Alkali ve Organik Asit Çözeltileri Kullanılarak Oksitlenmiş Pb-Zn Flotasyon Atıklarının Hidro- ve Biyo-Hidro-Metalurjik Yöntemlerle Geri Dönüşümü

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Recycling of Oxidized Pb-Zn Flotation Tailings Using Alkaline and Organic Acid Solutions by Hydro- and Biohydro- Metallurgical Methods

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by

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ETHICAL STATEMENT

I hereby declare that this thesis study titled “Recycling of Oxidized Pb-Zn Flotation Tailings Using Alkaline and Organic Acid Solutions by Hydro- and Biohydro- Metallurgical Methods” has been prepared in accordance with the thesis writing rules of Eskisehir Osmangazi University Graduate School of Natural and Applied Sciences under the academic consultancy of my supervisor Prof. Dr. Muammer Kaya. I hereby declare that the work presented in this thesis is original. I also declare that, I have respected scientific ethical principles and rules in all stages of my thesis study, all information and data presented in this thesis have been obtained within the scope of scientific and academic ethical principles and rules, all materials used in this thesis which are not original to this work have been fully cited and referenced, and all knowledge, documents and results have been presented in accordance with scientific ethical principles and rules. 28.06.2022

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Signature

ÖZET

Ortamdaki toksisiteyi azaltmak ve önemli metalleri geri kazanmak için maden atıklarının yönetimi ve arıtılması küresel bir endişe kaynağı haline gelmiştir. Bu çalışma, optimum geri kazanım, ekonomik ve teknik koşullar altında, hidrometalurjik ve biyo-hidrometalurjik yöntemlerle düşük dereceli karbonatlı çinko (smitsonit) ve kurşundan (seruzit) kurşun ve çinkonun geri kazanılmasını amaçlamaktadır. Bunu başarmak için çalışma üç ana aşamada gerçekleştirildi: İlk aşamanın amacı, alkali ve organik asit çözeltiler kullanılarak çinko ve kurşunun maksimum düzeyde birlikte çözünmesiydi. Yüklü liç çözeltisinden kurşunun çinkodan ayrılmasını amaçlayan ikinci aşama, reaktif olarak Na_2S kullanılarak kurşun sülfür (PbS) formunda kurşunun seçici olarak çökeltilmesi ile sağlandı. Bu aşamada kilit rol oynayan faktör çalışmamızda 1.4 olarak belirlenen Na_2S/Pb ağırlık oranıdır. İkinci aşamanın sonunda, PLS'deki saflaştırılmış çinko elektriklenmeye hazır hale gelirken, çökelti içindeki PbS formundaki kurşun biyo-liç aşamasına beslenir. Üçüncü aşamanın amacı, ikinci aşamada elde edilen kurşun sülfür çökeltisinden kurşunun etkili bir şekilde geri kazanılmasıydı. Bu, *L. ferrooksidans* bakterisi kullanılarak kurşun sülfürün biyo-liçi sağlandı.

Deneyler, 0.5 M NaOH, 0.2 M EDTA, 85 ^oC sıcaklık, S / L: 1/10, karıştırma hızı: 400 rpm, süre: 180 dakika koşulları altında kurşun ve çinkonun sırasıyla %95,4 ve %83,2 oranında birlikte ekstrakte edilmesinin mümkün olduğunu göstermiştir. Ayrıca, büyük bir safsızlığın Fe'nin çözelti içinde çözülmemesi, takip saflaştırmalarının gerekli olmaması nedeniyle büyük bir avantajdı. 1.4'lük bir Na_2S / Pb ağırlık oranındaki çökeltme reaksiyonu, biyo-liç deneyleri için besleme olarak kullanılan %99,99 Pb çökeltme sağlamıştır. Kurşun sülfürün biyo-liçinde Leptospirillum ferrooksidanlarının kullanılmasının çok etkili olduğu görülmedi, çünkü pH 2 ve %5 pülp yoğunluğunda maksimum %48,03 Pb elde edildi.

Anahtar kelimeler: Hidrometalurji, biyoliç, çökeltme, L. ferrooksidans. alkali çözeltiler

SUMMARY

The management and treatment of mine tailings in order to alleviate toxicity in the environment, and to recover important metals, has become a global concern. The present work is aimed at recovering zinc and lead from low-grade carbonaceous zinc (smithsonite) and lead (cerussite) by means of hydrometallurgical and bio-hydrometallurgical methods, under optimal recovery, economic and technical conditions. To accomplish this, the study was performed in three major stages: The objective of the first stage was to maximally co-leach lead and zinc using alkaline and organic acid solutions, as well as with the help of additive reagents and enhancers. The second stage which was aimed at separating zinc from lead in the pregnant leach solution, was achieved through selective lead precipitation as lead sulphide (PbS) using Na_2S as the reagent. The key playing factor in this stage is the Na_2S/Pb weight ratio which was determined to be 1.4 in our study. At the end of the second stage, the purified zinc in the PLS is ready for electrowinning (EW), while the lead in the form of PbS in the precipitate is fed to the bioleaching stage. The objective of the third stage was to effectively recover lead from the lead sulphide precipitate which was obtained in stage two. This was achieved by bioleaching of the lead sulphide using the bacterium *L. ferrooxidans*.

The experiments showed that it was possible to co-extract lead and zinc at 95.4% and 83.2%, respectively under the conditions: 0.5 M NaOH, 0.2 M EDTA, 85 ^{o}C temperature, S/L: 1/10, stirring rate: 400 rpm, time: 180 minutes. Also, the fact that Fe, a major impurity did not dissolve in the solution was a great advantage as follow-up purifications were not necessary. The precipitation reaction at a Na_2S/Pb weight ratio of 1.4 yielded 99.99% Pb precipitation which was used as the feed for the bioleaching experiments. The use of *Leptospirillum ferrooxidans* for the bioleaching of lead sulphide was not seen to be very efficient, as a maximum of 48.03% at pH 2 and 5% pulp density was obtained.

Keywords: Hydrometallurgy, bioleaching, precipitation, *L. ferrooxidans*, alkaline solutions.

DEDICATION

Dedicated to my mother and siblings

LIST OF CONTENTS

Page

ÖZET ..... **vi**
SUMMARY ..... **vii**
LIST OF CONTENTS ..... **ix**
LIST OF FIGURES ..... **xii**
LIST OF TABLES ..... **xvi**
LIST OF ABBREVIATIONS AND SYMBOLS ..... **xviii**
1. INTRODUCTION AND PURPOSE **1**
2. THEORY AND LITERATURE REVIEW **6**
2.1. Brief History and Origin of Zinc and Lead 6
2.1.1. Zinc (Zn) 6
2.1.2. Lead (Pb) 7
2.2. Physical and Chemical Properties of Zinc and Lead 8
2.2.1. Physical properties 8
2.2.2. Chemical properties 9
2.3. Zinc and Lead Minerals 10
2.4. World Lead-Zinc Reserves 12
2.5. Areas of Application of Zinc and Lead 14
2.6. Primary Production of Lead-Zinc 15
2.7. Recycling of Lead-Zinc from secondary resources 16
2.8. Toxicity of Pb-Zn 17
2.9. Lead-Zinc Recovery Methods 18
2.9.1. Hydrometallurgical Methods 19
2.9.1.1. Alkaline NaOH leaching 20
2.9.1.2. Organic Acid EDTA leaching 22
2.9.2. Bio-Hydrometallurgical Methods 23

LIST OF CONTENTS (Continued)

Page

2.9.2.1. Microbe - metal interactions 24
2.9.2.2. Mechanisms 25
2.9.2.3. Microorganisms used in Bioleaching 26
2.9.2.4. Leptospirillum ferrooxidans 30
2.9.2.5. Reasons for Biohydrometallurgy 31
2.9.2.6. Factors that Affect Biological Leaching 32
2.9.2.7. Applications of Bioleaching (to various solid wastes) 32
3. MATERIALS AND METHODS 34
3.1. Materials 34
3.1.1. For Chemical Leaching 34
3.1.1.1. Collection and preparation of Pb-Zn oxide flotation tailing sample 34
3.1.1.2. Characterization of the Pb-Zn oxide flotation tailing sample 35
3.1.2. For Bioleaching 44
3.1.2.1. Collection and Preparation of Sulphide Precipitate Sample 44
3.1.2.2. Characterization of Sulphide Precipitate Sample 45
3.2. Methods 48
3.2.1. Co-Extraction of Pb and Zn by Alkaline Leaching Method 49
3.2.2. Leaching Enhancement Method with Ultrasound 53
3.2.3. Purification Method 55
3.2.3.1. Zinc Recovery through Selective Sulphide Precipitation 55
3.2.4. Bio-leaching Method 58
3.2.4.1. The medium and culture of Leptospirillum ferrooxidans 59
3.2.4.2. Bioleaching experiments 60
4. RESULTS AND DISCUSSION 64
4.1. STEP I: Chemical Leaching for the co-extraction of Pb and Zn 64
4.1.1. Alkaline Leaching 64
4.1.1.1. Alkaline leaching with NaOH only 65

LIST OF CONTENTS (Continued)

Page

4.1.1.2. Alkaline Leaching with NaOH + NaCl 72
4.1.1.3. Alkaline leaching with NaOH + EDTA 74
4.1.2. Organic Acid Leaching with EDTA only 83
4.2. STEP II: Lead and Zinc separation through selective precipitation of lead 86
4.2.1. Effect of Na_2S/Pb weight ratio on selective precipitation of lead 87
4.2.2. Effect of temperature and time on selective precipitation of lead 89
4.3. STEP III: Bio-Leaching Tests for Lead Recovery from Sulphide Precipitate 92
4.3.1. Lead extraction 93
4.3.1.1. Effect of pulp density on Pb extraction 93
4.3.1.2. Effect of pH on Pb extraction 96
4.3.1.3. Effect of time on Pb extraction 98
4.3.2. Zinc Impurity extraction 100
4.3.3. Control Experiments 101
5. FINAL ASSESSMENT 106
5.1. Flowsheet Generation 106
5.2. Cost analysis 108
6. CONCLUSION AND RECOMMENDATIONS 110
REFERENCES 112

