.5) ZPR (Fig. 6.1b). ZPR contains high concentrations of heavy metals such as Cu (47%), Zn (28%), Cd (9.3%) and Pb (4.9%) and relatively lower amounts of Ni (0.34%), Co (0.34%), Fe (0.12%) and Mg (0.74%). Bulk metal analysis (hotplate aqua-regia digestion) results were quite comparable with the XRF results, except for Cd, Cu and Zn (Table 6.2).

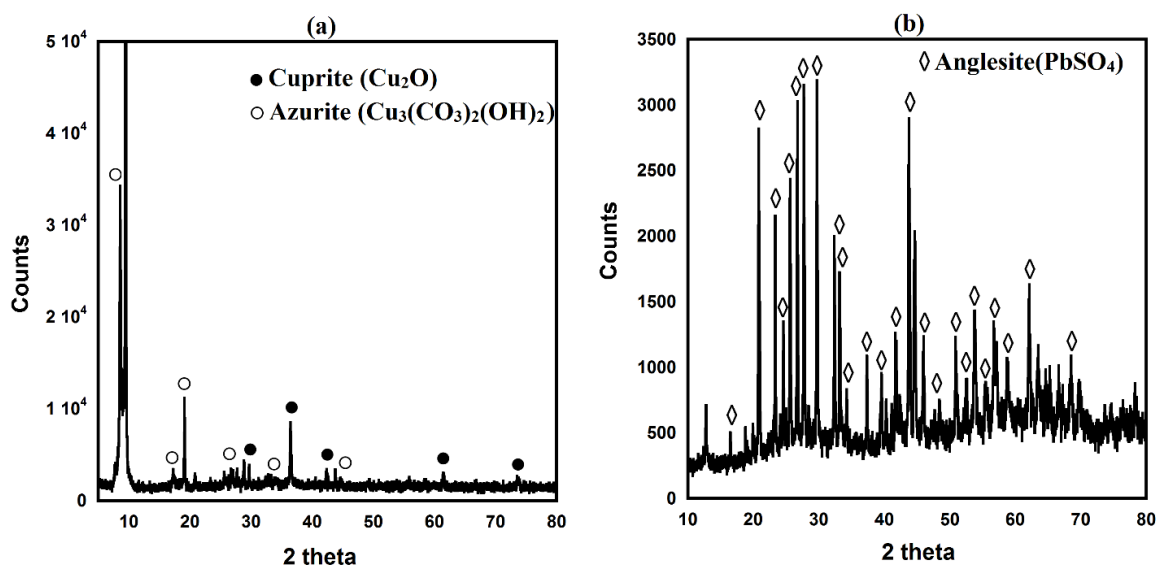


Fig. 6.1. XRD spectra of ZPR: (i) raw ZPR and (ii) ZPR leached at pH 2.5 (HNO_3).

Table 6.2. Total metal content of the ZPR from the Três Marias Zn plant.

Metals	Aqua regia digestate	XRF
	(g kg^{-1})	(wt %)
Cu	472.0 ± 26.3	32.69
Zn	285.6 ± 27.5	20.95
Cd	92.6 ± 5.9	14.34
Pb	48.5 ± 2.0	6.93
Mg	7.4 ± 1.2	0.36
Ni	3.44 ± 0.07	0.33
Co	3.25 ± 0.06	0.24
Mn	2.10 ± 0.05	0.11
Fe	1.20 ± 0.01	0.09

6.3.2. TCLP

The toxicity leaching results of Cd, Cu, Pb and Zn are presented in the Table 6.3. The pH of the leachates was increased from 4.93 to 5.75, which was attributed to the good acid buffering capacity of the samples. In the TCLP leachates, 39.8 mg L^{-1} of Pb and a much higher concentration of 718.9 mg L^{-1} of Cd was observed. Zinc and copper concentrations were also analyzed in the TCLP leachates. Zinc displays higher concentrations in the TCLP leachates compared to copper (677.97 mg L^{-1} and 319.3 mg L^{-1} for zinc and copper, respectively).

Table 6.3. Potential toxicity of the ZPR.

Metals	Regulatory threshold (USEPA) (mg L ⁻¹)	Regulatory threshold (Brazil) (mg L ⁻¹)	TCLP ZPR (mg L ⁻¹)
Pb	5.00	1.00	39.8 ± 1.5
Cu	-	-	319.3 ± 15.1
Cd	1.00	0.50	718.8 ± 32.9
Zn	-	-	677.9 ± 19.5

6.3.3. Sequential extraction

Figure 6. 2 gives the percentage of metal fractions released in each step of the BCR sequential extraction procedure. Copper was mainly observed in the oxidizable fraction (85%). Significant concentrations of Cu were observed in the acid extractable and reducible fractions, approximately 7% in both fractions. Cd was the most released metal in the acid extractable fractions (78%) and only 21% was recovered in reducing conditions. Zinc followed a similar release pattern as that of Cd and was also mainly confined to the acid extractable (63%) and reducible (36%) fractions. The concentrations of Cd, Cu and Zn in the residual fractions are lower (i.e. approximately 0.5%). On the other hand, Pb was mainly released in the oxidizable (66%) and residual (22%) fractions. Significant concentrations of Pb (11%) were released by acetic acid (i.e. acid extractable fraction).

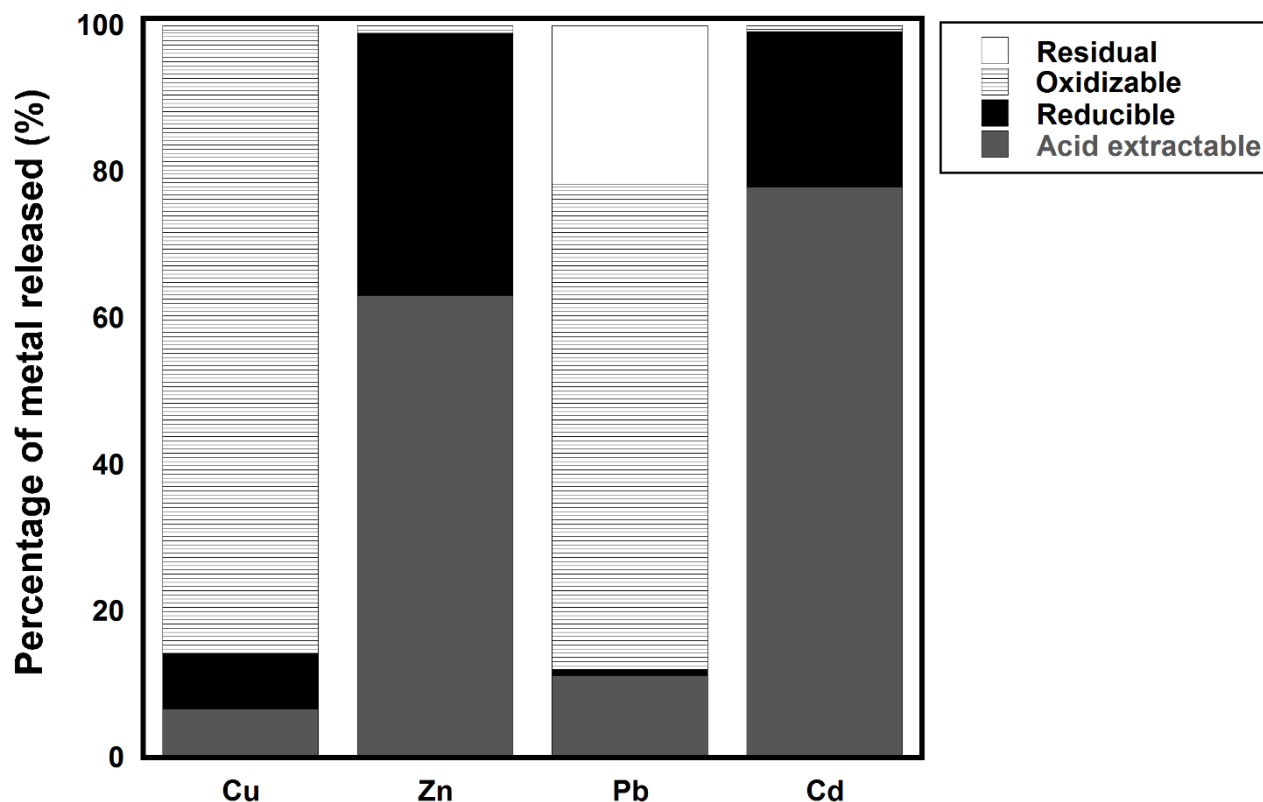


Fig. 6.2. Heavy metal fractionation in Três Marias ZPR evaluated by the accelerated BCR procedure.

6.3.4. pH stat leaching experiments

The pH stat leaching behavior of heavy metals (Cd, Cu, Pb and Zn) of ZPR is shown in Fig. 6.3. A maximum of 68% of Cu was leached at pH 2.5. The amount of Cu leached started decreasing when the pH increased from pH 3.5 to pH 4.5, leached Cu fractions were 50% and 3%, respectively, this further decreased to less than 0.01% at its natural pH (pH 6.9). Similarly, a 'L' shaped trend was observed for Cd and Zn. But for Zn and Cd, the leaching at pH 3.5 was equal or slightly higher than at pH 2.5. A further increase in pH, i.e. pH 4.5 –13, decreases Zn and Cd leaching. But at extreme alkaline pH 13, slightly higher concentrations of the metals (Cd, Cu and Zn) were observed than in the pH 6.9 (natural pH) –11.5 range. In contrast with the other metals, the Pb concentration below the detection limit in the range between pH 2.5 to pH 9.0 and increased leaching (0.3% to 10.5%) was observed in the pH range 10.5 - 13.

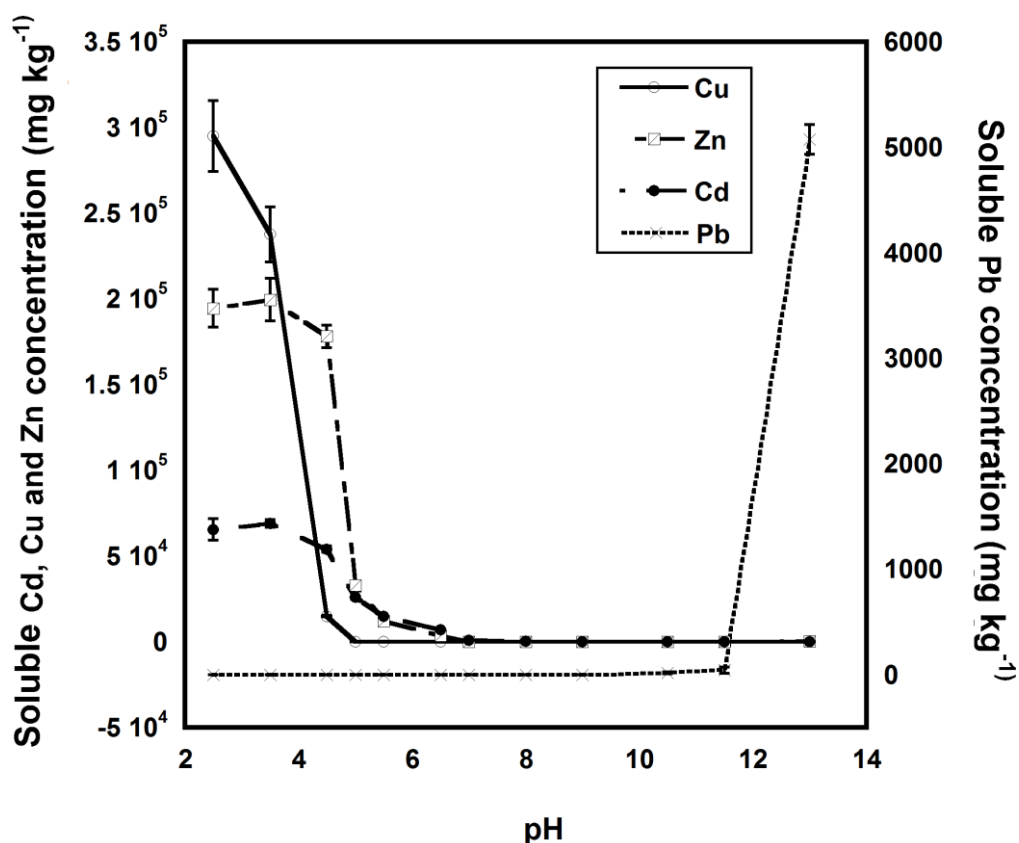


Fig. 6.3. Heavy metals leaching from the ZPR as a function of pH.

6.3.5. Optimization of leaching parameters

The effect of agitation on the Cu leaching kinetics against time (Fig. 6.4a) and Cd, Cu and Zn leaching (Fig. 6.4b) from the ZPRs was investigated. Fig. 6.4b shows that the agitation speed plays an important role in the leaching of the heavy metals, especially Cu. Cu leaching was increased from 52% to 66% upon increasing the agitation speed from 50 rpm to 450 rpm. Cd and Zn leaching was not significantly influenced by such a change in agitation rate.

The effect of temperature on the leaching of Cd, Cu and Zn is shown in Fig. 6.4 (c and d). Temperature did not have a substantial influence on the release of metals such as Cd, Cu and Zn. The percentage of Cu leaching efficiency from the ZPR was slightly increased from 59% to 69% when increasing the temperature from 40 °C to 80 °C. The difference in leaching efficiency was negligible between 20 - 40 °C and 60 - 80°C. For Cd and Zn also, the leaching yield was not significantly affected by the change in temperature (20 – 80°C). An average of 60 (± 2) % of Cd and 64 (± 3) % of Zn leaching was observed (after 6 hours of leaching) in the studied temperature range.

Fig. 6.4 (e and f) shows the effect of the sulfuric acid concentration on Cd, Cu and Zn leaching. The results showed that the acid concentration did not play a crucial role in the leachability of the studied metals. For Cu leaching, the sulfuric acid concentration ($0.5 \text{ M} > 2 \text{ M}$) did not influence the Cu dissolution significantly, while lower concentrations ($0.1 \text{ M H}_2\text{SO}_4$) leached a comparatively lower percentage of Cu (49%). On the other hand, Cd ($60 \pm 2\%$) and Zn ($63 \pm 3\%$) leachability were not influenced by the variation in leachant (H_2SO_4) concentration.

The effect of pulp density on the leaching of Cd, Cu and Zn from the ZPR is shown in Fig. 6.4 (g and h). The results revealed that the pulp density plays an important role on the metal leaching. Generally, the metal leaching efficiency was decreasing with increasing pulp density. For Cu, 63% was leached at 20 g L^{-1} pulp density and a comparable amount of 61% was leached at a 50 g L^{-1} pulp density, but when the pulp density is increased to 100 g L^{-1} and 200 g L^{-1} , the leaching efficiency was decreased to 46% and 8%, respectively. Similar to Cu, Cd and Zn leaching was also significantly influenced by pulp density. For Cd, the leaching yield was decreased from 61% to 34% with an increase in pulp density from 25% to 20%, while for Zn it was decreased from 62% to 47% for the same variation in pulp density.

Fig. 6.S1 shows the Cu leaching trend under optimized conditions: 20 g L^{-1} pulp density, $1 \text{ M H}_2\text{SO}_4$ and $80 \text{ }^\circ\text{C}$ at 450 rpm. The Cu leaching (under these conditions) follows an exponential increase in the initial stages and nearly 63% of the Cu is leached out within 15 minutes. Between 15 minutes to 240 minutes, the trend approaches a near plateau trend with a minor increase (11%) in Cu leaching. The plateau region was attained after 240 – 420 minutes, where the increase in Cu leaching was negligible ($< 5\%$).