LIST OF FIGURES

Figure **Page**

1.1. The dangers of tailing pollution (Gao et al., 2021) 1

2.1. Location of the major supergene nonsulfide Zn-Pb mineral deposits in the world(Mondillo, 2013) 12

2.2. Areas of application of (a) zinc and (b) lead and their percentages, reproduced from (Reuter et al., 2015) 15

2.3. NaOH chemical structure 20

2.4. (a) Chemical structure of ETDA and (b) molecular structure showing chelation 23

2.5. Different metal-microbe interactions occuring during bioleaching (reproduced from Sethurajan, 2016) 25

2.6. Flowsheet of metal recovery by bioleaching (Gao et al., 2021) 33

3. 1. Oreks tailing dam (a) area and (b) surface views and (c) drying of the roll crushed flotation tailing. 35

3.2. Particle size distribution of flotation tailing sample. 37

3.3. XRD pattern of the Turkish sample. 39

3.4. TGA curves for tailing sample 42

3.5. SEM-EDX anaylses of the flotation sample. 44

3.6. (a) dried precipitate after filtration, and (b) set-up for manual grinding of the dried precipitate. 45

3.7. Particle size distribution of sulphide precipitate 46

3.8. XRD pattern of sulphide precipitate 47

3.9. (a) Digital triple and (b) Single experimental leaching set-up 51

3.10. Ultrasound-assisted leaching set-up 53

LIST OF FIGURES (Continued)

Figure **Page**

3.11. Selective precipitation set-up,.....56
3.12. (a) before addition of Na_2S and (b) upon addition of Na_2S.....57
3.13. (a) Solid-liquid separation after selective precipitation, and (b) PLS before and after selective precipitation of lead.....58
3.14. Bioleaching set-up.....62

4.1. Effect of NaOH concentration on lead, zinc and Fe recovery at 85 ^{o}C, 180 minutes, 1/10 solid/liquid ratio and 400 rpm.....66
4.2. Effect of temperature on lead, zinc and Fe recovery at 5M NaOH concentration, 180 minutes, 1/10 solid/liquid ratio and 400 rpm.....68
4.3. Effect of time on lead, zinc and Fe recovery at 5.0 M NaOH, 85 ^{o}C, 180 minutes, 1/10 solid/liquid ratio and 400 rpm.....69
4.4. Effect of ultrasound on extraction efficiencies of zinc, lead, and iron at (a) without mixing and (b) with mixing at 5.0 M NaOH; 1hr; S/L=1/10; 400 rpm, 70 ^{o}C.....71
4. 5. Effect of NaCl concentration on zinc, lead, and iron extraction at 5.0 M NaOH; 180 mins; S/L=1/10; 400 rpm, 85 ^{o}C.....74
4.6. Effect of NaOH concentration on zinc, lead, and iron extraction at 0.2 M EDTA; 180 mins; S/L=1/10; 400 rpm, 85 ^{o}C.....76
4.7. Effect of EDTA concentration on zinc, lead, and iron extraction at 0.5 M NaOH; 180 mins; S/L=1/10; 400 rpm, 85 ^{o}C.....78
4.8. Effect of solid-liquid ratio on zinc, lead, and iron extraction at 0.5 M NaOH; 0.2 M EDTA; 180 mins; 400 rpm, 85 ^{o}C.....80
4.9. Effect of temperature on zinc, lead, and iron extraction at 0.5 M NaOH; 0.2 M EDTA; 180 mins; S/L=1/10; 400 rpm.....81

LIST OF FIGURES (Continued)

Figure **Page**

4.10. Effect of time on zinc, lead, and iron extraction at 0.5M NaOH; 0.2M EDTA; 85^{o}C mins; S/L=1/10; 400rpm 83
4.11. Effect of time on zinc, lead, and iron extraction at 0.2 M EDTA; 85 ^{o}C mins; S/L=1/10; 400 rpm 84
4.12. Schematic flowsheet for the co-dissolution of Pb and Zn from oxidized Pb-Zn flotation tailing by one-step alkaline leaching. 86
4.13. Effect of Na_2S/Pb weight ratio on the precipitation rates of Pb and Zn (Conditions: 60 mins, 50 ^{o}C) 89
4.14: Effect of time and temperature on the precipitation rates of Pb and Zn, at Na_2S/Pb weight ratio of 1.4 90
4.15. Schematic flowsheet for the separation of lead from zinc by selective precipitation of Pb using Na_2S, ... 92
4.16. Effect of pulp density on Pb extraction rate at pH (a)1.6 (b)1.8 and (c)2.0 over a 35-day period 95
4.17. Effect of pH on Pb extraction at 5% pulp density, after a 42-day period 97
4.18. Effect of time on Pb extraction rate, at pH (a)1.6, (b)1.8, and (c)2.0 over a 35-day period…. 99
4.19. Effect of time on the extraction of Zn impurity (Same graph at all pHs, and all pulp densities. Same graph too for control experiment) 101
4.20. Effect of time on Pb extraction rate of control experiment at pH (a)1.6 (b)1.8 and (c) 2.0 over a 35-day period 103
4.21. Schematic flowsheet for the bioleaching of lead sulphide precipitate using L. ferrooxidans 105

LIST OF FIGURES (Continued)

Figure **Page**

5.1. Final schematic flowsheet for the preparation of Zn and Pb concentrates from oxidized Pb-Zn flotation tailing by one-step alkaline leaching, one-step precipitation and bioleaching.… 107

LIST OF TABLES

Table **Page**

1.1. Comparison between hydrometallurgy and pyrometallurgy (Talan, 2016) 2
1.2. Main microorganisms used for the recovery of metals (Gao et al., 2021) 3

2.1. Physical and chemical properties of zinc (Goodwin, 2018; Sarilar, 2019) 8
2.2. Zinc and lead oxide minerals of economic value (reproduced from (Sarilar, 2019)) 11
2.3. Pb-Zn reserves around the world (Reproduced from (Hewitt and Wall, 2000)) 13
2.4. Mine production from 2017 to March 2022 (Reproduced from (International Lead & Zinc Study Group, 2022)). 16
2.5. Contamination levels detected in soils and regulatory guidelines regarding some toxic metals (Nguyen et al., 2021) 18
2.6. The micro-organisms used in bioleaching (Nguyen et al., 2021) 29

3.1. Particle size distribution of the tailing sample 36
3.2. XRF results of the tailing sample 38
3.3. ICP-AES results of flotation tailing sample 40
3.4. Particle size distribution of the sulfide precipitate sample. 46
3.5. Aqua regia analysis with triplicates of the sulphide precipitate 47
3.6. Experimental conditions for leaching tests 52
3.7. Experimental conditions for precipitation tests 56
3.8. Reagents used in the preparation of the medium of L. ferrooxidans 59
3.9. The experiments and the different conditions applied in the bioleaching of the sulphide precipitate. 63

4.1. Recovery efficiency for Pb, Zn, and Fe at varying NaOH concentrations. 66

LIST OF TABLES (Continued)

Table **Page**

4.2. Recovery efficiency for Pb, Zn, and Fe at varying temperatures 67
4.3. Recovery efficiency for Pb, Zn, and Fe at varying durations 69
4.4. Extraction efficiencies for zinc, lead and iron, with and without ultrasound. 70
4.5. Extraction efficiencies of zinc, lead and iron at different NaCl concentrations 73
4.6. Extraction efficiencies of zinc, lead and iron at different NaOH concentrations and 0.2 M EDTA 75
4.7. Extraction efficiencies of zinc, lead and iron at different EDTA concentrations and 0.5 M NaOH 77
4.8. Extraction efficiencies of zinc, lead and iron at different solid-liquid ratios 79
4.9. Extraction efficiencies of zinc, lead and iron at different temperatures 81
4.10. Extraction efficiencies of zinc, lead and iron at different durations. 82
4.11. Extraction efficiencies of zinc, lead and iron at different durations, at 0.2 M EDTA 84
4.12. Percentage of Zn and Pb precipitations at different weight ratios. 88
4.13 Percentage of Zn and Pb precipitations at different durations and temperatures. 90
4. 14. Lead extraction efficiencies at different pHs and pulp densities over a 35-day period 93
4.15. Pb extraction efficiencies at different pHs, at 5% pulp density, after a 42-day period 97
4.16. Lead extraction efficiencies for control experiments at different pHs and pulp densities over a 35-day period 102

5.1. Hydrometallurgical steps, their reagent consumptions, and metallurgical performance. 108
5.2. Prices of reagents, and consumption/ tonne of tailing 108
5.3. Prices of metals (solid and in solution) 109

LIST OF ABBREVIATIONS AND SYMBOLS

Symbol	**Description**
AAS	Atomic Absorption Spectroscopy
ARUM	Merkezi Arastırma ve Uygulama Merkezi
As	Arsenic
CRT	Cathode Ray Tube
EDTA	Ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$)
ESOGU	Eskisehir Osmangazi University
EW	Electrowinning
Fe	Iron
H_2SO_4	Sulphuric acid
ICP-AES	Inductive Coupled Plasma
L. ferrooxidans	*Leptospirillum ferrooxidans*
Na_2S	Sodium sulphide
NaOH or $PbCO_3$ or Na_2CO_3	Sodium hydroxide, Lead carbonate, Sodium carbonate
Pb	Lead
PLS	Pregnant Leach Solution
rpm	Rotations per minute
S/L ratio	Solid/Liquid ratio
TGA technique	Thermogravimetric Analysis technique
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
Zn	Zinc

1. INTRODUCTION AND PURPOSE

One of the main challenges in the world presently is mine tailing management. As mine tailings accumulate, there are numerous negative impacts on the environment, which has made the removal of heavy and toxic metals from these tailings inevitable. At the same time valuable metals are also recovered from these tailings, reason why recycling of mine wastes is gaining a growing interest in the last decades. One pivotal topic is lead (Pb)-zinc (Zn) recovery from mine tailings (Deep and de Carvalho, 2008). The reason is due to the simultaneous recovery of two important metals (Pb and Zn), the reduction of heavy and hazardous metals in waste including Pb, Zn, Cu, Cd, Mn, Ni, and As, and most importantly, due to the continual degradation of high grade Pb-Zn ores with time (Falagán et al., 2017). Figure 1.1 shows the dangers of tailing pollution.