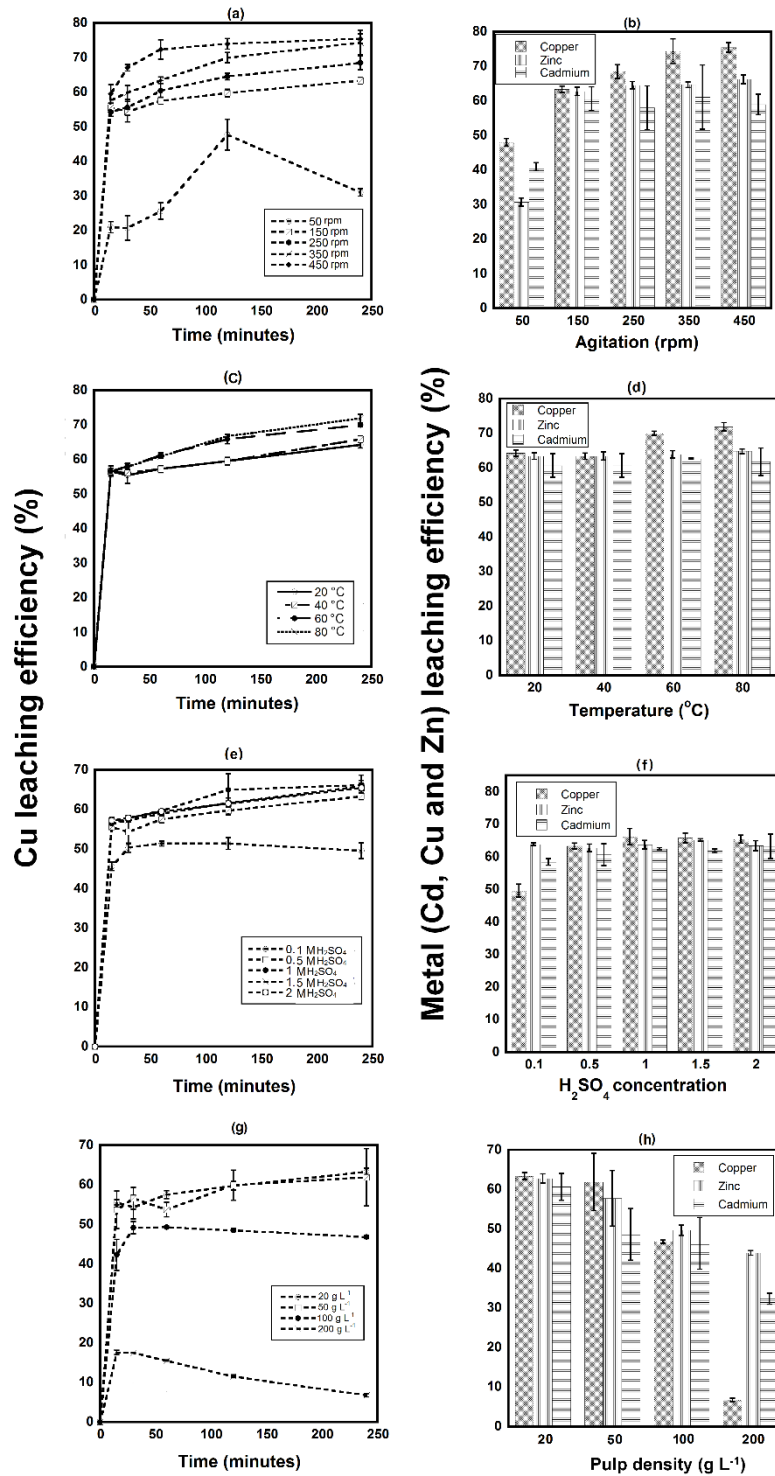


Fig. 6.4. Effect of (a) agitation, (c) temperature, (e) acid concentration and (g) pulp density on Cu leachability against time and effect of (b) agitation, (d) temperature, (f) acid concentration and (h) pulp density on metal (Cd, Cu and Zn) leachability after 6 hours of leaching.

6.3.6. Copper sulfide precipitation from the polymetallic ZPR leachate

The effect of the initial pH (of the leachate) on the metal (Cd, Cu and Zn) sulfide precipitation by 100 mg L⁻¹ dissolved sulfide is shown in Fig. 6.5. Prior to the sulfide dosage, metal loss due to the addition of NaOH was investigated (data not shown). From Fig. 6.S2 (effect of NaOH alone), it was concluded that no detectable loss of Cu, Cd and Zn was observed until pH 4.0. From pH 5.0 to 8.0, Cu solubility follows a U shaped trend meaning that in slightly acidic to neutral pH (pH 5.0 – pH 7), the concentration of Cu is decreasing and again at pH 8.0, it started increasing. The Zn concentration starts decreasing at pH 5.5, while the Cd concentration was decreased only at pH 8. Fig. 6.5 shows that more than 96% of the Cu (from the soluble metals in the leachates) can be precipitated as Cu-sulfide at pH 5.0. Approximately 20% of Cd and 20% of Zn is also found precipitating alongside at this pH. At extreme acidic pH range (pH 0.5 to 1.5) the Cu precipitation efficiency is low (< 20%), but no detectable precipitation of Cd and Zn is observed. Hence, an initial pH 1.5 was selected for the Cu:sulfide mass ratio optimization studies.

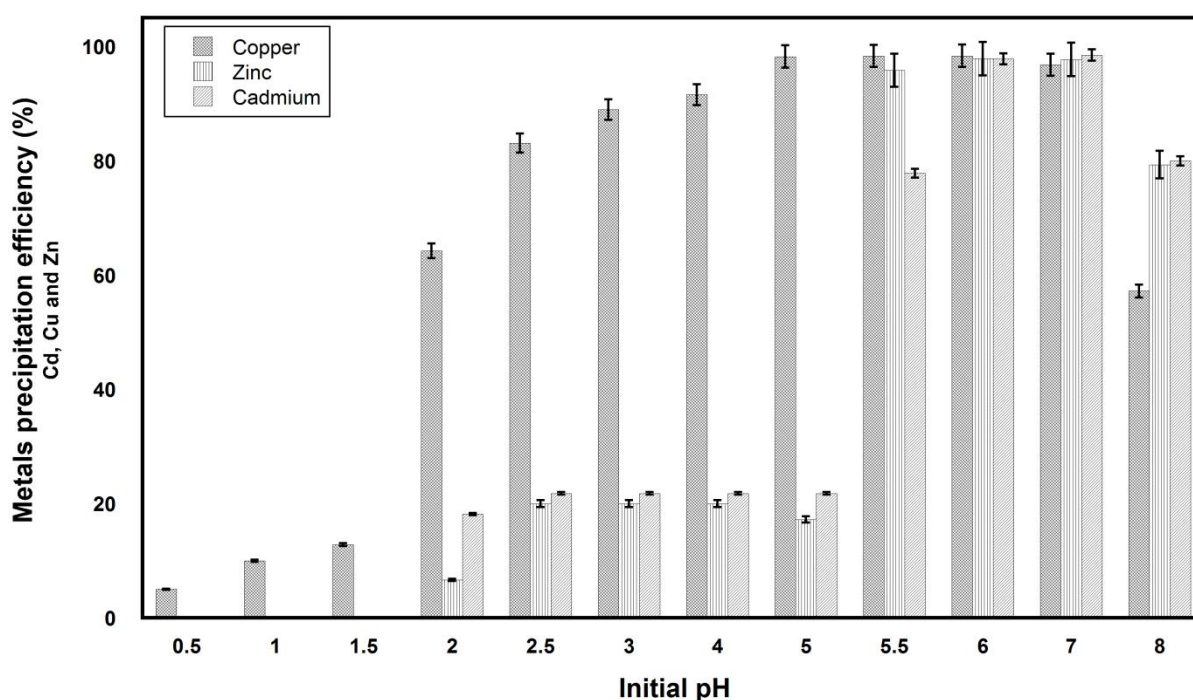


Fig. 6.5. Metal sulfide precipitation versus initial pH of the leachate (100 mg L⁻¹ of dissolved sulfide in 0.1 M NaOH, temperature 20 °C and agitation 150 rpm for 1 h).

The effect of the Cu to sulfide concentration ratio on the selective Cu-sulfide precipitation is shown in Fig. 6.6. Cu to dissolved sulfide mass ratios of 4:1; 2:1; 1:1 and 1:2 were investigated. The results revealed that a ratio of 2:1 of Cu:sulfide was the optimum sulfide dosage in the investigated range. Impurities such as 98% of the Fe and 55% of the Pb were precipitating in parallel. Approximately 5% of Zn and 8% of Cd precipitated at these conditions. These impurities (such as higher Fe and Pb concentration and lower Cd and Zn concentration) were also observed at low Cu/sulfide mass ratio. Fig. 6.S3 shows that most of the soluble Cu was precipitated just after the sulfide dosage (< 1 minute). The precipitates were stable and no dissolution was observed even after 24 h (data not shown). SEM-EDS (data not shown) analysis showed that the precipitates contain C, Cu, O and S. XRD analysis (Fig. 6.7) confirms the presence of covellite (CuS), chalcantite (CuSO₄) and natrochalcite (NaCu₂(SO₄)₂(OH)•H₂O). The average particle size of the precipitates was found to be 0.1 μm (data not shown).

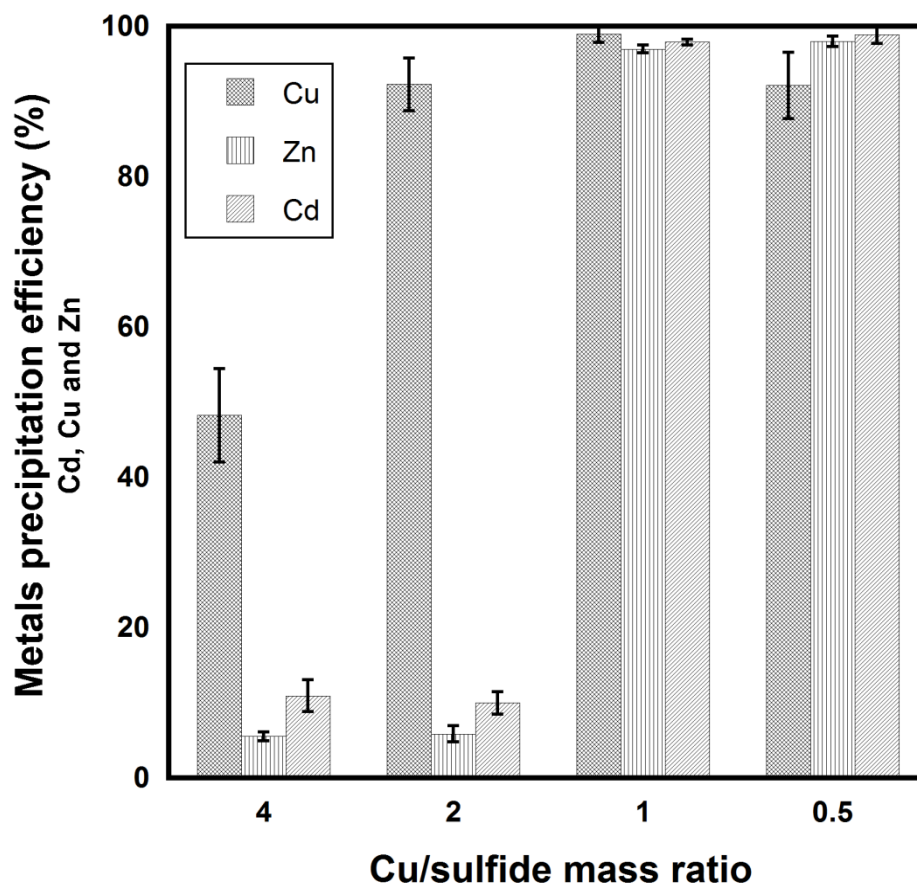


Fig. 6.6. Effect of sulfide dosage on metal sulfide precipitation from the polymetallic ZPR leachate (at initial pH 1.5, temperature 20 °C and agitation 150 rpm for 1 h).

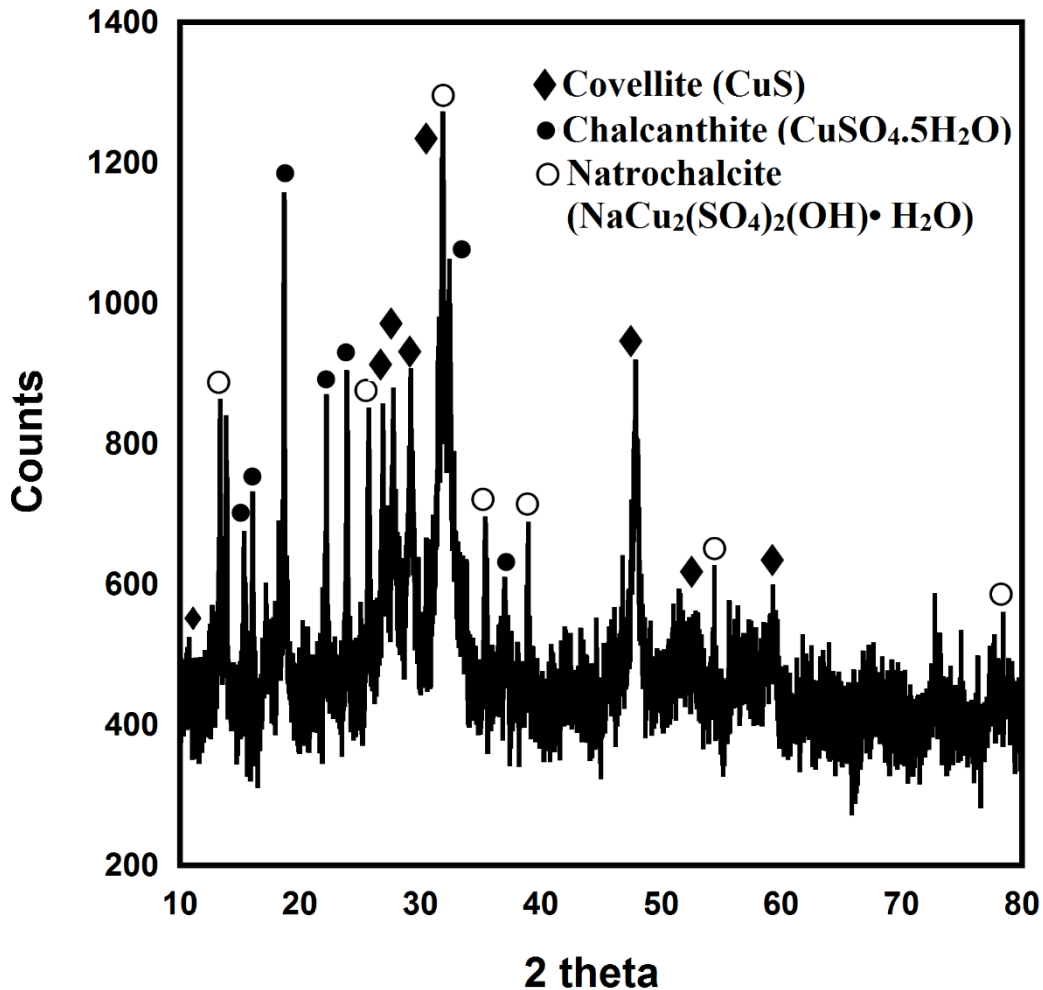


Fig. 6.7. XRD spectrum of the Cu precipitates.

6.4. Discussion

6.4.1. ZPR - an alternative resource for copper

This study showed that ZPR can be considered as a potential secondary resource for heavy metals, especially Cu. The ZPR investigated in this study is potentially hazardous to the environment, when disposed off in the environment (Table 6.3). Even long term storage of these ZPRs is a risk, as it can cause the release of the toxic metals Cd, Cu and Pb (Fig. 6.2) into the environment. Primary sulfidic ores for Cu (such as chalcopyrite (CuFeS₂), covellite (CuS) and chalcocite (Cu₂S)) have been depleting in the recent decades, which is a serious concern (Walting, 2006; Künkül et al., 2013). Based on the experimental data from this study, a hydrometallurgical flow route (Fig. 6.8) is proposed to selectively recover Cu (as covellite) from the hazardous ZPR. These hazardous ZPRs can be recycled and can be seen as a secondary

resource for Cu production. Thereby, the environmental concerns such as potential toxicity associated with the ZPRs and the primary depletion of ores can be addressed. A maximum of 350.2 g kg⁻¹ of Cu can be leached from the ZPR by 1 M sulfuric acid at optimized conditions (80° C, 20 g L⁻¹ pulp density at 450 rpm,). Approximately, 335.5 (± 11.2) g kg⁻¹ of Cu (71% of the total Cu content) can be recovered from the ZPR sulfuric acid leachates with sulfide precipitation (Figures 6. 5 and 6. 6). The metal sulfide precipitation efficiency of Cu from the polymetallic ZPR leachates was highly comparable with those from other polymetallic solutions, e.g. synthetic solutions (Gharabaghi et al., 2012); acid mine drainage (Avarez et al., 2007; Sahinkaya et al., 2009) and electronic waste leachates (Hu et al., 2012).