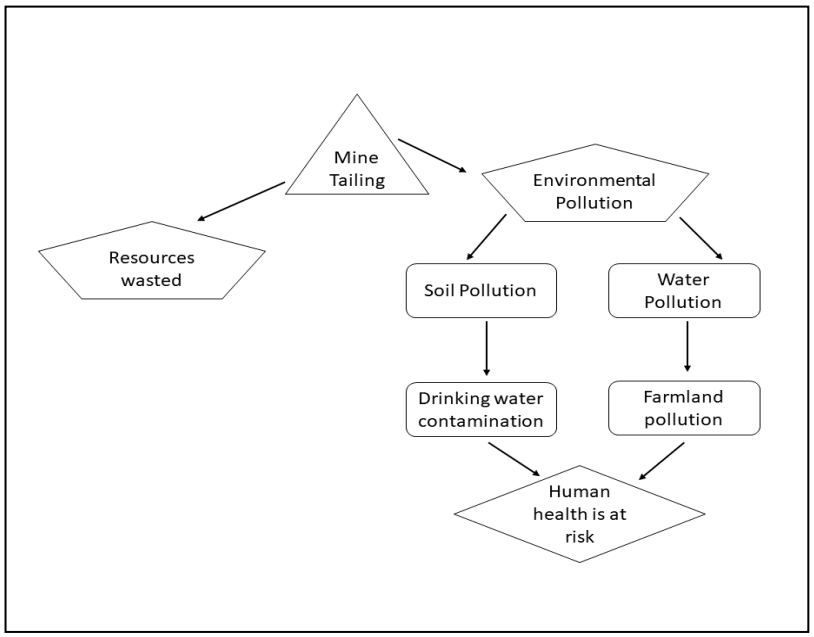


Figure 1. 1. The dangers of tailing pollution (Gao et al., 2021)

The recovery of metals from these tailings can be performed using traditional methods such as pyrometallurgy and hydrometallurgy, but in the last decades, hydrometallurgy is more preferred to pyrometallurgical methods for the treatment of mine tailings due to its high recovery efficiency, environmental friendliness, and its ability to treat low-grade ores/tailings (Hussaini et al., 2021b). Table 1.1 demonstrates a comparison between hydrometallurgy and pyrometallurgy.

Table 1. 1. Comparison between pyrometallurgy and hydrometallurgy (Talan, 2016)

Hydrometallurgy	**Pyrometallurgy**
Generally lower capital investment requirement	Generally higher capital investment requirement.
Treatment of low-grade ores	Treatment of high-grade ores
Chemically-similar material separation is possible	Materials with chemically similar properties are not easy to separate
No dust emission	Dust issue is common
Slower reaction rate	Faster reaction rate
Toxic gases are released less	Toxic gases are released more
Does not require complex engineering	Requires complex engineering
Material handling is easily done	Material handling is difficult

However, more sustainable and greener technology is being sought which has caused a significant progress in biological leaching technology where specific bacteria is used to improve on metal recovery at specific experimental conditions best appropriate to the species and the mineral type. Biohydrometallurgical processes consume very less energy, they are relatively cheap and environmentally safe. By exploiting metal accumulating and solubilizing properties of micro-organisms, these processes offer efficient technology for the extraction of important metals from low-grade ores, waste materials and rocks (Jain and Sharma, 2004). The literature has much, pertaining to bioleaching of sulfide ores, and generally chemolithoautotrophic micro-organisms

such as *Acidiothiobacillus ferrooxidans*, and *T. thiooxidans* have been used to efficiently recover the metals even commercially. Table 1.2 shows the main strains of bacteria used for the recovery of metals.

Table 1. 2. Main microorganisms used for the recovery of metals (Gao et al., 2021)

Microorganism	Shape	Convenient type of ores	Optimum pH range	Optimum temp. range (^{o}C)
Acidiobacillus ferrooxidans	Rod-shaped bacterium	sulfide	2 – 3	30 – 35
Leptospirillum ferrooxidans	Vibroid-shaped bacterium	sulfide	1.5 – 2	25 – 35
Aspergillus niger	flask-shaped fungus	oxide	5 – 5.5	30 – 40
Acidithiobacillus thiooxidans	Rod-shaped bacterium	sulfide	1.5 – 2	28 – 30

Nevertheless, the literature covering bioleaching of non-sulphidic ores is not yet very expanded. Non-sulphidic ores (carbonates, oxides, silicates) do not contain any energy source which the microorganisms will feed on. This is what poses the problem, and due to this, these types of minerals cannot be leached under the same conditions as sulphide ores. Researchers of the latter ores propose the using heterotrophic microorganisms, since as a source of energy and carbon for their growth, they require an organic carbon source (Jain and Sharma, 2004). These bacteria and fungi have a higher efficiency on metal extraction from non-sulphide ores.

Using microorganisms to extract heavy metals from tailings is more environmentally friendly, since it not only reduces tailings pollution but also reduces primary resource depletion and does not release hazardous gases that contribute to secondary pollution during the reaction (Gao et al., 2021).

Lead and zinc are among the oldest and most important metals in use, and their value is growing by the day. The production methods of lead-zinc, the rates, and the technologies for processing are being enhanced globally, to meet up with the demand of these metals in acceptable grade. There are numerous lead and zinc minerals which occur natural. The most common lead mineral with economic importance is lead sulphide, called galena (PbS). Others include cerussite ($PbCO_3$) and anglesite ($PbSO_4$). As for zinc, its most common mineral with economic importance is sphalerite (ZnS) making up to 85% of total zinc production. Others include smithsonite ($PbCO_3$), willemite ($\underline{Zn}_2\underline{SiO}_4$) and hemimorphite $Zn_4Si_2O_7(OH)_2H_2O$.

Albeit sulphide-type lead and zinc mineral beneficiation and concentration methods are more cost-effective and simple to implement, the depletion of sulphide mineral types of these metals, combined with the increased demand from developed countries, has sparked some interest in the non-sulphide lead and zinc deposits, and this has expanded the exploitation of oxide deposits. Some of the lead oxide minerals that exist include cerussite, anglesite, pyromorphite, crocoite, wulfenite, minettizite, plumbojarosite, while the zinc oxide minerals include smithsonite, willemite, calamine, clinohedrite, and zincite (Sarilar, 2019).

When it comes to the processing of sulphide ores, the most common method is selective froth flotation (Anyadike, 2002) which is advantageous in that it consumes less reagent and is easily operatable. However, on the contrary there are numerous challenges in using froth flotation for lead and zinc oxide minerals due to high reagent consumption, low grade and low recovery percentages. The use of hydrometallurgical methods for zinc and lead recovery from their oxide minerals is being highly considered in the literature owing to the low-grade nature of the oxide ore, and their higher solubility. The hydrometallurgical methods include leaching such as acid leaching and alkaline leaching, purification methods such as precipitation, and electrowinning processes to recover the metal. The type of method to use will depend on the characteristics of the ore/tailing, the metal to be recovered, and the impurities present (Hussaini et al., 2021b)

Purpose of the Study

The main motivation behind this work is to investigate and improve on the leaching, purification and bioleaching methods, for the obtention of pregnant leach filter liquors of lead and zinc, from carbonaceous lead and zinc (cerussite and smithsonite) in flotation tailings from the OREKS tailing dam, in Kayseri, Turkey, while taking into consideration the economic and technical aspects of the processes. The flotation tailing contains 7.50% lead and 5.77% zinc, and in three major steps, the recovery of zinc and lead at above 80% recovery is sought. Using NaOH (alkaline) leaching in the first step, different parameters such as concentration, temperature and time will be tested to improve on the co-leaching of zinc and lead at optimal recoveries. Also, enhancers will be used to boost the metal recoveries such as addition of other reagents such as NaCl, EDTA, and the use of ultrasound. Also, organic acid (EDTA) leaching will be performed in order to make a comparison with the alkaline leaching. Selective separation of the co-leached Zn and Pb will be investigated using a precipitation method, by adding Na2S at a specific Na2S/Pb weight ratio. This specific weight ratio will be achieved by testing different weight ratios, and choosing the one with maximum lead precipitation and minimum zinc precipitation. Finally, the purified zinc will remain in the PLS at high concentration and ready to be electrowon. On the other hand, the lead sulphide precipitate will be treated to the bioleaching phase using *L. ferrooxidans* as the leaching bacterium, and the objective is to extract pregnant filter liquor of lead, at considerable recovery levels, while testing different parameters like pulp density, pH, and time. Finally, the most technically feasible, economic, and considerable recovery methods will be determined and discussed.

2. THEORY AND LITERATURE REVIEW

2.1. Brief History and Origin of Zinc and Lead

2.1.1. Zinc (Zn)

Zinc has been known a long time ago as far as the 1100s, even though the zinc metal appeared considerably later in History compared to the other known metals such as copper, iron, tin, lead (Augustyn, 2021). The Romans were aware of zinc, even though it was scarcely utilized. Originally it was recognized as a separate metal in India, as a zinc smelter in Zawar, Rajasthan, produced waste which attests to the large-scale refinement around the years 1100 and 1500. Also, by the 1500s, China had developed a large-scale zinc refining industry. Evidence found from an investigation of ingots reclaimed from the coast of Sweden in 1745 after the sinking of an East India Company ship carrying Chinese zinc showed that the metal was almost pure zinc. In Europe, metallic zinc extraction from its oxide had been reported by P. Moras de Respour, a Flemish metallurgist in 1668, but Europe acknowledges Andreas Marggraf, a German chemist as the one who discovered zinc in 1746 and he was the first to recognize it as a new metal. (Emsley, 2012). Zinc stands as the fourth most common metal in use, after aluminium, iron and copper (Kropschot and Doebrich, 2011; Tolcin, 2021) with about 13 million tonnes as yearly production (Tolcin, 2021) . Out of all the zinc produced globally, approximately 70% comes from mining activity, while the remaining percentage comes from the recycling of secondary zinc resources (Lee, 2008) The primary ore mineral of zinc is sphalerite, which is a sulfide of zinc, but nonsulfide minerals of zinc also exist with zinc as main component. Early production of zinc mostly came from nonsulfide deposits, but production has shifted to sulfide deposits due to exhaustion of nonsulfide resources. New innovations in extractive metallurgy have also brought about increased interest in nonsulfide zinc deposits over the last decades (Kropschot and Doebrich, 2011).

2.1.2. Lead (Pb)

The Chinese are thought to have been aware of the use of lead metal as early as 2000 BC. There have been definitive proofs of the ancient Egyptians, Romans, and Greeks using lead in jewellery, water pipes, solder, and weights. Eastern Europe, Spain, and Sweden became key centres of lead mining during the Middle Ages. In 1621, the first lead mine was established in the United States (Chatterjee, 2007). Pb mining and use dates back millennia, with old mines across the Roman, Phoenician and other empires evolving to the widespread lead mining that occurred and continues to occur in more recent ages around the world. Pb was used to extract Ag and Au in ancient times, used as weatherproof seal for structures, was used for water pipes, paints, sheets, glass windows, and even cosmetics. Pb has been used as an electrical energy store in lead-acid batteries, as a petrol additive to improve the performance of engines, as a plastic additive, in older CRT-type of televisions (Mudd et al., 2017). During the early nineteenth century, the world's primary lead metal production was not up to 250000 tonnes, but increased to approximately 415.000 t in 1880, more than one million t in 1900, more than 2.1 million t in 1925, and approximately 3.5 million tonnes in 1968. However, the production fell in the 1990s, to around 3.2 million tonnes (Chatterjee, 2007). From the 1960s, awareness of the harmful effects of Pb exposure started increasing. This resulted in the gradual elimination of numerous dissipative usages from the 1970s and thereon (for example, Pb in paints or petrol), typically in response to the discovery of alternative materials to replace Pb as well as a focus on applications where recycling is a good option (Pb-acid batteries). Pb presently, is among the most recycled metals globally, with above 50% of global demand being met by secondary supplies. Pb is typically produced by pyrometallurgy, with a lead sulphide concentrate generally being produced, which is then melted and refined to pure metal (Mudd et al., 2017).

2.2. Physical and Chemical Properties of Zinc and Lead

2.2.1. Physical properties

Zinc (Zn) is a silvery white metal, transition element of Group IIb of the periodic table having a melting point of 419.5 °C. Its boiling of 907 °C is found to be comparatively low when compared to other metals. For example, lead melts at 327 °C and boils at 1740 °C, while tin melts at 232 °C and boils at 2270 °C. This significant disparity has an effect on zinc's extraction and application technology. It is a fairly good heat and electricity conductor. With a density of 7.14 g/ml, zinc relatively dense (especially compared to aluminium which has a density of 2.702 g/ml). Pure cast zinc does not have good mechanical properties due to its low melting point (Hewitt and Wall, 2000).

Lead (Pb) is a naturally occurring element belonging to Periodic Table Group IVA. The widespread use of lead is mostly due to its low melting point and strong corrosion resistance. Lead is bluish-grey, dense, malleable, and ductile metal with low mechanical strength, limited elasticity, and very soft (Sarilar, 2019). Table 2.1 shows the physical properties of zinc and lead.

Table 2. 1. Chemical and physical properties of zinc and lead (Goodwin, 2018; Sarilar, 2019).

Property	Zn	Pb
Colour	Silvery-white	Bluish-grey
Melting point in °C	419.5 °C	327.5
Boiling point in C	907 °C	1750
Density g/cm^3	7.13	
ΔH_{fusion}/ kJ/mol		5.121
ΔH_{vap}/ kJ/mol		179.4
Young's Modulus / GPa		16.1
Thermal Conductivity (27 ^oC) / W $m^{-1}k^{-1}$		35.2
Electrical resistivity (20 ^oC) / Ohm.m		20.648 x 10^{-8}

2.2.2. Chemical properties

When zinc is exposed to normal atmospheric conditions (such as humidity and carbon dioxide), it creates a matt inert layer on the surface called a patina, which considerably slows down subsequent reactions. This said property, added with the fact that it is able to protect steel, is what makes the foundation of zinc's most lucrative market – iron and steel protection from rusting. This quality, together with the capacity to provide cathodic protection to steel, forms the foundation of zinc's most important market - the prevention of rusting in iron and steel by galvanizing.

The acidity present in the air inhibits the patina formation which accelerates attack on zinc, and this happens where an atmosphere has heavy contamination with sulphur dioxide. The zinc coatings made on steelwork in some industrial settings were adversely affected, but thanks to the relentless pollution control improvements, corrosion rates have subsided considerably in these areas (Hewitt and Wall, 2000).

Lead's chemical and electrochemical properties make it a very useful material in batteries, which happens to be one of the most popular applications of lead. Lead has excellent corrosion resistance in acidic media, excellent electromechanical properties in a variety of media, and chemical stability in both water and air. Lead is known to have two oxidation states which are Pb (II) and Pb (IV). It undergoes a chemical reaction with sulphur and halogens when exposed to high temperatures. It reacts with water in the presence of oxygen to give Pb (II):

$$Pb(s) \rightarrow Pb^{2+} + 2^{e-} \qquad (2.\ 1)$$

In air, an adherent lead carbonate film forms by a quick reaction in two stages:

- Firstly, a reaction between oxygen and metallic lead forming lead oxide,

- Secondly, a reaction between the lead oxide and CO_2 forming a lead carbonate protective film.

The metallic lead underneath this protective film is prevented from corrosion.

When lead reacts with sulphuric acid, a protective lead sulphate film is formed. Also, lead is insoluble in the acid which protects it from continuous attack. A similar reaction occurs with phosphoric and chromic acids.

As for strong alkalis, lead is readily attacked by them, with no protective film being formed (Anyadike, 2002).

2.3. Zinc and Lead Minerals

Sphalerite is the most common zinc mineral, also called zinc blende. This mineral is rarely contaminated by other base metals and is found in almost all deposits of zinc. Smithsonite, usually called calamine is a zinc carbonate, and are also mined today. Galena, and pyrite (which are sulphides of lead and iron respectively), are most of the time associated with zinc in considerable quantities, while in lesser quantities, elements like gold, silver, copper, mercury, arsenic, germanium, cadmium, tin, and antimony could be found. Gangue minerals include calcite and quartz. Zinc ore grade seldom goes beyond 20% (Hewitt and Wall, 2000).

More than 60 lead minerals are known, but the most common is galena (Anyadike, 2002; Tita and Kaya, 2021). Galena is generally associated with zinc, silver, bismuth, copper, arsenic, etc. Other lead ores which are commercially important include cerussite and anglesite. Galena, cerussite and anglesite account for more than 95% of the total lead mined (Tita and Kaya, 2021).

Lead and zinc are generally mined together, with silver, copper, and a host of other metals. Over the years it has shown that global demand for zinc is only increasing more, relative to that of

lead. It was recorded in 1959 that for every 1000 kg of lead mined, about 1300 kg of zinc was mined, then towards the end of the ‘90s the ratio had almost doubled for zinc, with 2400 kg of zinc for every 1000 kg of lead (Hewitt and Wall, 2000). Table 2.2 shows zinc and lead oxide minerals while igure 2.1 shows the location of major Pb-Zn minerals in the world.

Table 2. 2. Zinc and lead oxide minerals of economic value (reproduced from (Sarilar, 2019))

Mineral	Formula	Specific Gravity in g/cm^3	Zn/Pb content (%)
Sphalerite	ZnS		
Calamine	$Zn_4(OH)_2.Si_2O_7.OH$	3.4 - 3.5	67.3
Smithsonite	$ZnCO_3$	4.3 - 4.4	35
Clinohedrite	$Ca_2Zn_2(OH_2)Si_2O.7H_2O$	3.4 – 3.7	60
Zincite	ZnO	5.5	20
Willmenite	Zn_2SiO_4	3.9 – 4.2	74
Galena	PbS		
Cerussite	$PbCO_3$	6.5	77
Anglesite	$PbSO_4$	6.3	68.3
Wulfenite	$Pb(MnO_4)$	7.1	55.8
Crocoite	$PbCrO_4$	5.9	64.6
Pyromorphite	$Pb_5(PO_4)_3Cl$	6.5	75.8
Minettizite	$Pb_3(AsO_4)_3Cl$	7 – 7.2	69.5

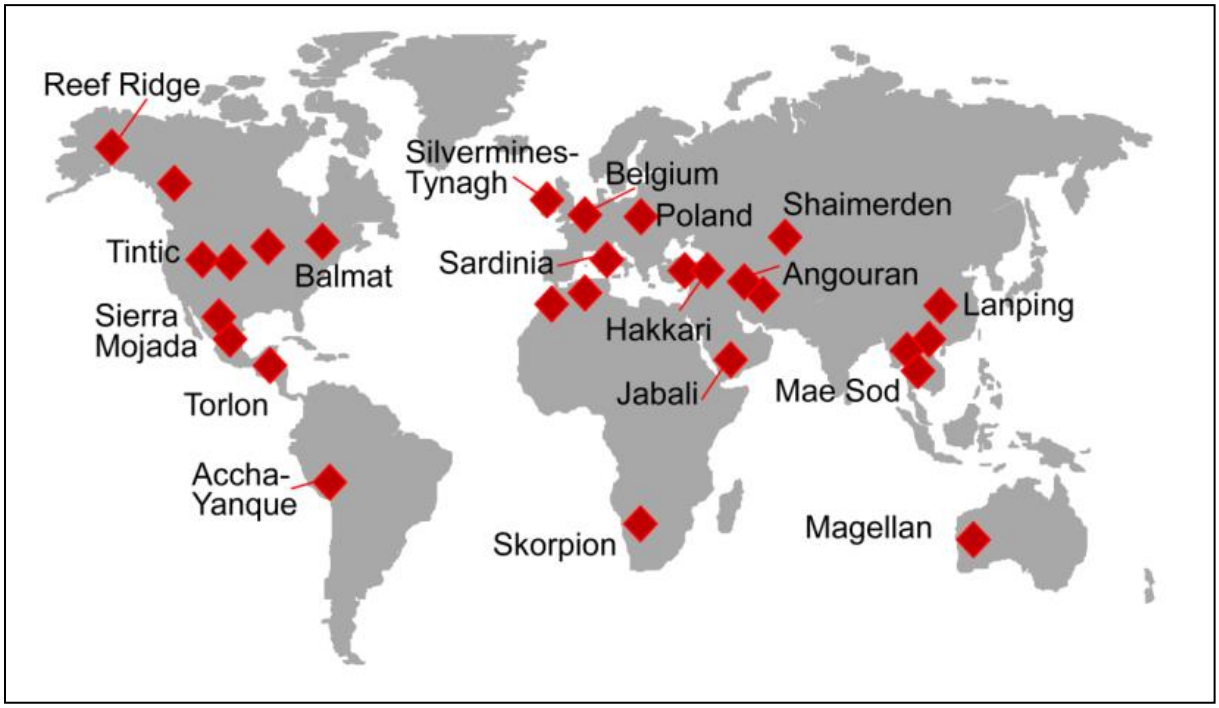


Figure 2. 1. Location of the major supergene nonsulphide Zn-Pb mineral deposits in the world (Mondillo, 2013)