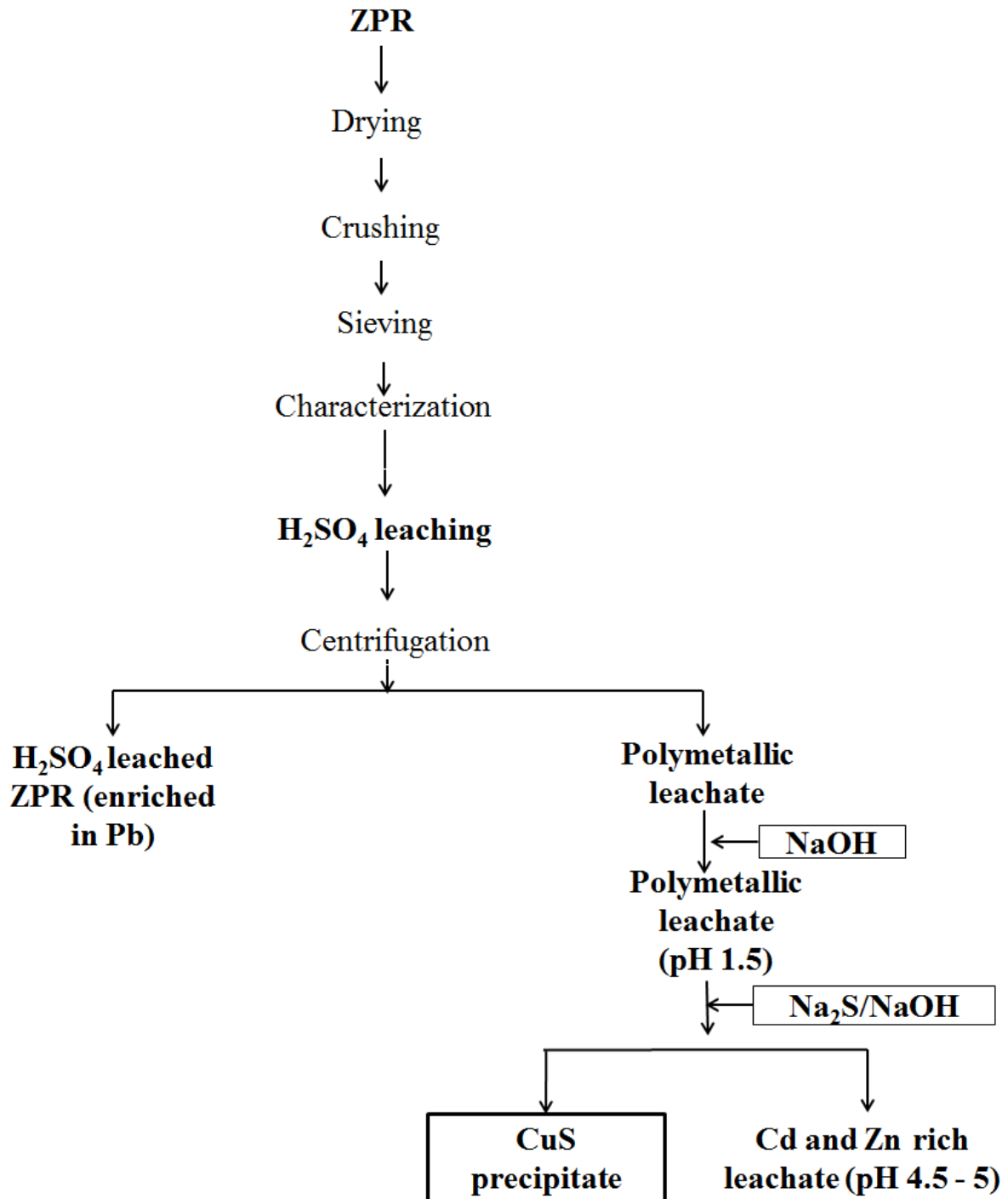


Fig. 6.8. Hydrometallurgical flow chart for the selective recovery of Cu as covellite from ZPR.

6.4.2. Characteristics of the ZPR

This study revealed that the ZPR samples are polymetallic, containing significant amounts (weight %) of Cu (47.2%), Zn (28.6%), Cd (9.3%) and Pb (4.9%) and most of them are present

in the extractable fractions (Table 6.3; Figures 6.2 and 6.3). XRF analyses endorse the polymetallic nature of the ZPR. The XRF results and the bulk chemical analyses were generally comparable (Table 6.2), but for Cd, Cu and Zn the elemental composition by aqua regia digestion and XRF are different which might be due to the heterogeneity of the samples. Cuprite (Cu_2O) and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) were the only mineral phases identified in the raw ZPR by the XRD analyses. Anglesite (PbSO_4) was identified in the ZPR leached at pH 2.5. XRD analysis suggests that the mineral composition of the samples was influenced by the impurities of the secondary minerals formed during the metallurgical processes.

The potential toxicity leaching tests (Table 6.3) revealed that Cd and Pb were several times higher than the permissible US EPA and Brazilian threshold values. As per U.S. EPA and Brazilian standards, no regulatory limits are set for zinc and copper. Based on these observations, it can be concluded that these wastes are highly hazardous if disposed uncontrolled into the environment. The metals released in the toxicity leachates (Table 6.3) were very much comparable to the metals released in the acid exchangeable fractions in the BCR analysis (Fig. 6.2). Carbonated and sulfated minerals were responsible for the metals released in the exchangeable fraction (Dold, 2003).

The heavy metal concentrations in the residual fraction were lower than in the other fractions. The metal released in the oxidizable and residual fractions are less significant than the exchangeable fraction (Min et al., 2013). The fractionation study revealed that most of the Cd and Zn present in the ZPR was associated to sulfates and/or carbonates. This suggests that the toxic heavy metals such as Cd, Cu, Pb and Zn can be easily mobilized into the surrounding environment by rainfall or alike conditions (Li et al., 2013). The percentage of metals (Cd, Cu and Zn) released in the toxicity tests and BCR F1 (acid exchangeable) fraction were also in agreement with the metals released by HNO_3 in the acidic pH range (1.5 – 3.5). The concentrations of Pb in the toxicity leachates and the BCR exchangeable fractions were higher when compared to the Pb concentration in the HNO_3 leachate. This is due to the higher solubility of Pb-acetate complexes than the Pb-nitrate complexes (Cappuyns and Swennen, 2008).

Significant amounts of metals such as Cd, Cu and Zn were also observed in reducing conditions (second step of BCR, Fig. 6.2). The metal fractions released in this BCR extraction (reducible fractions) are attributed to Fe/Mn oxides. Higher concentrations of Cu and Pb were observed in the oxidizable fractions (third step of BCR, Fig. 6.2). Generally, reduced mineral phases and metals associated to organic matter (Min et al., 2013) are responsible for the metal concentrations in this step. It is unlikely that the ZPR contain reduced mineral phases, as they

are oxidized due to various mineral processing unit operations. The higher concentration of Cu in these fractions is due to the leaching susceptibility of oxidized copper phases by ammoniacal solutions as they can form highly stable species (Mena and Olson, 1985; Künkül et al., 1994; Arzutug et al., 2004; Bingöl et al., 2005; Künkül et al., 2013).

Anglesite (PbSO₄) mineral phases were responsible for the non-exchangeable fractions of Pb (Fig. 6.1b), which is the most often observed Pb mineral phase in Zn-hydrometallurgical residues (Turan et al., 2004; Ruşen et al., 2008; Şahin and Erdem, 2015). Anglesite accumulates in the Zn-plant hydrometallurgical residues due to the sulfuric acid leaching of primary ores. The general solubility phenomena for lead (for pure minerals) in decreasing order of aqueous solubility is PbO = Pb₃(CO₃)₂(OH)₂ > PbSO₄ >> PbS (Bataillard et al., 2003).

6.4.3. Cu leaching from ZPR

This study showed that more than 70% of Cu can be leached from ZPR. Based on the XRD analysis (Fig. 6.1) and fractionation results (Fig. 6.2), the heavy metal leaching by sulfuric acid from ZPR can be explained by Equations 2 - 7: cuprite precipitates at standard conditions in metallic form (Equation 2) in sulfuric acid medium, but fully solubilizes in the presence of oxidants (like air) (Equation 3) (Mendes and Martins, 2003),



The increase in Cu leaching at increasing agitation speed (Fig. 6.4a) confirmed that the mass transfer is diffusion controlled. The change in acid concentration did not have a significant influence on Cu leaching (Fig. 6.4e). Similar observations (effect of agitation and acid concentration) on the Cu leaching from Cu-carbonate and CuO minerals by sulfuric acid were reported by Ata et al. (2001) and Habbache et al. (2009).

The pulp density is another important parameter which influences metal leaching. The decrease in Cu leaching (Fig. 6.4g) with increase in pulp density is due to the lower availability of H⁺ ions. The increase in pH was also observed at higher pulp densities (100 g L⁻¹ and 200 g

L⁻¹) because of the ZPRs high buffering capacity which will also affect Cu leaching (in accordance with pH static leaching, Fig. 6.3). The decrease in Cu leaching by sulfuric acid from copper carbonate minerals with respect to pulp density was also observed by Ata et al. (2001). Approximately 50% of Cd and 60% of Zn were observed in all the leaching tests irrespective of any process parameter variation (Fig. 6.4), which is due to the presence of easily soluble Cd and Zn sulfates. This Cd and Zn leaching is comparable with the acidic pH static leaching results (Fig. 6.3).

6.4.4. Selective Cu recovery from acidic ZPR leachates

This study revealed that more than 95% of dissolved Cu can be selectively recovered from the ZPR mainly as covellite (Fig. 6.7) and ZPR can thus be seen as a potential alternative feedstock for Cu. The initial pH plays an important role in metal sulfide precipitation (Lewis, 2010). A small amount of Cu (5% – 15%) was selectively precipitated in the pH range 0.5 to 1.5, with no detectable precipitation of Cd and Zn. The Cu-sulfide precipitation at this acidic pH range was similar to previous studies (Al-Tarazi et al., 2005; Alvarez et al., 2007; Sahinkaya et al., 2009; Gharabaghi et al., 2012). The Cu precipitation was found to increase with increase in initial pH. A maximum of more than 90% of Cu can be precipitated in the pH_{initial} range 4.0 to 7.0. But the increase in Cu precipitation in this pH range might also be influenced by Cu-hydroxides, because of the use of 0.1 M NaOH. Theoretical prediction by Visual MINTEQ showed that Cu-solubility is controlled by copper hydroxy sulfates (brochantite, Cu₄SO₄(OH)₆, data not shown). Furthermore, co-precipitation with iron hydroxides is highly probable in this pH range. Additionally, Cd and Zn were also precipitating in the above mentioned pH range (Fig. 6.5).

Fig. 6.6 clearly shows that a maximum of more than 95% of Cu can be precipitated at an initial pH of 1.5 with a Cu/sulfide mass ratio 1:0.5. The observed results are very similar to previous studies on Cu-sulfide precipitation (Al-Tarazi et al., 2005; Alvarez et al., 2007; Sahinkaya et al., 2009; Gharabaghi et al., 2012). The final pH of this solution increased to 4.7 (± 0.3), because of the use of 0.1 M NaOH to dissolve sodium sulfide. Even though more than 60% of lead and 90% of iron (data not shown) was also precipitated at this pH, their total concentration in the leachate is much lower (9 mg L⁻¹ Pb and 35 mg L⁻¹ Fe) compared to Cu (650 mg L⁻¹). But, minor impurities of Cd (8%) and Zn (5%) were also found co-precipitating at this Cu/sulfide mass ratio. These impurities were observed at an even lower Cu:sulfide mass ratio of 1: 0.25. However, based on the pH dependence of metal sulfides, Cd-sulfide and Zn-

sulfide formation at this pH is unlikely (Lewis et al., 2010; Chapter 2). They might be influenced by hydroxide precipitation or co-precipitation with iron oxides.

SEM - EDS analyses (data not shown) further endorse that the precipitates are composed of copper and sulfur. Covellite (CuS) and chalcocite (Cu_2S) are the most often observed polymorphs of Cu-sulfides, which are dependent on the redox state of Cu. There are some other crystalline Cu sulfides such as anilite ($\text{Cu}_{1.75}\text{S}$) and djurleite ($\text{Cu}_{1.96}\text{S}$) reported in the literature (Anthony, 1990). XRD analyses confirms the presence of covellite in the precipitates (Fig. 6.7). Visual MINTEQ modelling also predicted the precipitation of covellite (data not shown). Most of the dissolved Cu (more than 90%) was precipitated within 5 minutes of sulfide dosage and no dissolution of the Cu-sulfide precipitates occurred (data not shown). XRD analyses (Fig. 6.7) found the presence of chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and natrochalcite ($\text{NaCu}_2(\text{SO}_4)_2(\text{OH}) \cdot \text{H}_2\text{O}$) which might be due to the usage of strong sulfuric acid (for leaching) and sodium sulfide (for precipitation). The formation these mineral phases could be influenced by the higher sulfate concentration in the polymetallic leachates and sodium sulfide addition (Chapter 4). However, these Cu-sulfates were not predicted by the modelling which might be due to the fact that Visual MINTEQ does not consider any sulfide oxidation (to sulfates) in the acidic pH range.

6.5. Conclusions

This study showed that zinc plant purification residues can be used as an alternative feedstock for Cu extraction. The ZPR is polymetallic in nature, rich in Cu (47%), Zn (29%) and Cd (9%). Cuprite, azurite and anglesite were the crystalline minerals identified by XRD analyses. Fractionation of the ZPR with different extractants (acetic and nitric) revealed the potential toxicity of the ZPR to the environment. Sulfuric acid leaching is able to leach more than 70% of Cu from the ZPR. More than 96% of this Cu can be selectively precipitated (as covellite) at an initial pH 1.5 with a Cu to sulfide mass ratio of 1:0.5. Copper could be selectively precipitated with an average particle size of 0.1 μm .

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Chapter 7

General discussion, conclusions and perspectives

7.1. General overview of the research

The ultimate objective of this research was to investigate the potential of metallurgical residues as secondary resources for metal recovery. Two different metallurgical residues namely zinc leach residues (ZLRs, three different leach residues based on their age of production and deposition) and zinc-plant purification residues (ZPR) were collected from a Zn-metallurgical plant located in Três Marias, Brazil. In order to achieve the above-mentioned objectives, the research plan was sub-divided into three main phases (Fig. 7.1), namely (i) characterization, (ii) leaching and (iii) recovery.

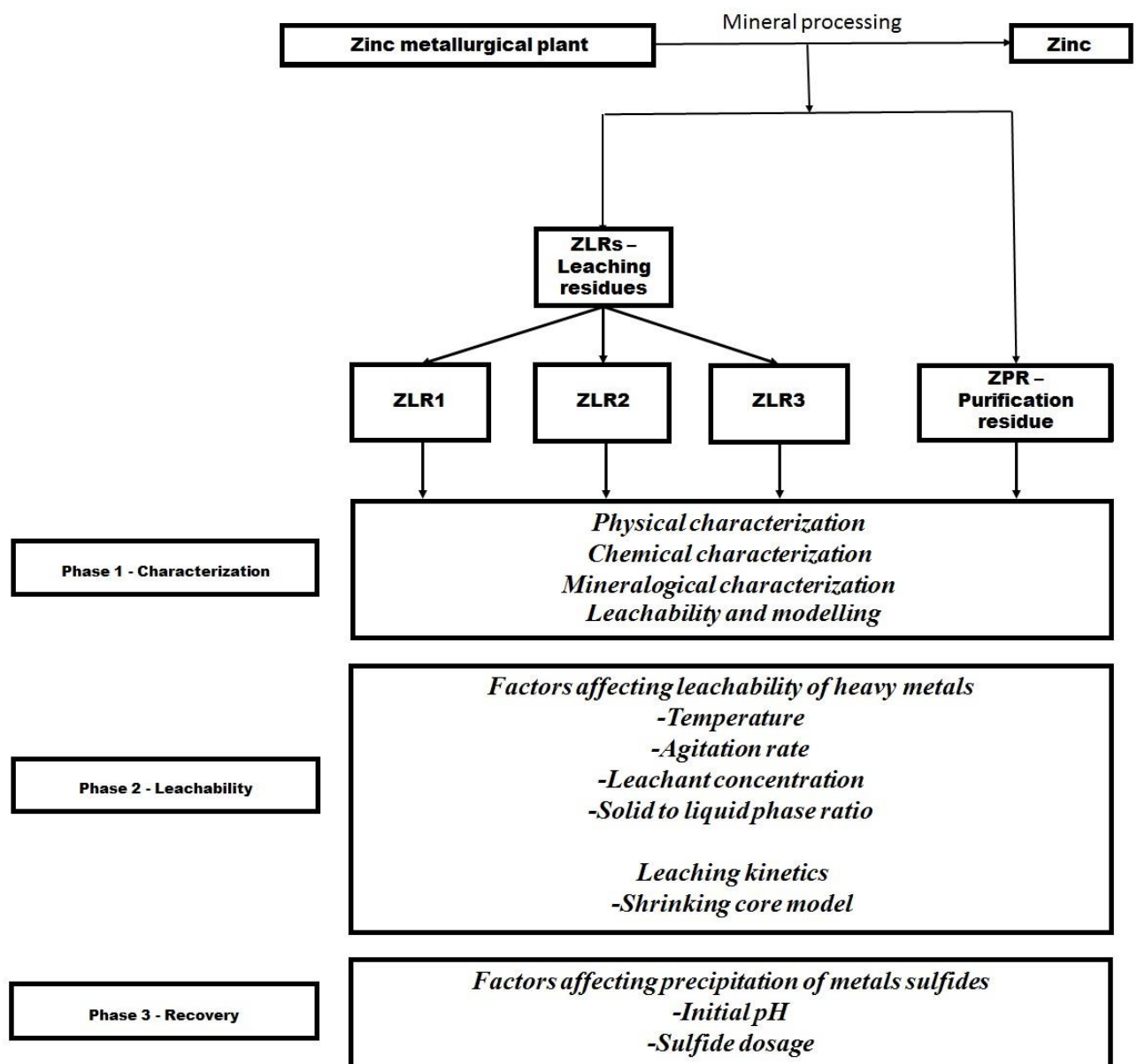


Figure 7.1. Overview of PhD research components.

7.1.1. Characterization of the sludges

Phase 1 was dedicated and focused on the characterization of the metallurgical residues. Various characteristics of the residues, such as physico-chemical characteristics, mineralogy, total metals content, potential toxicity and fractionation, influence of pH on the liquid-solid partitioning and geochemical modelling to predict the mechanisms that control the solubility of the mineral phases were investigated. The general research components of the characterization phase are provided in Fig. 7.2 and detailed experimental setups were described in chapters 3 and 6. The results (Fig. 7.2) showed that these residues are polymetallic but generally rich in Zn content (2.5% - 5% ZLRs, 28% ZPR). ZLRs also contain significant concentrations of Pb (1.7% to 2.3%), Mn (0.05% - 0.9%), Cu (0.07% - 0.2%), and Al (0.3% - 0.4%) and Cd (0.02% - 0.05%). The ZLRs are rich in Fe (6.5% - 11.5%) and Ca (7% - 8.5%) content. The ZPR contains high concentrations of Cu (47%), Cd (9%) and Pb (5%) (Chapter 3). The ZPR also contains Ni (0.32%), Co (0.34%) and Mn (0.2%) metal fractions. In contrast to the ZLRs, ZPR contains much lower quantities of Fe and Ca. Both the ZLR and ZPR contain considerable concentrations of Mg (ZLR 0.6% - 1.1% whereas ZPR 0.7%) (Chapter 6). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was the major crystalline mineral identified in ZLRs and cuprite (Cu_2O) and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) were identified in raw ZPR. Anglesite (PbSO_4) was also identified in the ZPR leached at acidic conditions (pH 2.5, 2 M HNO_3) (Chapter 6).

7.1.2 Acid leachability of heavy metals from the sludges

7.1.2.1. Fractionation and pH dependent leaching

The heavy metals (Cd, Cu, Pb and Zn) present in the ZLRs and ZPR were found to be easily leachable under acidic/rainfall conditions. These residues can be considered as hazardous for the environment. But the hazardous nature of the ZLRs is diminishing over the years, i.e. the recently generated ZLR3 is less hazardous than the decades old ZLR1 and ZLR2. The Zn solubility in the ZLRs is mainly controlled by dissolution and precipitation mechanisms. The experimental data and the geochemical models show that the Zn leaching is controlled by Zn sulfate and carbonate and likely by the dissolution of Zn co-precipitated with Al/Fe oxide. The characterization studies reveal that there is a significant concentration of Zn (ZLRs) and Cd, Cu and Zn (ZPR) present in the exchangeable/non-residual fractions.

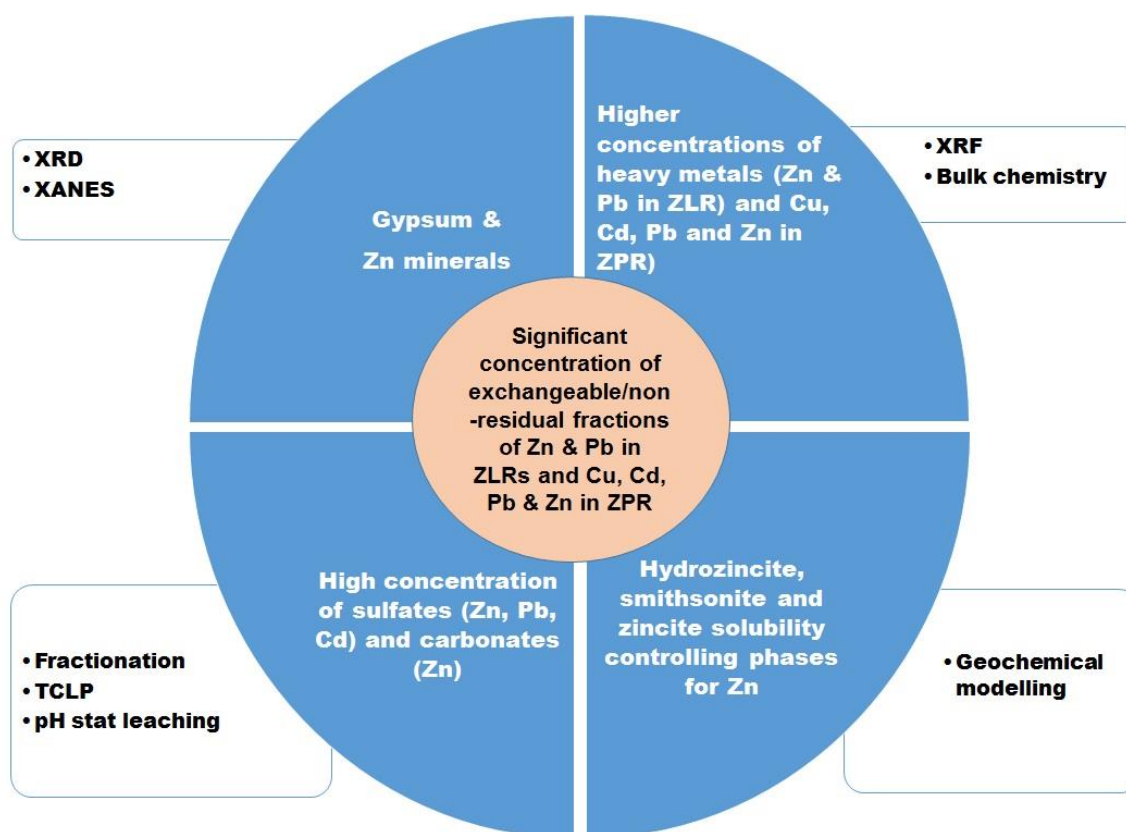


Figure 7.2. Characterization of the Zn-plant residues performed in this study.

7.1.2.2. Optimization of leaching parameters

Based on the results of the characterization studies, phase 2 was designed and dedicated to the optimization of the leaching parameters to solubilize maximum of Zn (ZLRs) and Cu (ZPR) (Fig. 7.3). Sulfuric, hydrochloric, nitric and acetic acids were used for the preliminary leaching studies (data not shown). Sulfuric acid was chosen for the leaching experiments based on the preliminary tests. The factors influencing the metal leaching such as temperature, solid to liquid ratio, agitation speed and the acid concentration were investigated for the maximum leaching of metals Zn (ZLRs) and Cu (ZPR). A detailed experimental setup regarding the leaching experiments performed for the optimization of the parameters is presented in Fig. 7.4. The leachate samples were collected at regular time intervals to examine the leaching kinetics of Zn and Cu.

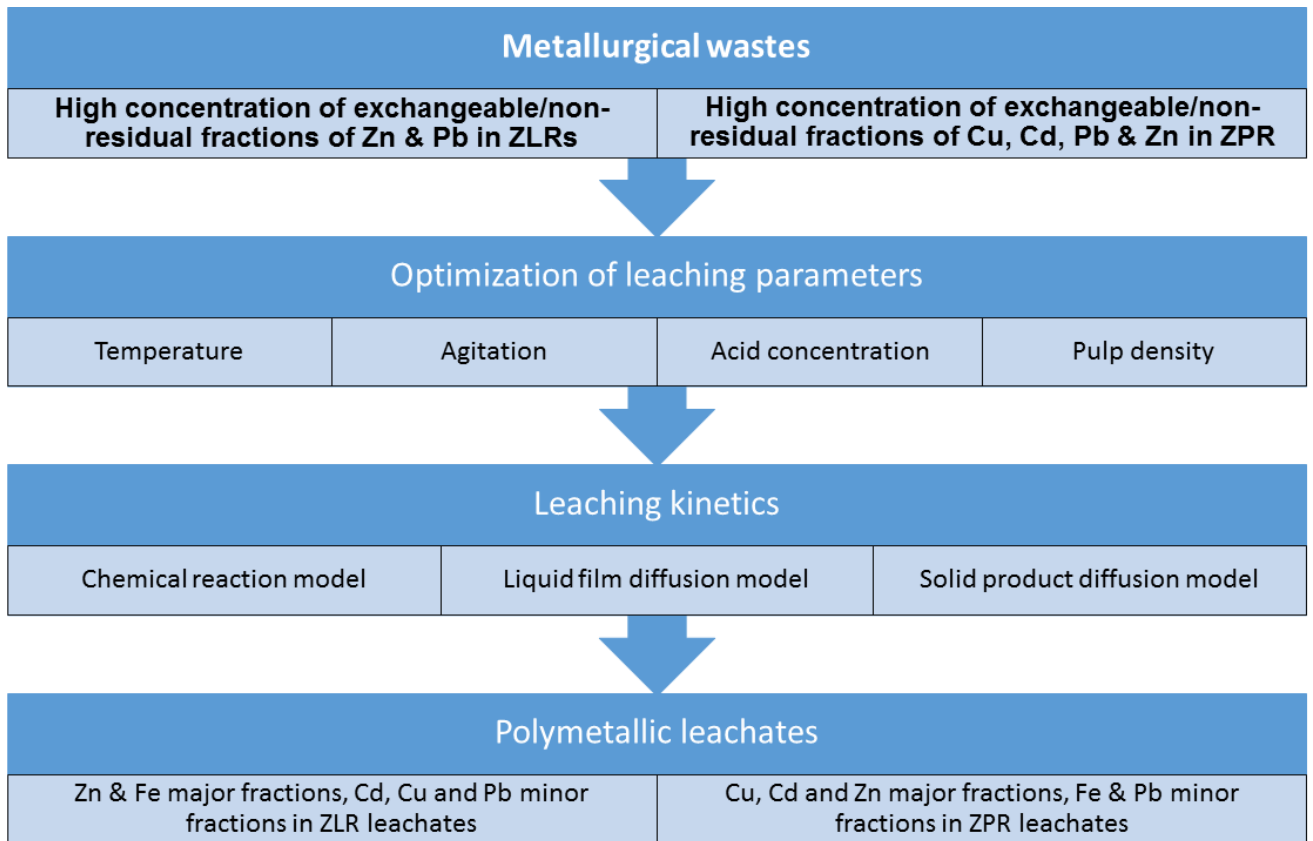


Figure 7.3. A schematic representation of the experiments performed in phase 2.

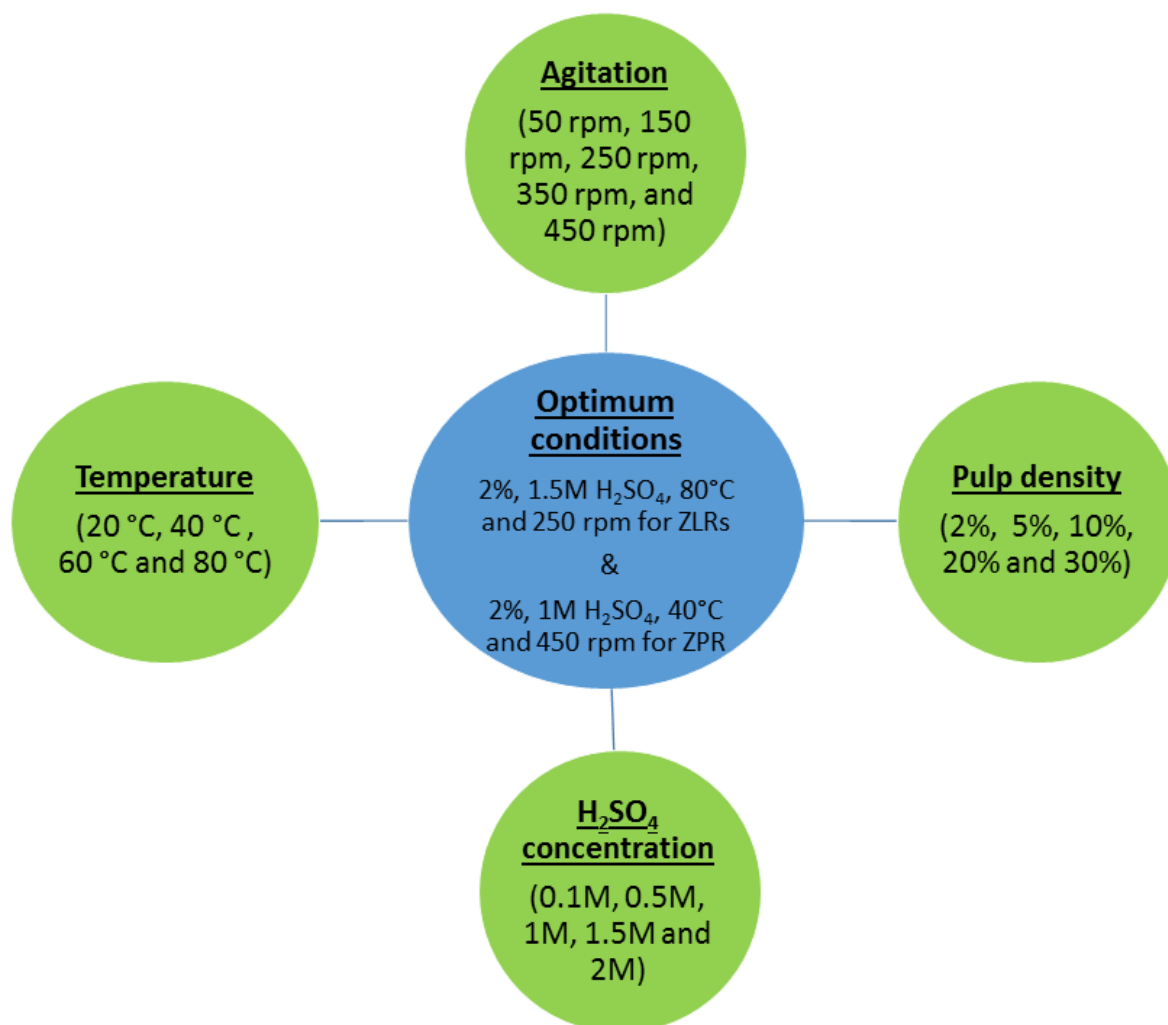


Figure 7.4. Details of the parameters investigated for the optimization of Zn and Cu leaching from ZLRs and ZPR.

In metallurgy, the leaching kinetics can be divided into two processes: (i) the particle size of the ores/solids changes significantly (shrinking core model, SCM) and (ii) the size of the solids does not change (Levenspiel, 1999). Out of these two heterogeneous solid-fluid processes, hydrometallurgy belongs to the former category i.e. the SCM. In the SCM, the leaching can be controlled by diffusion through the liquid boundary layer or diffusion through the solid product layer on the one and or the chemical reaction at the surface of the solids on the other hand (Levenspiel, 1999). Based on the results of the leaching studies, the Zn leaching (from ZLR) is temperature and acid concentration dependent. The pulp density of ZLRs does not have a significant impact due to the low buffering capacity of the samples against strong acids. The kinetic analyses endorse the same observation, such temperature dependency and acid strength. The apparent activation energy and acid strength required to leach more than 90%, 85% and 70% of ZLR1, ZLR2 and ZLR3, respectively, are estimated as 2 - 12 Kcal/mol

and 0.2 – 0.9 (dimensionless). Bioleaching of Zn by *A. thiooxidans* (sulfuric acid producing bacteria) was also performed on the ZLRs (Chapter 5). The Zn bioleaching (by biogenic sulfuric acid) from the ZLR3 is comparable with the chemical sulfuric acid leaching. The Zn bioleaching also follows solid product shrinking core diffusion kinetics. On the other hand, Cu leaching (from ZPR) is dependent on pulp density and agitation speed. Temperature and acid concentration do not have a significant effect on Cu leaching from ZPR. Under the optimum conditions, more than 70% of Cu can be extracted from ZPR within 4 hours (Chapter 6). Cu leaching from ZPR also follows shrinking core kinetics. To understand about the Cd, Cu and Zn leaching kinetics, a more precise sampling interval is required as the majority (50 - 60%) of these metals were leached within 5 minutes.

7.1.3. Recovery of the heavy metals from the polymetallic sludge leachates

Later phase 3 (Fig. 7.5) was devoted to the selective recovery of Zn from the ZLR leachates and Cu from the ZPR leachates. The major objective of phase 3 was to selectively recover the metals in their sulfidic form, as most of the commercial metal production depends on the sulfidic primary ores of Zn. Hence, metal sulfide precipitation (MSP) was chosen and investigated on the acidic leachates. As these samples are polymetallic in nature, the leachates are also polymetallic. The major process parameters affecting metal sulfide precipitation are pH and metal to sulfide ratio (Lewis, 2010).