2.4. World Lead-Zinc Reserves

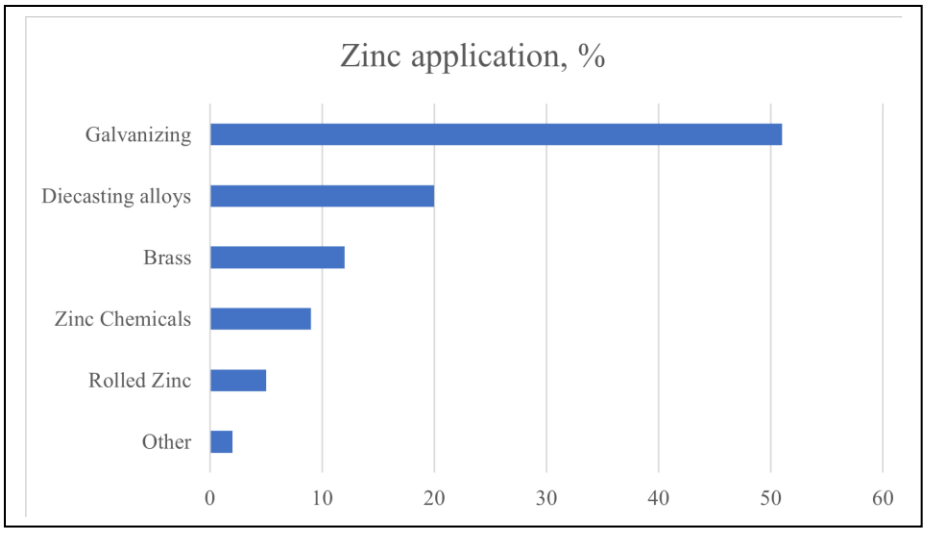
There exist five different occurrences of Pb-Zn ore deposits: massive sulphide, supergene non-sulphide, sedimentary exhalative, intrusion, and Mississippi valley. The cut-off grade in 2017 for zinc was 6% for underground mines, 4% for open mines, and 10 to 32% for oxidized zinc ores. In the same year, global zinc production in descending order was 37% for China, 11% for Peru, 7% for India, and 6% for Australia, USA and Mexico (Kaya et al., 2020). Table 2.3 shows the different deposit types, their ore reserves in different mines around the world, with their lead and zinc content.

Table 2. 3. Pb-Zn reserves around the world (Reproduced from (Hewitt and Wall, 2000))

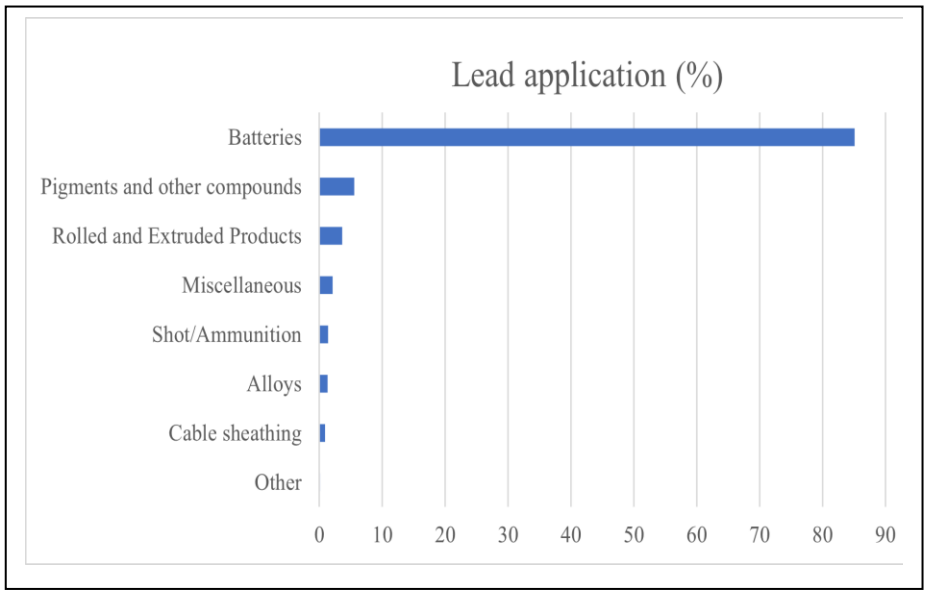
Deposit type	Mine	Ore reserve in Mt	Pb content (%)	Zn Content (%)
Sediment host type 1: Carbonate hosted	Navan, Ireland	70	2	10
	Polaris, Magnetic North Pole, Canada	25	4	14
	Black Angel, Greenland	9	5	14
	Pine Point, Northwest Terr., Canada	68	2.1	5.3
	Spain	30	1.5	14
Volcanogenic	Kidd Creek, Manitoba	170		
	Spanish Pyrite Belt, Spain	340	0.9	2.1
Sediment host type 2: Shale or clastic hosted	Dugald River, Queensland	22	2.5	14.4
	Hilton, Queensland	45	6.6	9.6
	Broken Hill, NSW, Australia	85	9.8	11.3
	Faro, Yukon Territory	75	3.7	5.6
	Meggen, Germany	63	1.3	10
	Rammelsberg Germany	30	0.9	19
	Mount Isa, Queensland	89	7.1	6.1
	Sullivan, BC, Canada	164	6.1	5.9
	Red Dog, Alaska	85	1.3	10

2.5. Areas of Application of Zinc and Lead

Within the world economy, both lead and zinc have significant applications. Zinc is primarily utilized in the automotive and construction industries for galvanizing steel, also in brass, bronze, zinc-based alloys, and chemicals production. As for lead, it is mostly utilized to produce lead-acid batteries, which are in high demand in the automobile industry (Mohr et al., 2018). Figure2.2 shows the different modes of application of zinc and lead, and their percentages.



(a)



(b)

Figure 2. 2. Areas of application of (a) zinc and (b) lead and their percentages, reproduced from (Reuter et al., 2015)

2.6. Primary Production of Lead-Zinc

Pb and Zn minerals are naturally occurring. The majority of zinc mines are underground (80%) while 8% accounts for open-pit. The remaining 12% is a combination of underground and open-pit. With respect to production volume, up to 64% of total zinc production comes from underground mines, 15% from open-pit mines, and 21% for a combination of underground and open-pit mine. Table 2.4 shows the global mine production from 2017 to March 2022.

Table 2. 4. Mine production from 2017 to March 2022 (Reproduced from (International Lead & Zinc Study Group, 2022)).

Mine Production (x 1000 tonnes)	2017	2018	2019	2020	2021	Jan to March 2021	Jan to March 2022	Dec-2021	Jan-2022	Feb-2022	Mar-2022
Lead	4602	4572	4678	4467	4572	1003	1023	405.9	340.5	322.6	360.1
Zinc	12683	12744	12814	12274	12783	3000	3063	1123.8	995.8	990.7	1076.7

Production of zinc from primary resources is difficult and quite costly (Kaya et al., 2020). Because the zinc ores generally contain only 5-15% Zn when mined, they are hardly used by smelters directly without concentration. This is why concentration processes are very instrumental, and the most commonly used method for zinc concentration is froth flotation. Concentration of Zn by froth flotation requires crushing, followed by grinding to ensure maximum liberation from other minerals in the ore. The comminution and flotation processes are preferably done at the mine to save transport costs. A Zn concentrate will contain approximately 55% Zn and around 25 – 30% sulphur. The ZnS need to be converted to ZnO, and this can be done by sintering or roasting. The zinc metal can be recovered from the zinc oxides by pyrometallurgy or hydrometallurgy (Kaya et al., 2020).

2.7. Recycling of Lead-Zinc from secondary resources

The importance of lead and zinc recycling from secondary resources is increasing over the past four decades. In the year 2000, more than half of Western World's total lead supply was from secondary resources, while in Europe, about half of the 1.6 million tonnes produced each year has gone through recycling. The majority of secondary lead is recycled from lead batteries. After lead is recovered from the batteries, the acid is drained, neutralised and carefully disposed of. Zinc on the other hand also, can be recycled without any loss of chemical or physical properties. A fraction of 9/25 of the world's zinc consumption is accounted for, by recycled zinc which is about 2.8

million tonnes. Zinc has a long-life span, so most of the produced zinc in the past is still being used. Also, most of the available recyclable zinc is being recycled currently (about 80%). Just the recycling of brass alone gives about 600 000 million tonnes of zinc yearly (Anyadike, 2002).

The most popular Pb – Zn secondaries include electric arc furnace dust (EAFD), galvanizing process wastes, hydrometallurgical residues (Waelz Oxide), lead-zinc mine tailings, and metallurgical wastes (Kaya et al., 2020).

2.8. Toxicity of Pb-Zn

One of the most significant issues that the world's Pb-Zn sector faces is environmental pollution management issues within guidelines while meeting ever-increasing global Pb-Zn demand. Pb particularly, over the years, is known to have negative effects on the health of workers and users. Also, it poses a high health risk to young children and infants, as its accumulation in the bloodstream will retard intellectual development, especially their cognitive and mental functions. Generally, guidelines have become very stringent in the last decade for the use of Pb and its levels in the environment (Mudd et al., 2017). Contamination levels detected in soils and regulatory guidelines regarding Pb, together with some toxic metals is shown in table 2.5.

Although zinc is not considered toxic, its natural association with lead, mercury, and cadmium has resulted in strict control regimes around the world. These include worker health and safety, air emissions, liquid effluent discharge, and solid waste disposal. As expected, these controls have always had a significant impact on how the zinc industry operates (Hewitt and Wall, 2000).

The majority of mine tailings are deposited in tailing ponds during mining operations. Disposing of these wastes without any proper treatment may result in toxic metal leakage and

subsequent migration into the environment. This could lead to hazards such as groundwater pollution, contamination of soil, and destruction of ecology. Mine tailing storage is becoming more and more of a global concern, as more of these tailings are being generated from mining activity. As a result, the management and treatment of mine tailings using appropriate and cost-effective strategies is indispensable (Nguyen et al., 2021).