Initially, a theoretical prediction of the MSP was performed using Visual MINTEQ (based on the leachate composition). On the basis of the theoretical prediction, different initial pH values were chosen (more details can be found in chapters 4 and 6). In case of ZLR, the major hindrance for the selective Zn recovery was due to Fe the content. There were many commercial processes viz jarosite process (Hu et al., 2012; Yazici et al., 2014a), goethite process (Yazici et al., 2014b) and paragoethite process (Loan et al., 2006) reporting for iron removal (Buban et al., 1999). The implementation of such processes is dependent on leachate composition. In this study (Chapter 4), a different but simple 2 steps approach was tailor made for these ZLR acidic leachates. At the first stage, impurities such as Cd, Cu, Fe and Pb were removed by adjusting the initial pH and sulfide dosage. The impurities depleted ZLR leachates were subsequently subjected to Zn recovery. At initial pH 4, the Zn can be recovered as ZnS. SEM-EDS analysis confirms the presence of ZnS. A poorly crystalline sphalerite was identified by XRD in the ZLR precipitates. Biogenic sulfides were also tested for their ability to

selectively recover Zn (Chapter 5). The biogenic sulfides were also able to precipitate more than 95% of total soluble Zn.

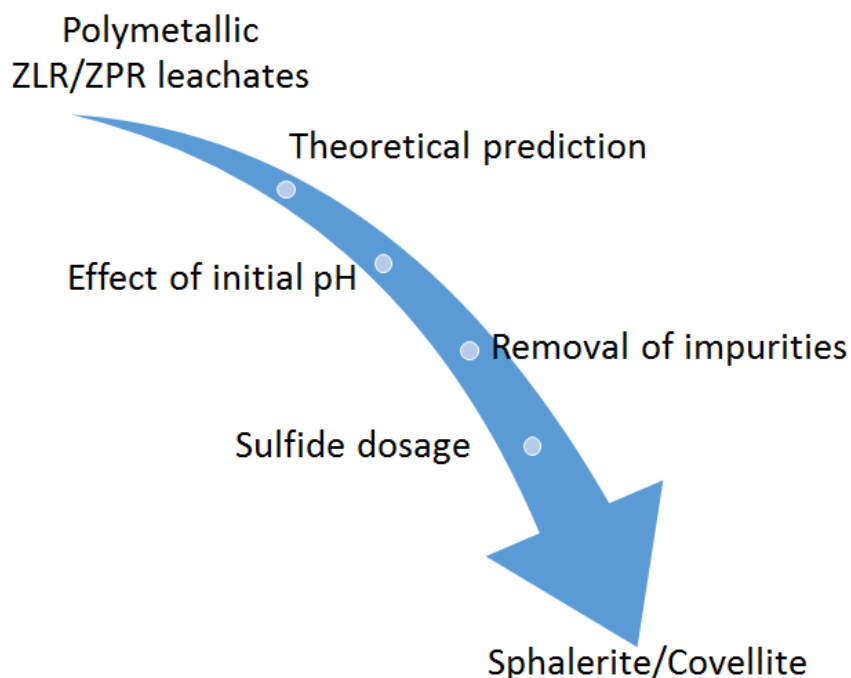


Figure 7.5. Pictorial representation of the stepwise approach for the selective recovery of metals (Cu & Zn) from the ZLR/ZPR leachates.

On the other hand, the Fe content in the ZPR leachate was lower, when compared to the total Cu concentration. But it contains significant concentrations of Cd and Zn along with Cu. The effect of the initial pH and the Cu to sulfide mass ratio was investigated for the selective Cu recovery (Chapter 6). At an initial pH 1.5 and Cu:sulfide mass ratio 1:0.5, a maximum of 97% of Cu was precipitated. XRD and SEM – EDS analysis confirms the presence of CuS (covellite) minerals in the precipitates. Thenardite (Na_2SO_4) and natrochalcite ($\text{NaCu}_2(\text{SO}_4)_2(\text{OH}) \cdot \text{H}_2\text{O}$) were also observed in the sphalerite and covellite precipitates, due to the usage of sodium hydroxide and sodium sulfide. Thus, a maximum of zinc can be recovered from ZLR1, ZLR2 and ZLR3 was $41.7 (\pm 0.4)$, $22.8 (\pm 0.1)$ and $17.1 (\pm 0.1)$ mg g^{-1} respectively, and $335.5 \text{ mg g}^{-1} (\pm 11.2 \text{ mg g}^{-1})$ of Cu can be recovered from ZPR. This PhD research demonstrates the potential of these hazardous residues as secondary resources for Zn and Cu. The environmental impacts associated with the storage and deposition of these wastes can be minimized. Consequently, the capital cost for the storage of these wastes can be reduced.

Moreover, the gradual depletion of the high grade mineral resources for Zn and Cu can be addressed. Based on the scientific findings from this research, an alternative metal strategy (Fig. 7.6) can be proposed for these metallurgical sludges.

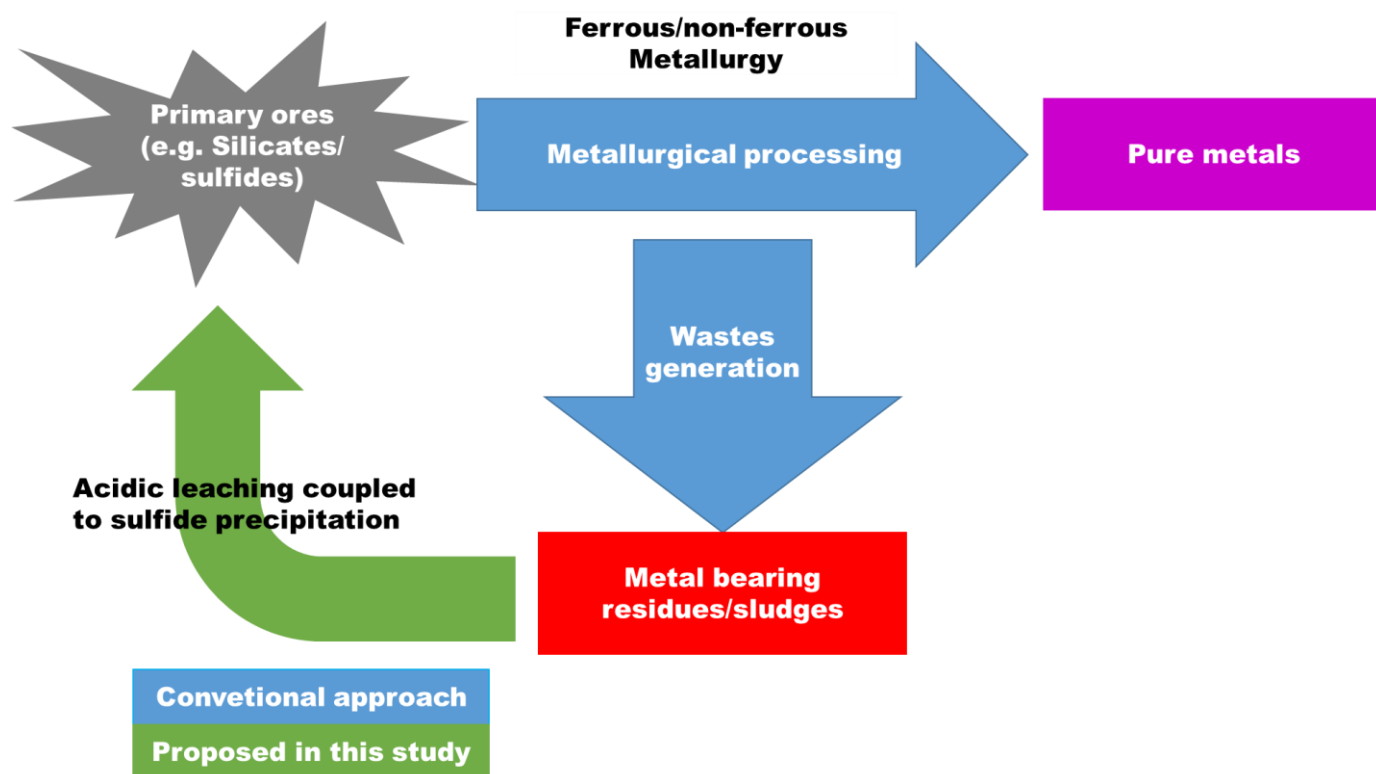


Figure 7.6. Alternative metal recovery strategy proposed in this PhD research.

7.2. Conclusions

This study demonstrates the potential of metallurgical sludges as alternative resources for the extraction of heavy metals (Cu and Zn). Based on the above scientific findings, discussions and perspectives, it can be concluded that, the ZLRs/ZPR contain more than 90% of total solids and their pH ranges from mild acidic to neutral. They are mainly constituted of oxidized minerals (sulfates, oxides, silicates, and carbonates). These sludges are hazardous to the environment, if they are disposed off improperly. Bioavailable fractions of Cd and Pb are responsible for the potential toxicity of these sludges. The heavy metals leaching in these sludges are pH dependent. The experimental data and the geochemical models show that the Zn leaching is controlled by Zn sulfate and carbonate dissolution and likely by the dissolution of Zn co-precipitated with Al/Fe oxide. Then Zn solubility is controlled by the precipitation of smithsonite, zincite and hydrozincite minerals in the alkaline conditions. The hazardous

nature of the sludges is reduced over the years. The majority of heavy metals are associated to non-residual fractions. Sulfuric acid was found to be the best leachant for the leaching of Zn (ZLR) and Cu (ZPR) based on higher leaching of desired metals (Zn and Cu) and lower Pb leaching) (among the studied acids i.e. sulfuric, hydrochloric and nitric acid). Zn leaching from the ZLRs is temperature and acid concentration dependent. Hot acidic leaching is required to extract maximum Zn from the ZLRs, because of the presence of zinc ferrites. The activation energy required was determined as 2 - 12 Kcal/mol and the order acid concentration required was estimated as 0.2 – 0.9 for the ZLRs. Cu leaching from ZPR is pulp density and agitation dependent. The activation required to leach Cu from ZPR was determined as 2.88 Kcal/mol. A maximum of 92%, 85% & 70% of Zn from ZLR1, ZLR2 & ZLR3 and 73% of Cu from ZPR can be leached, respectively (under the optimum conditions such as 2% pulp density, 80 °C, 250 rpm, 1.5 M H₂SO₄ and 6 hours). Zn leaching from the sludges follows solid product diffusion model (shrinking core kinetics). Selective recovery of the Zn and Cu from the polymetallic leachates of ZLRs and ZPR can be achieved by metal sulfide precipitation. For Zn recovery, a two stage recovery method was proposed. In the first stage (initial pH 1.5), impurities like Cd, Cu and Fe were removed by the addition of sodium hydroxide and sodium sulfide. In the second stage (initial pH 4.0), Zn-sulfide was recovered as sphalerite by the addition of sodium sulfide. More than 90% of soluble Zn can be precipitated by the proposed methodology from the ZLR leachates. With the proposed hydrometallurgical route 41.7 (\pm 0.4), 22.8 (\pm 0.1) and 17.1 (\pm 0.1), mg per g of Zn can be selectively recovered from ZLR1, ZLR2 and ZLR3, respectively. Cu recovery from the ZPR leachate was also achieved by the addition of sodium sulfide. The sulfide precipitation process parameters such as initial pH and metal to sulfide mass ratio were optimized as 1.5 (pH units) and 1:0.5 (Cu:sulfide). 97% of Cu can be recovered (mainly as covellite, CuS) from the ZPR leachates.). 33.5 (\pm 1.1) mg per g of Cu (71% of the total Cu content) can be recovered from the ZPR sulfuric acid leachates with sulfide precipitation. This study can be further extended to investigate the selective recovery of Pb from the H₂SO₄ leached ZLRs/ZPR. Bioleaching and biological recovery of Zn and Cu from the sludges will also be interesting to investigate. Overall, these hazardous metallurgical sludges can be as a potential secondary resource for the heavy metals (Zn and Cu).

7.3. Perspectives

However, this research also leaves few other potential perspectives that can further be extended as follow up.

- (i) Recycling perspectives.

As shown in Fig 7.6, the end products (metal sulfides) of this PhD research are of great potential to be recycled in metallurgical industries to produce pure metals.

- (ii) Secondary source for lead

ZLRs/ZPR after sulfuric acid leaching yields polymetallic leachates and non-reacted solids. These non-reacted solids generated after the acid leaching stage is enriched in Pb concentration. It can be further investigated for selective Pb recovery.

7.3.1. Recycling perspectives

From the end results and discussion of chapters 4, 5 and 6, these sludges could be proposed as alternative resources for primary sulfidic ores for the Cu and Zn recovery. Further metallurgical investigations on the end products of chapters 4, 5 and 6 i.e. ZnS and CuS precipitates are of great interest. As discussed earlier (Chapter 1), the sludges are originating from a Zn-metallurgical industry which processes Zn-sulfide and Zn-silicates ores to produce Zn metal. The end products (metal sulfides) of this PhD research are of great potential to be recycled (as illustrated in Fig. 7.7) in their pyro/hydro metallurgical unit operations to produce pure metals. The Zn metallurgical plant (origin of these investigated sludges) is processing Zn-sulfide ore in roasting-leaching-electrowinning processes (chapter 1, Fig.1.1) to produce Zn metal. The Zn-plant applies a sequence of unit operations such as (Souza, 2000; Souza et al., 2007) (i) Flootation and thickening & filtration, (ii) roasting, (iii) neutral leaching, (iv) purification, (v) filtration, and (vi) electrowinning. Of which the objective of the first stage i.e. floatation and thickening & filtration is to produce a Zn-sulfide concentrate. Then the ZnS concentrate will be subjected to roasting to produce ZnO. Neutral leaching (with mild sulfuric acid) of the calcinated/roasted ZnO will be done to leach out Zn. In the treatment of natural ores, strong sulfuric acid will also be used to leach Zn from Zn-ferrites. But this step will not be required in the processing ZnS precipitates (end products of this research) as they are Fe depleted (chapter 4) (and no franklinite or other Fe minerals present in the precipitates). Then

the sludge (product of neutral leaching) will be subjected to purification of the impurities such as Cd, Co, Cu, Pb and Ni (present in the natural ores). This step also will not be required in the processing of the precipitates (this study), as they are impurities such as Cd, Cu, Fe and Pb depleted. Then the sludge will be subjected to filtration and electrowinning for the pure metal production.

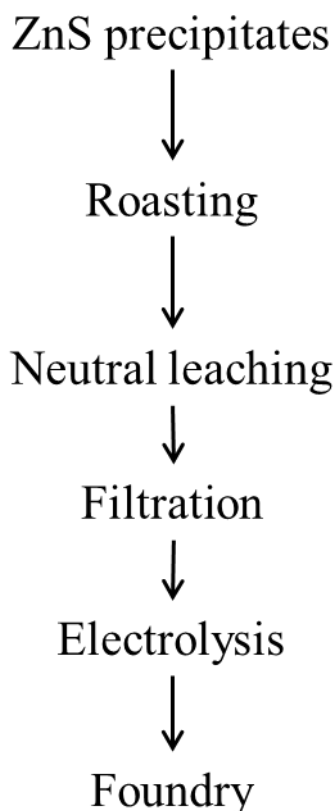


Figure 7.7. Recycling unit operations to produce Zn from the ZnS precipitates.

On the other hand, heap leaching of the precipitates are also a possibility. Heap leaching was mostly proposed for the Cu-sulfidic ores. Heap leaching is quite well established for the extraction of low grade or secondary resources (Petersen and Dixon, 2007). There are many studies reporting on the heap leaching of low-grade sulfides or secondary resources. Petersen and Dixon (2002) proposed a thermophilic heap leaching for the processing of chalcopyrite concentrate. Copper extraction from a low grade chalcopyrite by a biological heap (contains mainly *Acidithiobacillus ferrooxidans*) was also demonstrated (Panda et al., 2012). Other copper sulfides (low grade) such as chalcocite and covellite were also susceptible for biological heap leaching (Renman et al., 2006). A commercial Hydrozinc™ Process (heap leaching coupled to metal recovery) was also proposed for low grade Zn-sulfides ores (Lizama et al., 2003). Based on the literature and the results, a lab scale column heap leaching coupled to a

metal recovery unit is recommended (Fig 7.8). However, a lot of laboratory trials are required. The CuS precipitates should be packed in a column (of about 70% of the total height). Before packing into the column, the precipitates should be dried and agglomerated to ensure the leachant flow and proper leaching. Concentrated acids or biological agents (for instance chemolithotrophs such as *Acidithiobacillus*, *Leptospirillum* etc) can be sprinkled at the top of the column continuously. Leach liquor should be collected in the pregnant leach solution (PLS) tank placed at the bottom of the column. Before the samples (precipitates) packed onto the column, a filter material (which prevent the sample from escaping the column but allow the leachate to reach the PLS tank) has to be placed in the bottom end of the column. The collected leach liquor must be supplied to a metal recovery unit. These leachates might be depleted of impurities (because the precipitates used are selectively recovered), electrowinning or solvent extraction is suggested to recover pure metals from the pregnant leach solution.

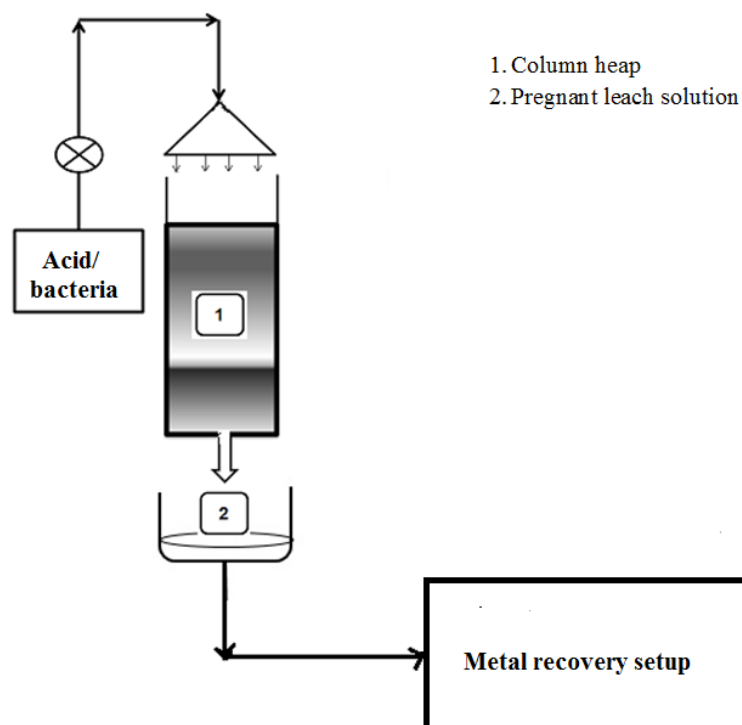


Figure 7.8. Proposed process diagram for the lab scale heap leaching and recovery of the metals from the precipitates.

7.3.2. Potential secondary source for lead

Selective recovery of lead (Pb) in the form of Pb-sulfide (galena, which is the most commonly used primary ore for Pb recovery) is another perspective of this research. Even though Pb is a toxic element to humans (Gillis et al., 2012), it has many significant applications such as batteries, paints, electronics etc (Oh et al., 1999; Qin et al., 2009). Usually Pb is extracted from natural lead – sulfide (PbS, Galena) ores (Mejía et al., 2012). The extraction of Pb from secondary resources also forms significant amounts of worldwide Pb production (Agarwal et al., 2004). Lead is the most often found metal in the Zn-plant residues (Tural et al., 2004; Rusen et al., 2008; Ngenda et al., 2009). Mostly Pb, is found in the ZLRs as semi-soluble anglesite minerals (Turan et al., 2004; Rusen et al., 2008) and sometimes as PbO (Şahin and Erdem, 2015). These anglesite minerals are secondary oxidation products of primary Pb phases during the hydrometallurgical processes to recover Zn.

There are many studies reported on the recovery of Pb from different industrial wastes. Brine leaching was the most common technique used to leach Pb from the PbSO₄ bearing wastes (Table 7.1). The brine leaching of Pb from the Pb-sulfates follows diffusion controlled first order kinetics (Geidarov et al., 2009). The Pb leaching by brine solution is temperature dependent, the activation required to leach maximum Pb was ranging from 2.7 kJ/mol - 12.41 kJ/mol (Geidarov et al., 2009; Şahin and Erdem, 2015). Şahin and Erdem (2015) proposed alkali leaching of Pb from the ZLRs. Even though, the leaching efficiency was high; this approach was not a selective recovery of Pb as Zn was also leached alongside Pb. Raghavan et al. (2000) proposed direct sulfidation and brine leaching coupled to sulfide precipitation to recover Pb as PbS from two different ZLRs generated from different smelters. Direct sulfidation of the ZLRs was not so efficient (26% and 60%), while brine leaching coupled to sulfide precipitation yielded better recovery efficiency (more than 85%). However, in this case the initial pH suggested was pH 2.0, which is not suitable for most of the ZLRs leachates. Because ZLRs most often contain Cu and Fe impurities and they will interfere in the selective recovery. Şahin and Erdem (2015) also proposed sulfide precipitation using Na₂S and carbonate precipitation using CO₂. Sulfide precipitates contain ZnS (würtzite) impurities along with galena while the carbonate precipitate contain crystalline phases of sodium lead carbonate hydroxide (NaPb₂(CO₃)₂OH).

Table 7.1. Various studies reported on the leaching of Pb from ZLRs.

Residue type (Lead content - %)	Mineral phase	Treatment	Leaching yield	Reference
Blended zinc leaching residues from Zn plants located in Iran and Turkey Pb - 15.5 %	Anglesite (PbSO ₄)	NaCl (300 g L ⁻¹)	Pb extraction up to 98.9% of Pb was leached at 95 °C with 5 % pulp density within 10 minutes.	Ruşen et al., 2008
Zinc plant residues from Zn plants in Turkey Pb - 24.6 %	Anglesite (PbSO ₄)	NaCl (200 g L ⁻¹)	89% Pb was leached at a pulp density of 20 g L ⁻¹ at 25 °C in 10 minutes.	Turan et al., 2004
Zinc plant residues from Zn plants in Turkey Pb - 19.2 %	Anglesite (PbSO ₄) Massicot (PbO)	NaOH (11%), followed by sulfidation using Na ₂ S	99.6% Pb was leached at a pulp density of 5% at 100 °C in 60 minutes.	Şahin and Erdem, 2015
Lead sulphate concentrate, Debari Zinc Smelter, India Pb - 21.4% Lead sulphate concentrate, Vizag Zinc Smelter, India. Pb - 36%	Anglesite (PbSO ₄)	Two different treatments (i) direct sulfidation (Na ₂ S) (ii) NaCl (300 g L ⁻¹) leaching + sulfidation	100 % recovery of Pb as PbS, at a pulp density 2%, within 30 minutes at pH 2.0.	Raghavan et al., 2000
Zinc plant residue from Zn-plant located in Iran	Anglesite (PbSO ₄)	NaCl (300 g L ⁻¹)	89.4% of Pb was recovered with solid to liquid ratio 0.3 at 400 rpm within 30 minutes	Farahmand et al., 2009

The ZLRs and ZPR investigated in this research are also rich in Pb content (Fig 7.9). The crystalline Pb minerals in ZLRs were not identified by XRD but crystalline PbSO₄ was identified in nitric acid (2 M) leached ZPR. Based on the results of selective Zn recovery from

ZLRs (chapter 4) and selective Cu recovery from ZPR (chapter 6), Pb was not leached by H_2SO_4 (meaning that the Pb concentration in the leachate was below detection limits). This negligible Pb leaching of $PbSO_4$ by sulfuric acid is well in accordance with the previous studies (Turan et al., 2004; Rusen et al., 2008).

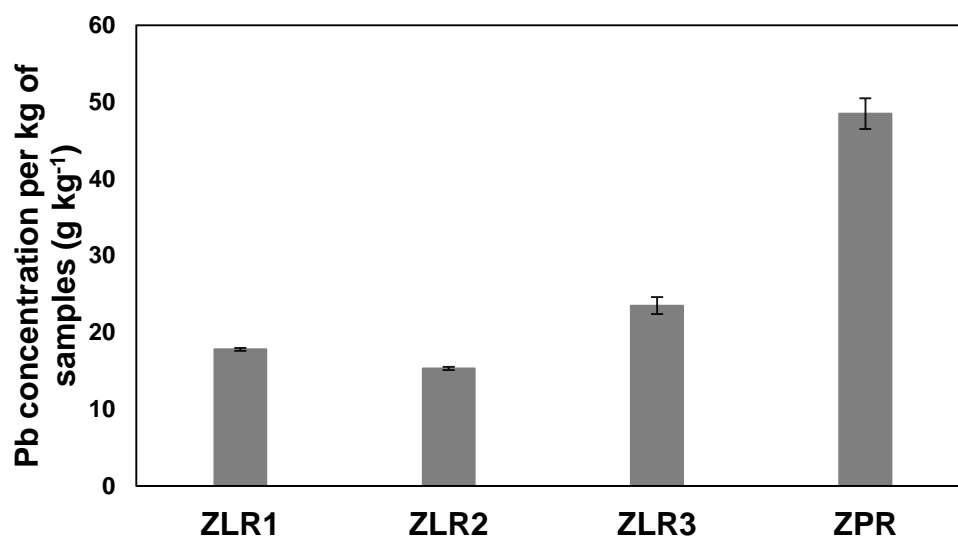


Figure 7.9. Total Pb content present in the investigated samples.

On the other hand, hydrochloric acid leaching (1 M) of ZLRs extracts more than 60% of Pb (along with Zn) from all the investigated ZLRs (Fig. 7.10). This study can be further extended with an objective of selective recovery of Pb from the sulfuric acid leached ZLRs/ZPR. The sulfuric acid leached ZLRs and ZPR are depleted of the impurities such as Cd, Cu, Zn and most of the Fe. Hence, a selective leaching of Pb can be expected by brine leaching followed by sulfide precipitation (pH 1 – 2) can be expected to yield galena rich Pb-precipitates.

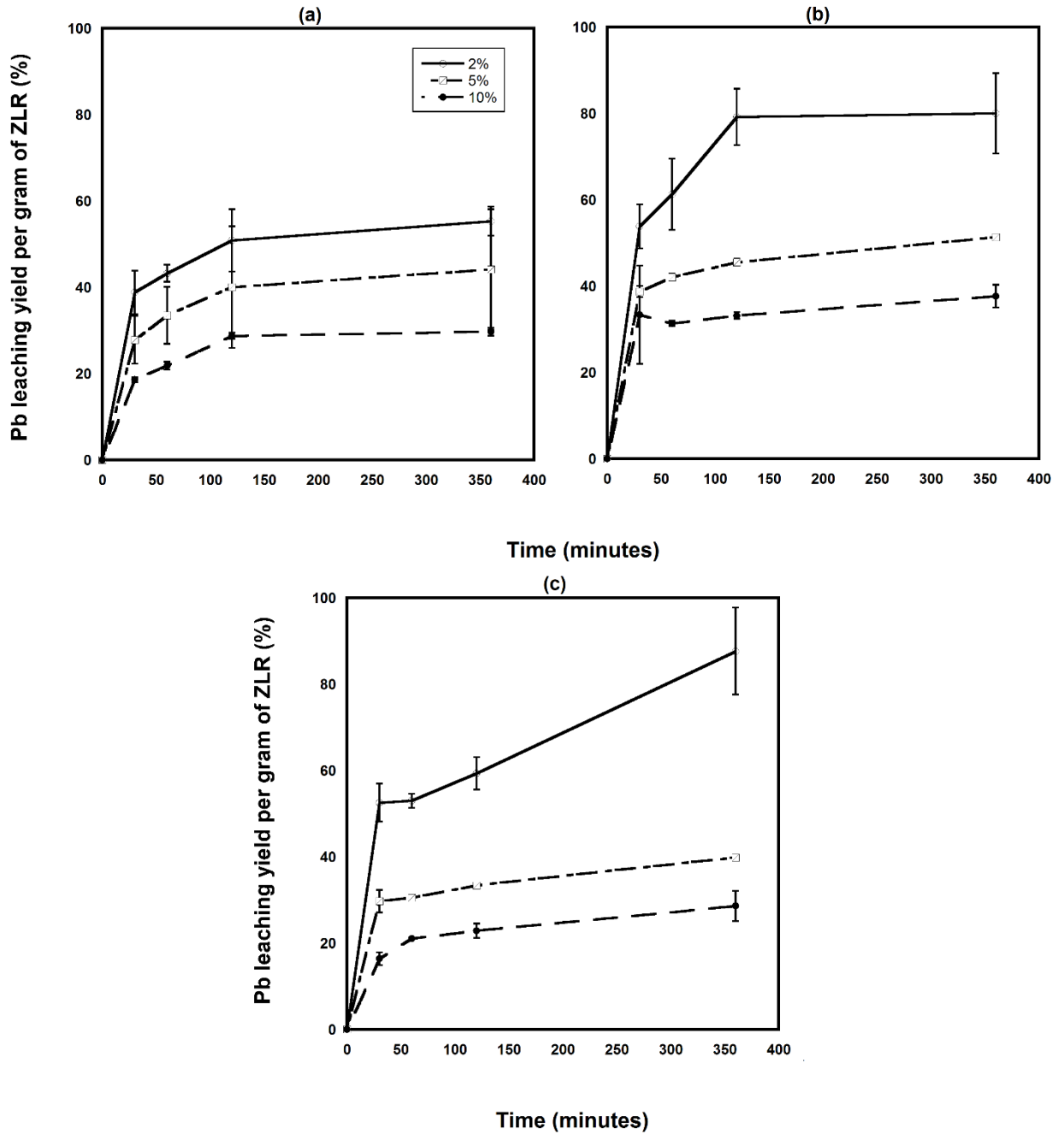


Figure 7.10. Effect of pulp density on Pb extraction from ZLRs, (a) ZLR1, (b) ZLR2 and (c) ZLR3 (temperature – 20 °C, agitation – 150 rpm, 1 M HCl) (legends shown inside panel (a)).

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Supplementary Information

Supplementary Information**Table S1. Limits of Detection (LD) and quantitation (LQ) of the ICP-OES.**

Metals (wavelength, nm)	LD ($\mu\text{g L}^{-1}$)	LQ ($\mu\text{g L}^{-1}$)
Pb 220.353	1.77	5.83
Fe 238.204	0.43	1.42
Ca 317.933	12.24	40.40
Ca 315.887	11.30	37.30
Mg 285.213	7.57	24.97
Mg 279.077	8.58	28.32
Mn 257.610	4.70	15.52
Cu 324.752	1.58	5.21
Cd 228.802	1.42	4.68
Al 396.153	1.08	3.57
Zn 213.857	56.09	185.11

Table S2. Quality control results obtained for the industrial waste sludge BCR146R.

Element	Experimental value (mg kg⁻¹ ± S.D.)	Certified value (mg kg⁻¹ ± S.D.)	Recovery (%)
Cd	18.86 ± 0.52	18.4 ± 0.4	102.5
Cr	161.35 ± 3.52	174 ± 7	92.7
Cu	766.41 ± 12.88	831 ± 16	92.2
Mn	289.62 ± 14.14	298 ± 9	97.2
Ni	57.14 ± 0.90	65 ± 3	87.9
Pb	532.01 ± 37.17	583 ± 17	91.3
Zn	2804.75 ± 64.84	3040 ± 60	92.3

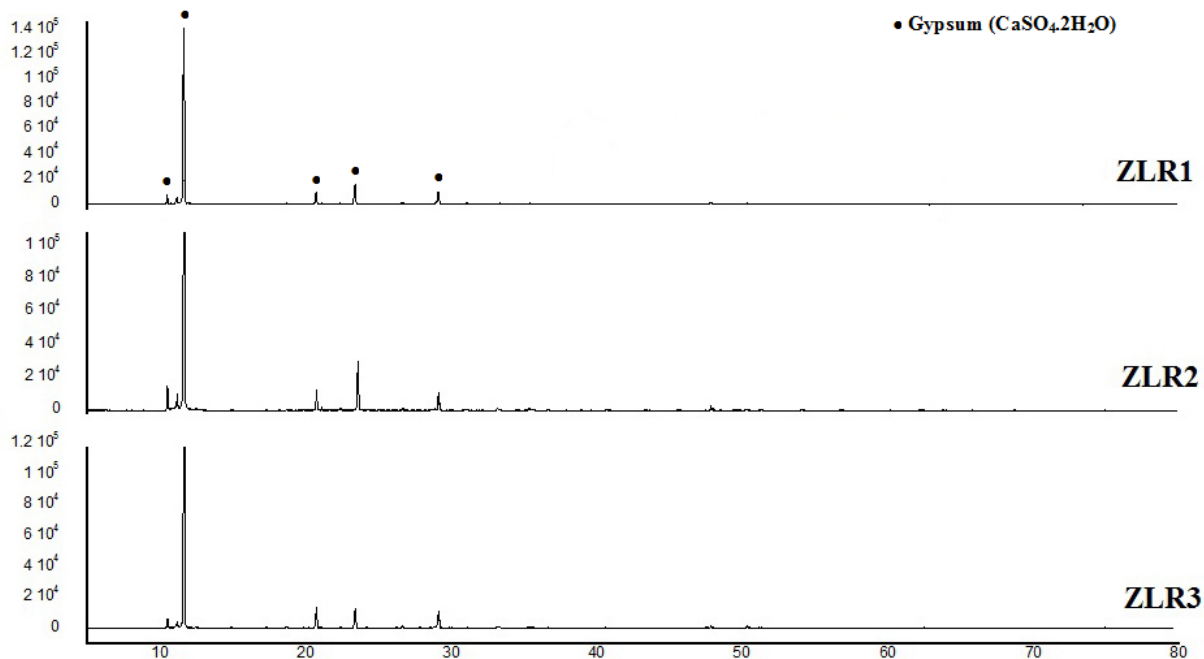


Fig. S1a. X-ray diffractograms of zinc plant leach residues.