Table 2. 5. Contamination levels detected in soils and regulatory guidelines regarding some toxic metals (Nguyen et al., 2021)

Metal	Pb	Zn	Cd	Cr	Co	Hg	Cu	Ni	Sb	As
Contamination range (mg/kg)	69000	5000	345	700 - 1500	120 - 154	1800	214	250 - 26000	1081	1000 - 3000
Guideline values from the EU (mg/kg)	200	250	10	200	100	2	150	100	10	50

Another serious challenge during Pb-Zn mining is acid mine drainage or acid and metalliferous drainage (AMD) where there is exposure of sulphides to the environment, leading to weathering, oxidation, and formation of sulphuric acid, which in turn leaches out heavy metals and some salts. Areas like the Zeehan Pb-Zn-Ag field, the Rosebery Pb-Zn-Ag-Cu-Au mine in Australia, the Iberian Pyrite belt in Portugal, all have had AMD issues over the years (Mudd et al., 2017).

2.9. Lead-Zinc Recovery Methods

Generally, the three recovery methods which exist are pyrometallurgical, hydrometallurgical, and bioleaching (Deshpande et al., 2018). The methods involved in pyrometallurgy include smelting, sintering, melting, and dossing. Due to exhaustion of high-grade ores, the use of pyrometallurgy has greatly declined due to higher cost, and new processes are

being introduced for metal recovery from low-grade ores. As for hydrometallurgy, the use of chemical reagents such as acids, bases, chelating agents are being employed to recover the metal. Bioleaching involves microbial oxidation, or the leaching of metals by products of microbial metabolism (Deshpande et al., 2018). Only hydrometallurgical and bio-hydrometallurgical methods will be discussed in this section.

2.9.1. Hydrometallurgical Methods

Hydrometallurgy is the main aqueous method used metallic extraction from their ores or wastes, and from the name hydrometallurgy, "hydro" means water, while metallurgy refers to metallic production (Free, 2013). Hydrometallurgy can be traced as far back as the alchemist era, but modern hydrometallurgy started towards the end of the 19^{th} century with the MacArthur-Forest process for gold, and the Bayer process for alumina. Later on, solvent extraction and ion exchange emerged, due to the growth of the nuclear industry during WWII. Subsequently, pressure leaching came about, for the treatment of sulphide ores. As ore grade keeps reducing, and as reserves continue depleting, hydrometallurgy plays an important role in the extraction of base metals (Jia et al., 2020).

The first stage of hydrometallurgy is generally leaching (Faraji et al., 2020) which could be divided into several types, depending on the mode of operation: heap leaching, in-situ leaching, dump leaching, agitated leaching, and vat leaching (Sarilar, 2019), and the reagents vary with respect to the ore characteristics. In Hydrometallurgy, an important factor which is considered during the leaching process is the leaching kinetics. Leaching kinetics plays a vital role in metal extraction, and is highly related to the profitability and the engineering designs (Faraji et al., 2020; Ghasemi and Azizi, 2018). Faraji et al., (2020) defined kinetics as *"a tool for the investigation of chemical reaction rates and comprehending the way various processes are being affected"* (Faraji et al., 2020), and the popular used models for investigating the kinetics of processes are the progressive conversion model (PCM) and the shrinking core model (SCM). With respect to NaOH,

the leaching process kinetics is as such: 1) Transportation of NaOH from the solution the surface of the particle, 2) Diffusion of NaOH from particle surface to the unreacted core, 3) NaOH – oxide ore reaction on unreacted core, 4) Diffusion of NaOH – oxide reaction product from core to particle surface, and 5) Transportation of the reaction product from particle surface to the solution (Ghasemi and Azizi, 2018)

Leaching is done with a vast number of reagents: acids (organic and inorganic), alkali, chelating agents, thiosulphate, acetate, water, etc. In this section we will only do a review on alkaline (NaOH) leaching and organic acid and chelating agent (EDTA) leaching.

2.9.1.1. Alkaline NaOH leaching

Sodium hydroxide is an inorganic compound having the chemical formula NaOH. It is also called lye or caustic soda, and an ionic compound white in colour, made up of sodium cations (Na^+) and hydroxide anions (OH^-). NaOH is a strong alkali that can cause severe chemical burns and is capable of decomposing proteins at room temperature. It is highly soluble in water, and the reaction between solid NaOH and water is highly exothermic, meaning much heat is liberated. Figure 2.3 shows the structure of NaOH. Aqueous NaOH is known for its use in hydrometallurgy, for the dissolution of minerals of some heavy metals like Zn, Pb, Cu, Fe, Ni, Co, Mn, Al, Hg and Cd

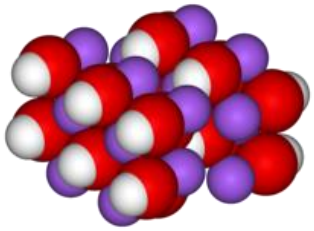


Figure 2. 3. NaOH chemical structure

The alkaline leaching for Pb and Zn extraction from oxidized ores or wastes is seen to be simple, easily operatable, and cost-effective. Also, impurities such as Fe, Ca, Mg, Al, Cu, Co, Cd,

Ni, do not dissolve in alkaline medium, which make separation of target metal from impurity easier (Chenglong and Youcai, 2009), as well as a considerably lower consumption of electricity in EW, compared to acidic EW (Youcai and Stanforth, 2001). The specific energy needed for the electrolysis of Zn in alkaline leach solution is between 2.4–2.6 kWh/kg, while about 3.3 kWh/kg is needed in the conventional electrolysis of Zn in acidic sulphate electrolytes. Another advantage is the recyclability of NaOH after most of the Zn has been electrowon (Zhao and Stanforth, 2000). NaOH being able to dissolve both Zn and Pb at the same time serves as an advantage because multi-step leaching will not be required to individually extract the Zn and Pb, leading to a considerably reduced leaching agent consumption.

The dissolution of cerussite and smithsonite in NaOH can be described as shown in Equations 2.2 and 2.3 (Ghasemi and Azizi, 2018).

$$ZnCO_{3(s)} + 4OH^-_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \quad (2.2)$$

$$PbCO_{3(s)} + 4OH^-_{(aq)} \rightarrow Pb(OH)_4^{2-}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \quad (2.3)$$

The use of NaOH as leaching agent in the recovery of Zn and Pb from low-grade ores and from waste, has been observed severally in the literature. Low-grade smithsonite was leached by Zhao and Stanforth (2000) using 5M $NaOH_{(aq)}$ at almost boiling point temperature yielding more than 85% Zn extraction (Zhao and Stanforth, 2000). Also, alkaline leaching by NaOH, for the co-leaching of Pb and Zn from a low-grade mine tailing was carried out by Ghasemi and Azizi (2018). At 4M NaOH, 70 ^oC, 500 rpm stirring speed, and L/S ratio of 20, they obtained 81% and 64% Zn and Pb dissolutions respectively (Ghasemi and Azizi, 2018).

A very important advantage of using NaOH is that it does not dissolve iron. Iron, which is generally abundant in several ores and wastes, poses an issue as a major impurity in the material. Because of this, a couple of purification steps need to be employed to separate it from the desired material, but using NaOH eliminates all these steps, as it is unable to dissolve iron, so the iron can be easily filtered out with the residue (Hussaini et al., 2021b)

2.9.1.2. Organic Acid EDTA leaching

Ethylenediaminetetraacetic acid (EDTA) also called edetic acid, is an aminopolycarboxylic acid which is white in colour, having a molecular mass of 292,24 g/mol and a density of 0.86 g/cm^3. The formula of EDTA is $[CH_2N(CH_2CO_2H)_2]_2$ or $C_{10}H_{16}N_2O_8$. It has a very low water solubility, and it is not soluble in common organic solvents. It is a carboxylic acid, a lead chelator, as well as an anti-coagulant. EDTA is stable and can only be chemically attacked by very strong oxidants. When EDTA combines with metals, it forms chelates and the stability of these chelates are arranged as such: $Na^+ < Ca^{2+} < Fe^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+} < Pb^{2+} < Fe^{3+}$. EDTA is produced as salts, such as disodium EDTA, tetrasodium EDTA, and sodium calcium edetate. Figure 2.4 shows the structure and chelation of EDTA.

EDTA has advantages such as low biodegradability, availability of appropriate techniques for recycling, high efficiency in metal removal, less environmental impact compared to other reagents, such as soil microorganism and enzyme activity. EDTA is also a relatively cheap chemical sold around 1.5 Euro/kg, and easily recyclable. EDTA is greatly used for remediation of contaminated soils.

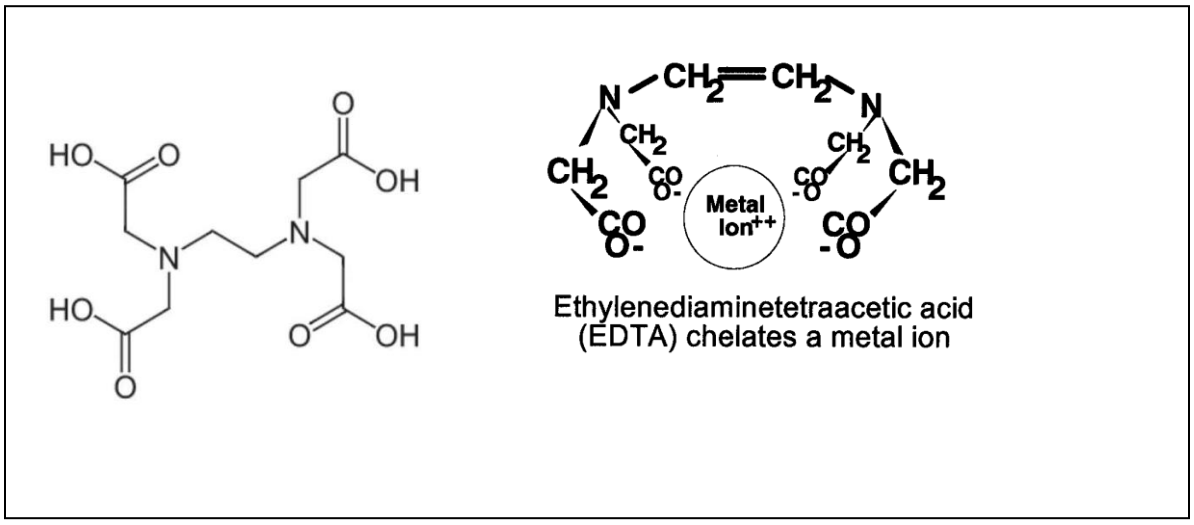


Figure 2. 4. (a) Chemical structure of ETDA and (b) molecular structure showing chelation

2.9.2. Bio-Hydrometallurgical Methods

Biohydrometallurgy is a relatively new development in the mining sector, in which microorganisms are used to improve on metal leaching. Biohydrometallurgy is the use of microorganisms to convert insoluble metals in ores or waste into soluble forms. The microorganisms are used to extract metals from concentrates, ores, and waste, in aqueous solutions. When compared to traditional chemical/heat treatment methods, microbial extraction and recovery of metals has gotten a lot of attention in the last three decades because of its relative simplicity, eco-friendly operation, and cheap capital requirement (Johnson, 2013). Bioleaching has also been used commercially in a number of cases (Sethurajan, 2016).