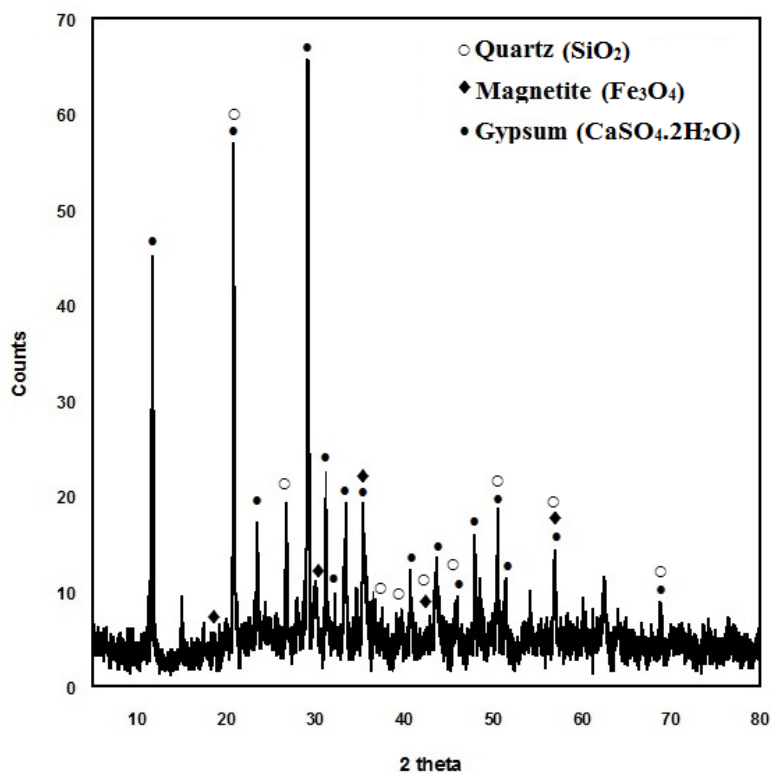


Fig. S1b. X-ray diffractogram of pre-concentrated ZLR1.

Supplementary Information

Table S3. Volume of acid/base required to bring the desired pH for pH dependent leaching.

Samples	pH2.5*	pH3.5*	pH4.5*	pH5.5*	Natural pH	pH7 [#]	pH8.5 [#]	pH10.5 [#]
ZLR1	7.0 mL	5.1 mL	3.3 mL	0.1 mL	-	0.8 mL	2.5 mL	7.3 mL
ZLR2	2.7 mL	2.3 mL	1.6 mL	0.5 mL	-	0.15 mL	1.0 mL	6.0 mL
ZLR3	0.9 mL	0.6 mL	0.2 mL	0.075 mL	-	0.3 mL	1.6 mL	10 mL

“*” – mentioned volume of acid (2 M HNO₃) + ultrapure water (final working volume 50 mL)

“-” – Ultrapure water (final working volume 50 mL)

“#” – mentioned volume of base (1 M KOH) + ultrapure water (final working volume 50 mL)

Table S4. Input molar concentrations used for visual MINTEQ modelling (based on the pH 2.5 leachate composition).

Species	ZLR1 (mg L⁻¹)	ZLR2 (mg L⁻¹)	ZLR3 (mg L⁻¹)
Zn ²⁺	3400	680	165
Cu ²⁺	97	10	35
Cd ²⁺	60	10	2.3
Mn ²⁺	388	210	15
Al ³⁺	111	25	48
Pb ²⁺	6	5	3
Fe ^{3+*}	15	40	190
Ca ²⁺	1923	1668	963
Mg ²⁺	180	300	240
Cl ⁻	3475	3950	3870
SO ₄ ²⁻	2190	1350	1150
NO ₃ ⁻	12400	4690	2840
PO ₄ ³⁻	15	15	15
CO ₃ ²⁻	80	105	110

* - total Fe concentration (by ICP-OES) was assumed as Fe³⁺ concentration

Supplementary Information

Table S5a – Saturation indices of the selected solubility controlling mineral phases for ZLR1 (calculated by Visual MINTEQ) (oversaturated SI were highlighted by bold italic) (in the descending order Al, Cd, Cu, Mn and Zn).

Mineral phase	pH 2.5	pH 3.5	pH 4.5	pH 5.5	pH 7.0	pH 8.5	pH 10.5
AlOHSO _{4(s)}	-1.209	-0.203	<i>0.733</i>	<i>0.779</i>	-0.206	-4.496	-10.399
Diaspore	-3.584	-0.595	<i>2.334</i>	<i>4.357</i>	<i>6.368</i>	<i>5.059</i>	<i>3.069</i>
Ettringite	-54.336	-42.308	-30.432	-20.327	-7.278	-0.818	<i>7.539</i>
Cd ₄ (OH) ₆ SO _{4(s)}	-34.086	-28.07	-22.065	-16.715	-7.042	<i>1.967</i>	<i>13.272</i>
Atacamite	-8.384	-5.384	-2.385	<i>0.607</i>	<i>4.435</i>	<i>5.371</i>	<i>5.976</i>
CuCO _{3(s)}	-6.645	-4.646	-2.663	-0.972	<i>0.665</i>	<i>0.117</i>	-1.356
Cupric ferrite	-1.064	<i>6.036</i>	<i>11.862</i>	<i>16.308</i>	<i>22.024</i>	<i>25.553</i>	<i>23.458</i>
MnHPO _{4(s)}	<i>1.079</i>	<i>1.881</i>	<i>1.984</i>	<i>2.95</i>	<i>4.721</i>	<i>4.714</i>	<i>1.138</i>
Pyrochroite	-13.135	-11.135	-9.135	-7.137	-4.135	-1.148	<i>0.687</i>
Hydrozincite	-33.228	-23.233	-13.268	-3.887	<i>9.059</i>	<i>19.996</i>	<i>18.407</i>
Smithsonite	-5.711	-3.713	-1.73	-0.036	<i>1.937</i>	<i>3.065</i>	<i>1.087</i>
Zincite	-8.332	-6.332	-4.333	-2.335	<i>0.665</i>	<i>3.559</i>	<i>4.347</i>

Supplementary Information

Table S5b – Saturation indices of the selected solubility controlling mineral phases for ZLR2 (calculated by Visual MINTEQ) (oversaturated SI were highlighted by bold italic).

Mineral phase	pH 2.5	pH 3.5	pH 4.5	pH 5.5	pH 7.0	pH 8.5	pH 10.5
AlOHSO _{4(s)}	-1.79	-0.776	<i>0.164</i>	<i>0.408</i>	-0.887	-5.236	-11.2
Diaspore	-4.071	-1.083	<i>1.85</i>	<i>4.085</i>	<i>5.787</i>	<i>4.43</i>	<i>2.436</i>
Ettringite	-55.876	-43.823	-31.938	-21.44	-9.032	-2.711	<i>5.401</i>
Cd ₄ (OH) ₆ SO _{4(s)}	-37.366	-31.342	-25.336	-19.328	-10.332	-1.34	<i>9.916</i>
Atacamite	-10.083	-7.083	-4.083	-1.091	<i>3.005</i>	<i>4.727</i>	<i>4.866</i>
CuCO _{3(s)}	-7.436	-5.438	-3.449	-1.601	<i>0.322</i>	<i>0.19</i>	-1.783
Cupric ferrite	-0.848	<i>6.169</i>	<i>11.085</i>	<i>16.307</i>	<i>22.158</i>	<i>26.076</i>	<i>23.748</i>
MnHPO _{4(s)}	<i>0.751</i>	<i>1.526</i>	<i>2.427</i>	<i>3.307</i>	<i>4.776</i>	<i>4.691</i>	<i>1.085</i>
Pyrochroite	-13.311	-11.311	-9.311	-7.311	-4.315	-1.344	<i>0.56</i>
Hydrozincite	-36.075	-26.081	-16.104	-6.404	<i>6.819</i>	<i>17.665</i>	<i>15.205</i>
Smithsonite	-6.221	-4.223	-2.234	-0.383	<i>1.736</i>	<i>2.861</i>	<i>0.545</i>
Zincite	-8.941	-6.942	-4.942	-2.943	<i>0.052</i>	<i>2.918</i>	<i>3.642</i>

Supplementary Information

Table S5c – Saturation indices of the selected solubility controlling mineral phases for ZLR3 (calculated by Visual MINTEQ) (oversaturated SI were highlighted by bold italic).

Mineral phase	pH 2.5	pH 3.5	pH 4.5	pH 5.5	pH 7.0	pH 8.5	pH 10.5
AlOHSO _{4(s)}	-1.435	-0.4	<i>0.559</i>	<i>0.703</i>	-0.589	-4.896	-10.88
Diaspore	-3.678	-0.712	<i>2.227</i>	<i>4.342</i>	<i>6.043</i>	<i>4.731</i>	<i>2.734</i>
Ettringite	-56.049	-43.941	-32.006	-21.675	-9.252	-2.866	<i>5.132</i>
Cd ₄ (OH) ₆ SO _{4(s)}	-39.886	-33.829	-27.81	-21.782	-12.784	-3.808	<i>7.379</i>
Atacamite	-8.848	-5.857	-2.858	<i>0.14</i>	<i>3.78</i>	<i>5.203</i>	<i>5.677</i>
CuCO _{3(s)}	-6.813	-4.819	-2.831	-1.052	<i>0.844</i>	<i>0.655</i>	-1.238
Cupric ferrite	<i>1.321</i>	<i>8.054</i>	<i>13.55</i>	<i>18.279</i>	<i>24.047</i>	<i>27.692</i>	<i>25.531</i>
MnHPO _{4(s)}	-0.837	-0.076	<i>0.884</i>	<i>1.925</i>	<i>3.844</i>	<i>3.775</i>	<i>0.679</i>
Pyrochroite	-14.392	-12.396	-10.397	-8.394	-5.398	-2.447	-0.014
Hydrozincite	-38.802	-28.831	-18.856	-9.288	<i>4.093</i>	<i>15.193</i>	<i>12.404</i>
Smithsonite	-6.759	-4.765	-2.777	-0.995	<i>1.204</i>	<i>2.507</i>	<i>0.072</i>
Zincite	-9.491	-7.497	-5.497	-3.496	-0.502	<i>2.329</i>	<i>3.023</i>

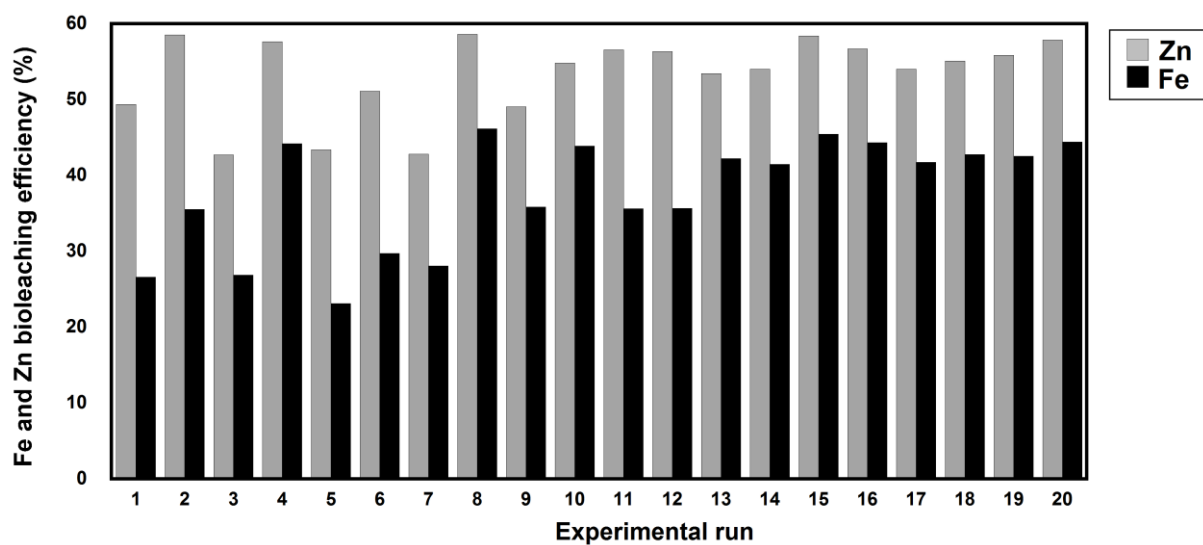


Fig. S5.1. Zn and Fe bioleaching efficiencies (%) achieved during the 20 experimental runs, after 30 days of bioleaching (experimental run refers to the std order in Table 1).

Supplementary Information

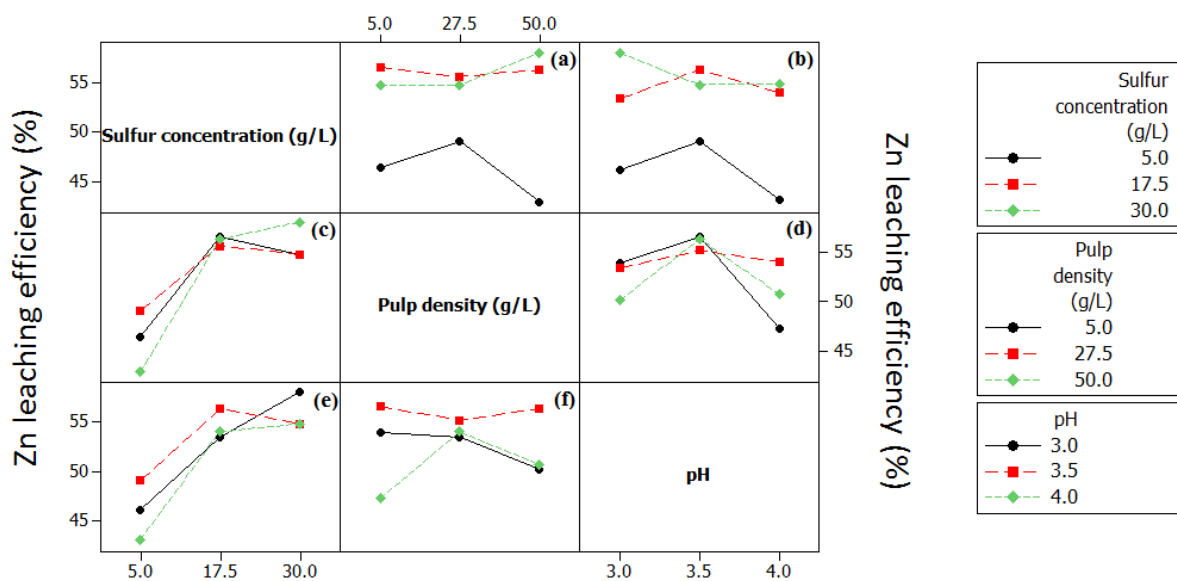


Fig. S5.2. Interaction plots for the bioleaching process variables (other variables were held constant at their centre point values).

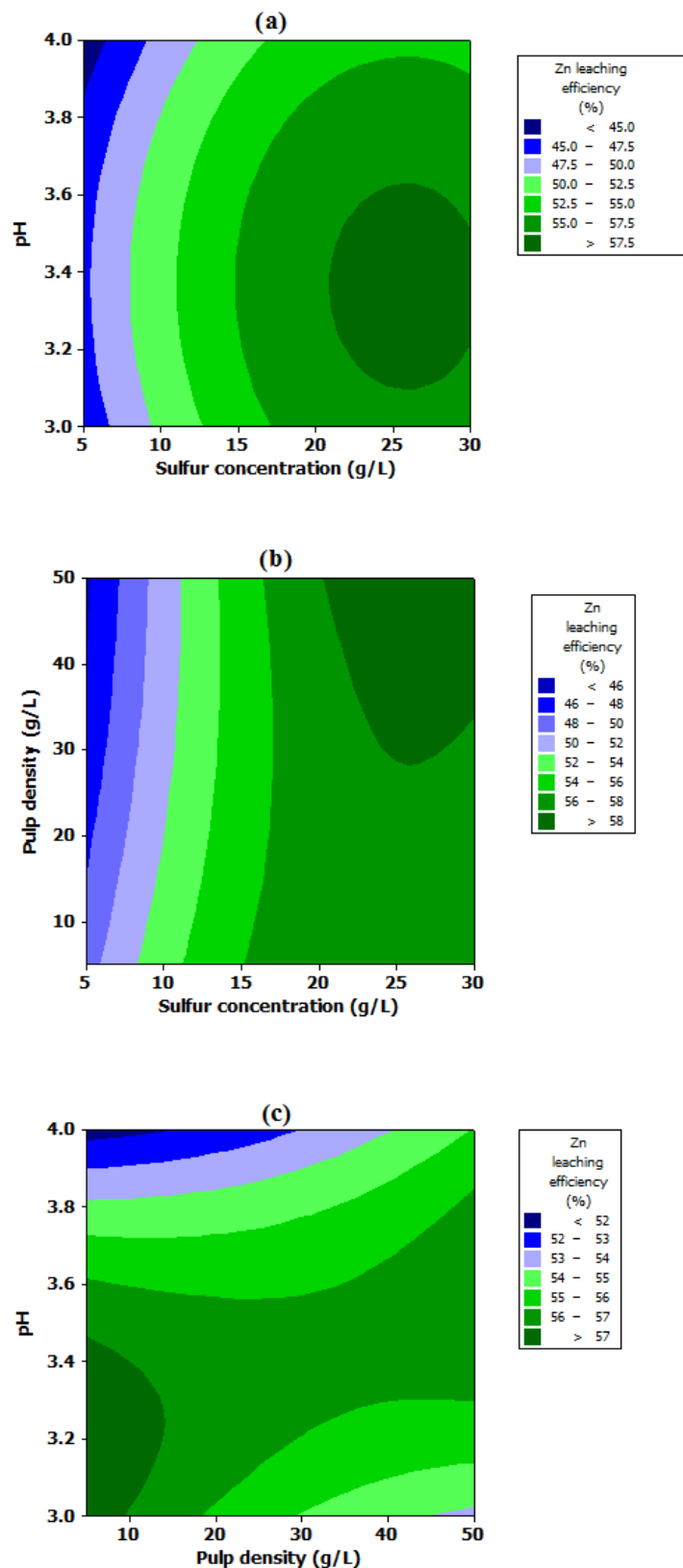


Fig. S5.3. Contour plots for the optimization of Zn bioleaching from ZLR (a) sulfur concentration vs pH, (b) sulfur concentration vs pulp density and (c) pulp density vs pH.

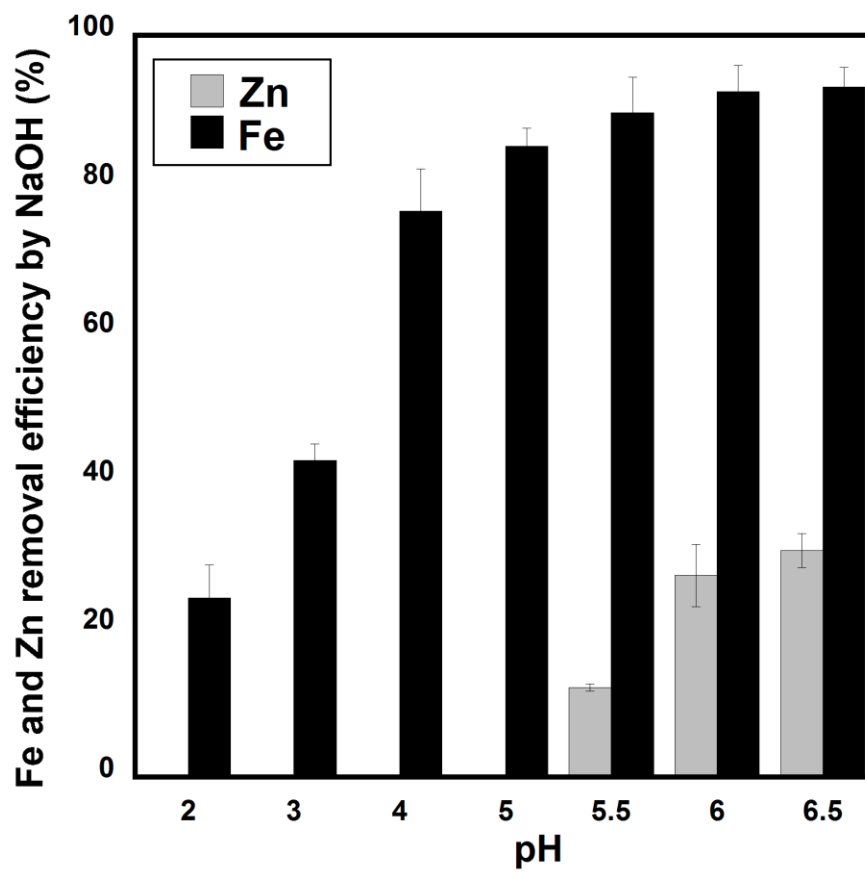


Fig. S5.4. Metal removal efficiency (%) by the addition of 10 M NaOH.

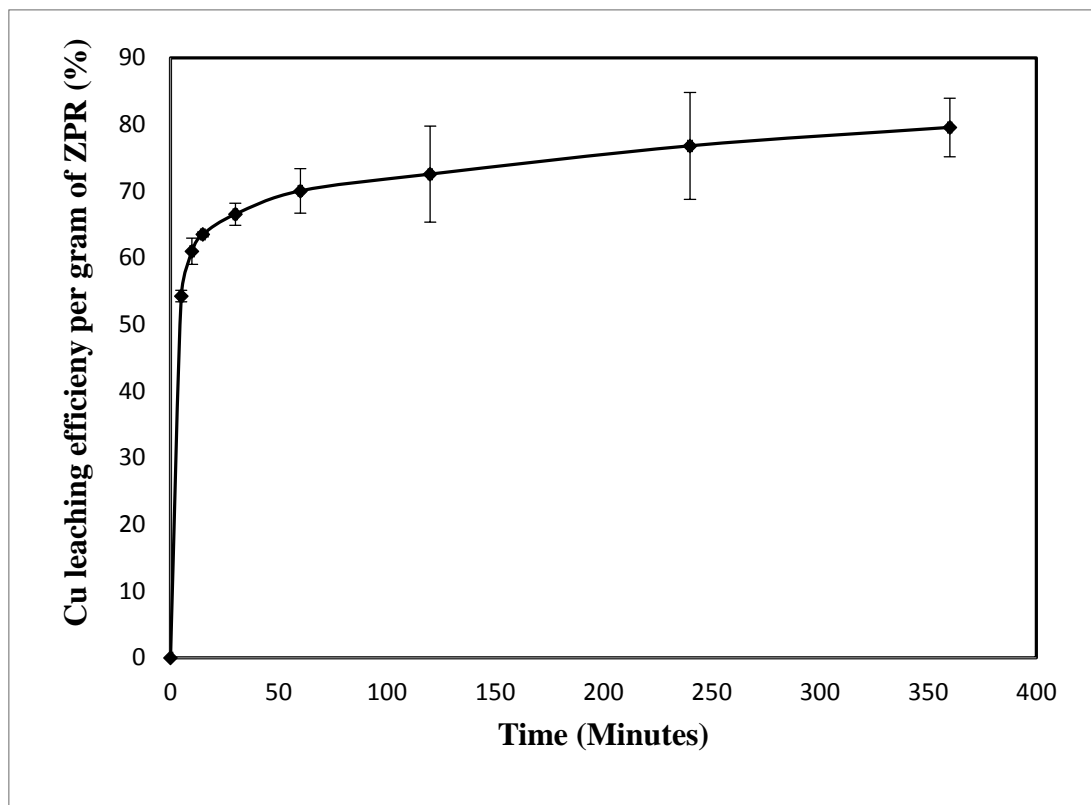


Figure S6.1. Copper leaching under optimized conditions.

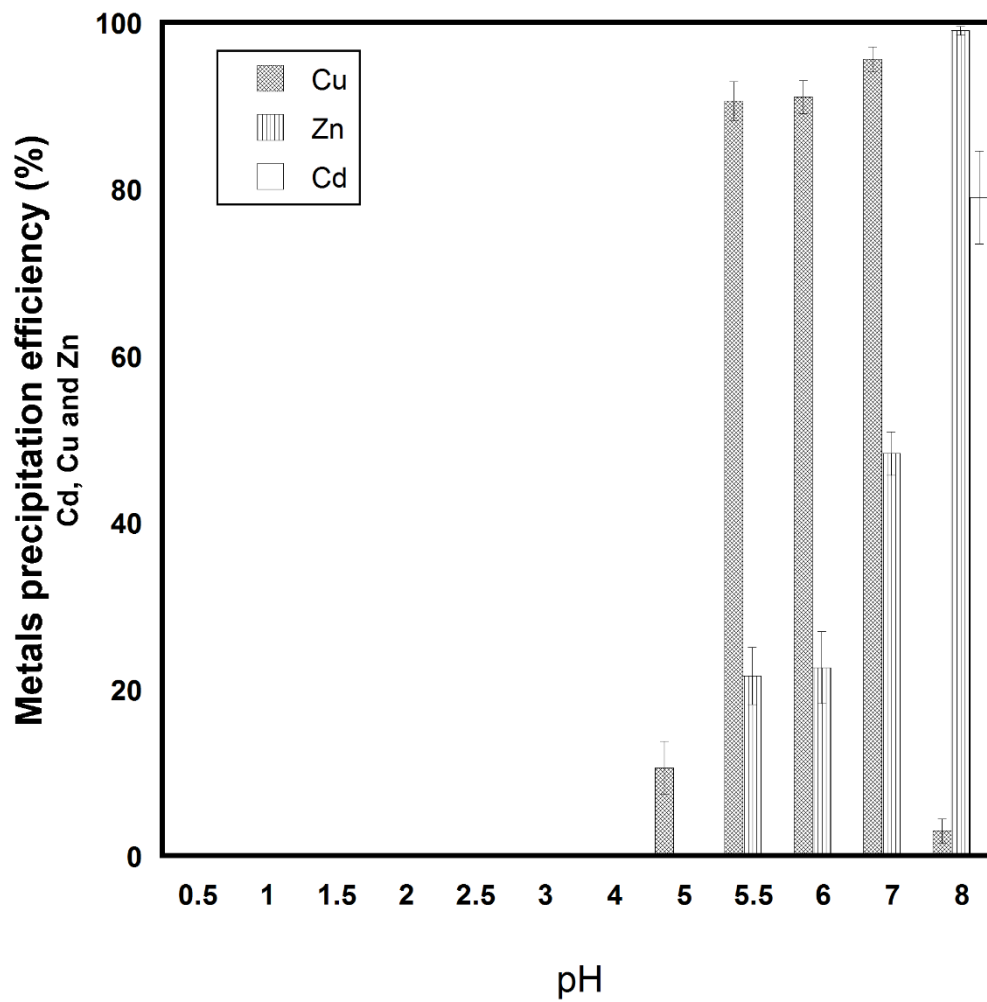


Figure S6.2. Metals (Cd, Cu and Zn) precipitation at different pH.

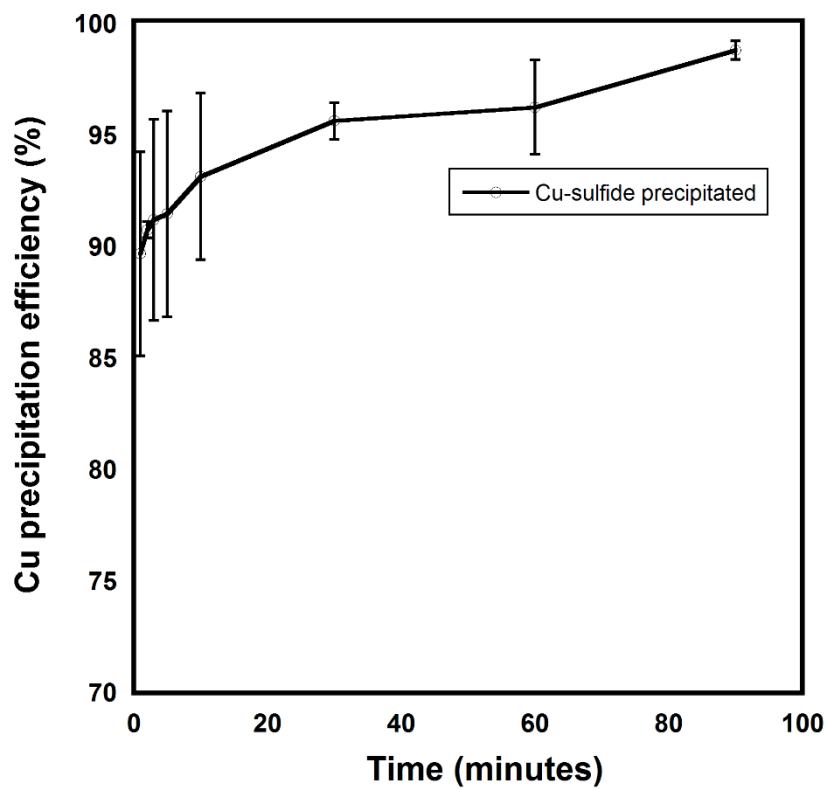


Figure S6.3. Cu-sulfide precipitation against time (initial pH 1.5, Cu:sulfide mass ratio 1:0.5, temperature 20 °C and agitation 150 rpm).

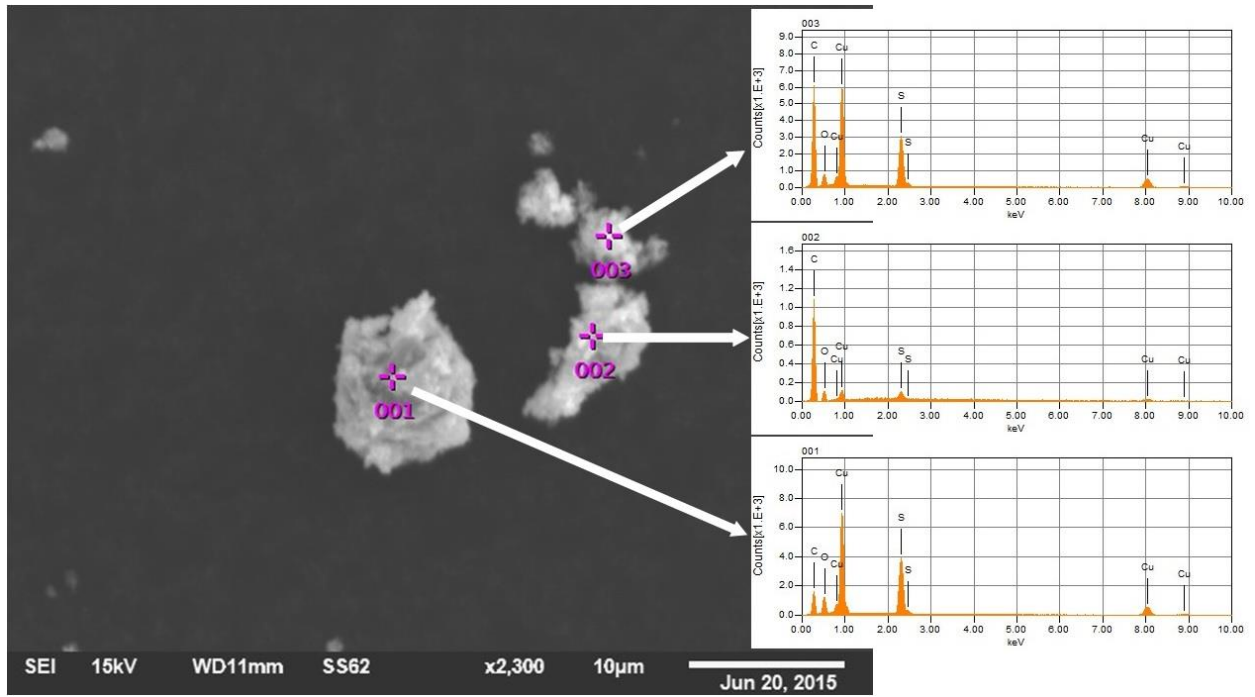


Figure S6.4. SEM - EDS micrographs of the precipitates.

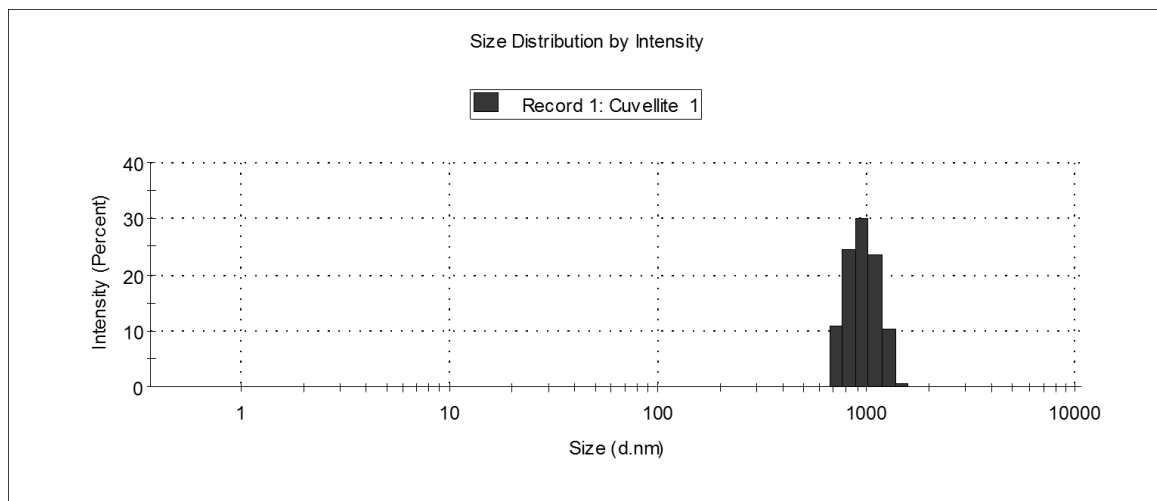


Figure S6.5. Particle size distribution of the Cu-sulfide precipitate.

Yesterdays's wastes

Today's resources

(Gadsden times- August 5, 1985)