Currently, there is much interest in sulphide mineral bioleaching, especially for zinc and copper sulphides, but for galena, very little attention has been paid due to the fact that galena oxidises to insoluble $PbSO_4$ in a sulphate system. This lead sulphate formation is a major issue in

lead recovery, either from bacterial or ferric sulphate leaching, since it inhibits lead recovery, and is also environmentally hazardous owing to its higher solubility over galena (Baba et al., 2011)

For the successful recovery of metals from metallurgical wastes, understanding and knowledge of metal-microbe interactions as well as bioleaching mechanisms are essential (Sethurajan, 2016). Figure 2.5 demonstrates the metal-microbe interaction.

2.9.2.1. Microbe - metal interactions

For the successful recovery of metals from metallurgical wastes, understanding metal-microbe interactions as well as bioleaching mechanisms are essential. Microorganisms such as bacteria and fungi have the ability to extract metals from soils, ores, and wastes. The process(es) involved that permit this extraction ability include: (Sethurajan, 2016):

- Specific interactions at cell wall
- Non-specific interactions outside the cell wall
- Bioaccumulation
- Secretion of chemicals by microbes which form a complex with the metals (metallo-chemical complex)
- Metal precipitation by bacterial metabolites
- Volatilization of metals.

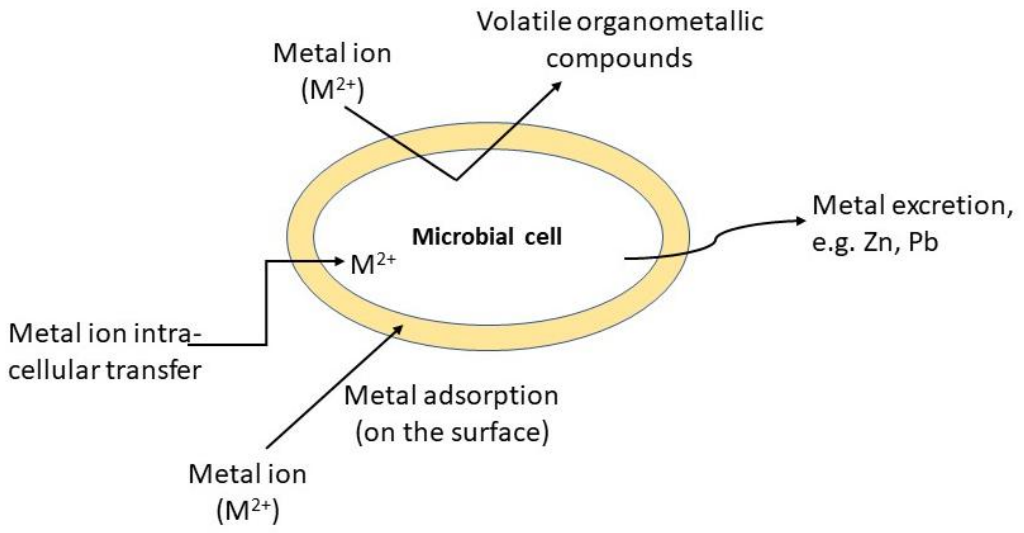


Figure 2. 5. Different metal-microbe interactions occuring during bioleaching (reproduced from Sethurajan, 2016)

2.9.2.2. Mechanisms

The bioleaching mechanisms can be divided into three : Contact/Direct mechanism, Indirect mechanism, and Cooperative mechanism of bioleaching (Deshpande et al., 2018).

- **Direct mechanisms:**

In direct/contact mechanisms, sulphide minerals are oxidized by microbes through direct attack on the surface of the mineral, and potentially by the cell's specific oxidise system, which oxidizes the sulphide minerals directly. The simultaneous production of hydrogen ions causes a drop in the pH of the surrounding system and a rise in the redox potential, culminating in soluble sulphate formation. However, because the bacterial cell wall and the sulphide molecular layer are difficult to separate, this method is better suited to contact leaching (Gao et al., 2021). The following equation (2.4) can be used to express this:

$$MS + 2\,O_2 \xrightarrow{A.ferrooxidans;A.thiooxidans} MSO_4 \quad (2.4)$$

- **Indirect Mechanisms**

The metabolites of Fe or S/Fe and S – oxidizing microbes are employed in redox reactions with sulphide minerals resulting in the formation of a redox circulatory system, and the pH of the surrounding system is lowered to about 2.0, by the sulphuric acid produced. This considerably aids heavy metal dissolution. Equation (2.5) summarises indirect mechanisms, while using pyrite to illustrate (Gao et al., 2021):

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{bacterium} 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (2.5)$$

- **Cooperative bioleaching Mechanisms**

Here, a cooperation exists between microorganisms that are attached to the mineral surface, and the free bacteria present in the solution. The microbes attached to the mineral surface release chemicals into the solution which act as the source of energy for the free microorganisms in solution. (Deshpande et al., 2018)

The mechanisms that exist in heterotrophic bacteria are different, since they need organic carbon as their energy and carbon source. The mechanisms include bioreduction, acidification, ligand production/complexolysis, and alkalinization (Jain and Sharma, 2004).

2.9.2.3. Microorganisms used in Bioleaching

Bioleaching microbes are classified as chemolithotrophs or chemoorganotrophs based on their requirements of metabolism (energy source). Chemolithotrophs (acidophiles) thrive at low pH and are given this name for their capacity to use inorganic materials like sulphur and iron, as a

source of energy. Chemolithotrophs are classified into three groups based on their preferred ideal growth temperatures, namely: mesophilic, moderately thermophilic, and thermophilic. Bacteria make up the majority of mesophiles and moderate thermophiles, while archaea make up the majority of thermophiles. Chemolithotrophs can also be divided into chemolithotrophic autotrophs and chemolithotrophic heterotrophs: autotrophs use CO_2 as the source of carbon, while heterotrophs use organic carbon as the source of carbon, along with the inorganic source of energy. Organotrophs get their energy from organic carbon. Organotrophs include fungi and cynogenic microorganisms, which use organic carbon, and they are both classified as chemoorganoheterotrophs since they are thought to use organic carbon as a carbon source (Srichandan et al., 2019). Table 2.6 shows the different microorganisms used in bioleaching.

a) Chemolithotrophs

As mentioned earlier, these bioleaching microbes thrive at low pH (around pH of 2), and are made up of mesophilic, moderately thermophilic, and thermophilic which are differentiated mainly by their optimum growth temperature.

- **Mesophiles**

These are chemolithotrophs that have optimum temperature growth range between 28–37°C (Chen et al., 2015). Because they use inorganic matter as their energy source, and CO_2 as their source of carbon, they are considered chemolithoautotrophs. Examples of mesophilic leaching bacteria include *Acidithiobacillus thiooxidans, Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans, Leptospirillum ferriphilum*.

Mesophiles like *Leptospirillum ferriphilum* and *Leptospirillum ferrooxidans* grow in an iron (II) oxidizing environment (Olson et al., 2003). It is also important to note that the first isolated and the most extensively studied bacterium for the bioleaching of ores and wastes is *Acidithiobacillus ferrooxidans* (Gao et al., 2021; Giaveno et al., 2007), which is an iron- and a sulfur-oxidizing acidophile.

- **Moderate thermophiles**

Compared to the mesophiles, moderate thermophiles can grow at higher temperatures ranging from 40 to 60 °C. Bioleaching moderate thermophiles are generally eubacteria, and they include: *Acidimicrobium sp., Sulfobacillus sp. Ferromicrobium sp., Sulfobacillus thermosulfidooxidans , and Acidithiobacillus caldus.*

- **Thermophiles**

These chemolithotrophs belong to archea, and operate best at temperatures between 60 and 80 °C. Examples include Sulfolobales (such as *Sulfolobus, Acidianus, Sulfurisphaera, and Metallosphaera*). The Sulfolobus sp. includes *Sulfolobus metallicus, Sulfolobus Sulfurisphaera, Sulfolobus acidocaldarius, Sulfolobus brierley, Sulfolobus solfataricus, and Sulfolobus Ambioalous* (Srichandan et al., 2019).

b) Organotrophs

These are bioleaching microbes that consist of fungi and cyanogenic microbes. With organic carbon as their energy source, these microbes produce substances that carry out the bioleaching process: fungal bioleachers produce organic acid, and the cyanogenic bioleachers produce hydrogen cyanide. Examples of fungal bioleachers include *Aspergillius niger, Penicillium chrysogenum*, *Aspergillius flavus*, and *Penicillium simplicissimum*. Optimum temperature for bioleaching using these fungi is around room temperature (25-35 °C), and pH between 3.0–7.0 (Amiri et al., 2011). Examples of cyanogenic bacteria include *Pseudomonas fluorescens*, *Pseudomonas putida, Pseudomonas aeruginosa*, *Chromobacterium violaceum, Pseudomonas chlorophis, Bacillus megaterium*, *Escherichia coli*, and *Pseudomonas aureofaciens*. Cyanogenic bioleaching is generally carried out between 25 and 35 °C, and pH of 7.0 to 11.0 (Valix, 2017)

Table 2. 6. The micro-organisms used in bioleaching (Nguyen et al., 2021)

Micro-organism	Metabolism type	Temperature, ^{o}C
Archea		
Acidianus brierleyi	heterotroph	45 - 75
Acidianus infernus	heterotroph	n.d
Ferroplasma acidiphilum	autotroph	15 - 45
Metallosphaera sedula	autotroph	Extreme thermophilic
Sulfolobus acidocaldarius	autotroph	55 - 85
Sulfolobus solfataricus	autotroph	Extreme thermophilic
Sulfolobus thermosulfidooxidans	autotroph	Extreme thermophilic
Bacteria		
Acidithiobacillus caldus	autotroph	45
Acidithiobacillus ferrooxidans	autotroph	28 -35
Acidithiobacillus thiooxidans	autotroph	Oct-37
Acidiphilium cryptum	heterotroph	mesophilic
Bacillus megaterium	heterotroph	n.d
Leptospirillum ferrooxidans	autotroph	30
Leptospirillum thermoferrooxidans	autotroph	45 - 50
Pseudomonas putida	heterotroph	n.d
Sulfobacillus thermosulfidooxidans	autotroph	50
Thiobacillus acidophilus	mixotroph	25 - 30
Thiobacillus albertis	autotroph	28 - 30
Thiobacillus thioparus	autotroph	11-25
Fungi		
Aspergillus awamori	heterotroph	28
Aspergillus fumigatus	heterotroph	n.d
Aspergillus niger	heterotroph	30
Penicillum chrysogenum	heterotroph	28
Penicillum funiculosun	heterotroph	n.d
Trichoderma lignorum	heterotroph	24-26
Yeasts		
Candida lipolytica	heterotroph	30
Saccaromyces cerevisiae	heterotroph	28

n.d: no dat

2.9.2.4. Leptospirillum ferrooxidans

Leptospirillum ferrooxidans is a gram-negative, aerobic, non-spore-forming, acidophilic chemolithotrophic microbe that thrives in a pH range of 1.5 to 4 on an iron-rich mineral media (Deshpande et al., 2018). *L. ferrooxidans* and Thiobacillus thiooxidans are often utilized in biooxidation procedures for copper and zinc-lead ore treatment (Rawlings et al., 1999a). A native *L. ferrooxidans* strain was used to bioleach complicated, low-grade sulphide ores, (Giaveno et al., 2007) but after comparing it to *Acidithiobacillus ferrooxidans* bioleaching, it was discovered that zinc recovery was higher with the former than the latter. It was concluded from here that even in the absence of sulphur oxidizers, the *Leptospirillum ferrooxidans* strain was particularly efficient at digesting complex sulphides (Giaveno et al., 2007).

The metabolic activity of *L. ferrooxidans*, which is quite similar to that of the most extensively studied and isolated iron-oxidizing microbe, *Acidithiobacillus ferrooxidans,* requires the oxidation of ferrous iron utilizing as electron acceptor, molecular oxygen (Stoytcheva et al., 2009). The reaction is shown in Eq. 6:

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{L.ferrooxidans} 4Fe^{3+} + 2H_2O \quad (2.6)$$

In bioleaching, L. ferrooxidans is applied in commercial biooxidation and bioleaching of sulphide ores such as pyrite, and other similar ores and wastes. (Rawlings et al., 1999b)

- **Comparison of *L. ferrooxidans* with *A. ferrooxidans***

Acidithiobacillus ferrooxidans is the first isolated and the most extensively studied bacterium for the bioleaching of ores and wastes (Gao et al., 2021; Giaveno et al., 2007), which is

an iron- and a sulfur-oxidizing acidophile. Furthermore, there is adequate data to suggest that *A. ferrooxidans* thrives in environments with higher concentrations of ferrous ion. However, *L. ferrooxidans* has a 10 times greater inhibitory concentration of ferric ion, compared to *A. ferrooxidans*, as well as a strong tolerance for acid may promote its growth in acidic biotopes (Giaveno et al., 2007; Stoytcheva et al., 2009). As a result, *L. ferrooxidans* is likely to be just as beneficial as *A. ferrooxidans* in the indirect leaching mechanisms (Giaveno et al., 2007). Another advantage of *L. ferrooxidans* over *A. ferrooxidans* is its abundance in several environments, and it appears to be the most abundant microbe in continuous-flow bio-oxidation tanks in industry (Giaveno et al., 2007). The numerical dominance of *L. ferrooxidans* has also been indicated by Fairview, in South Africa. (Dew et al., 1997) Also, *L. ferrooxidans* is strictly an autotroph, using only Fe^{2+} as its only energy source, whereas *A. ferrooxidans* grows in both sulphur media and ferrous iron (Stoytcheva et al., 2009).

Bioleaching has several notable advantages, including low requirement of power, environmental friendliness, cost-effectiveness, ability to treat low grade ores or wastes, and affordability and ease of use of equipment. The common disadvantages include poor treatment with primary sulphides, the need for large area, low rates of reaction, as well as longer operation time (Deshpande et al., 2018).

2.9.2.5. Reasons for Biohydrometallurgy

It is a promising and environmentally friendly option, especially for the treatment of low grade ores, as well as complex ores. The fact that bio-hydrometallurgical processes are generally inexpensive, involve little energy usage, and are environmentally friendly has sparked a rise of interest in them recently. By utilizing the solubilizing and metal accumulating capabilities of microbes, biohydrometallurgy provides a simple and effective process for extracting rich metals such as copper, zinc, gold, nickel, uranium, cobalt, as well as many others from low-grade ores, from rocks, and from waste materials. Microbial leaching offers some promise for rehabilitation

of mining sites, treatment of metal-containing waste products, and detoxification of sewage sludge, in addition to its industrial application in raw material supply. It's evolved into a cutting-edge multidisciplinary technology that incorporates chemistry, microbiology, and chemical engineering, and process engineering (Jain and Sharma, 2004)

2.9.2.6. Factors that Affect Biological Leaching

Factors that affect bioleaching include microorganismal characteristics, and physicochemical parameters such as temperature, pH and redox potential, oxygen and carbon dioxide supply, stirring rate, nutritional composition of the medium, salinity, pulp density, and others. According to (Nguyen et al., 2021), the most important factors that affect the process of bioleaching are the microorganisms used and the mineralogical and chemical composition of the material. Now, to obtain maximum yields of the metal extraction, the optimum growth conditions for that particular microbe must be determined such as pH, temperature, nutrients, water, O_2 and CO_2 concentrations, mineral substrate, etc. pH control and temperature control are also very pertinent during bioleaching (Nguyen et al., 2021). Figure 2.6 shows the flowsheet of metal recovery by bioleaching.

2.9.2.7. Applications of Bioleaching (to various solid wastes)

Metal extraction from low-grade ores and concentrates: Bioleaching is effective and simple for metal extraction from mineral concentrates and low grade ores, especially owing to the fast depletion of many commercial ores and reserves, as well as uneven geographical distribution of these reserves.

Beneficiation of coals and ores: Biobeneficiation is a selective type of bioleaching where the undesirable mineral of the ore is being dissolved by microbial action, hence enhancing the ore's quality. Biobeneficiation of several ores is still being developed. (Jain and Sharma, 2004)

Recovery of metals from waste materials: As time goes on ore reserves are slowly getting exhausted, and to reduce this overdependence, wastes are being considered as source of metals. Bioleaching stands as a technology to recover these metals from waste streams. These metals include Zn, Pb, Cu, Fe, etc.

Heavy metal detoxification: Huge amounts of toxic materials are being exposed to the environment, and heavy pollutants are being sent to the atmosphere, worse still, these pollutants making their way into human food chains. Biobeneficiation plays a role in solubilizing toxic materials from solids and waste (Jain and Sharma, 2004).

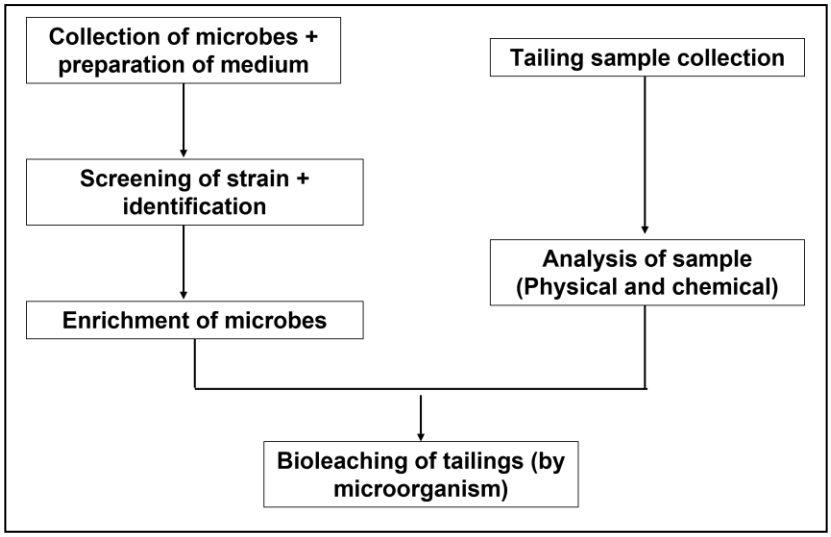


Figure 2. 6. Flowsheet of metal recovery by bioleaching (Gao et al., 2021)

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. For Chemical Leaching

3.1.1.1. Collection and preparation of Pb-Zn oxide flotation tailing sample

The flotation tailing samples were collected from Oreks Mine tailing dam in Yahyalı-Kayseri, Turkey. About 100 kg representative sample was collected from the tailing dam to the Mineral Processing laboratory of ESOGU University, and to facilitate characterization and laboratory experiments, the representative samples were prepared. This flotation tailing is very fine, around 50% -13 μm, containing major minerals such as smithsonite ($ZnCO_3$), cerussite ($PbCO_3$), goethite (FeOOH) and corkite ($PbFe_3(PO_4)(SO_4)(OH)_6$), with minor gangue minerals such as calcite and quartz.

For the deagglomeration of the tailing mass, roll crushing was employed, followed by its drying by spreading for one week on the floor at room temperature. Caking occurred in some of them after drying, but simply squeezing with the hand was enough to break the lumps. After drying, most of the sample passed through a 3.175 mm (8 mesh) sieve of a Russel sieving machine. The oversize fraction was ground in a laboratory ball mill for 5 minutes (6.7 kg of balls with 3 kg of sample). The mixing and homogenization of all the ground samples was thoroughly done and the sample kept in closed buckets, ready for the proceeding experiments. All these activities took place in our Mineral Processing laboratory at ESOGU. Figure 3.1 shows the tailing dam area (a), and surface (b), and the roll crushed flotation tailing (c).

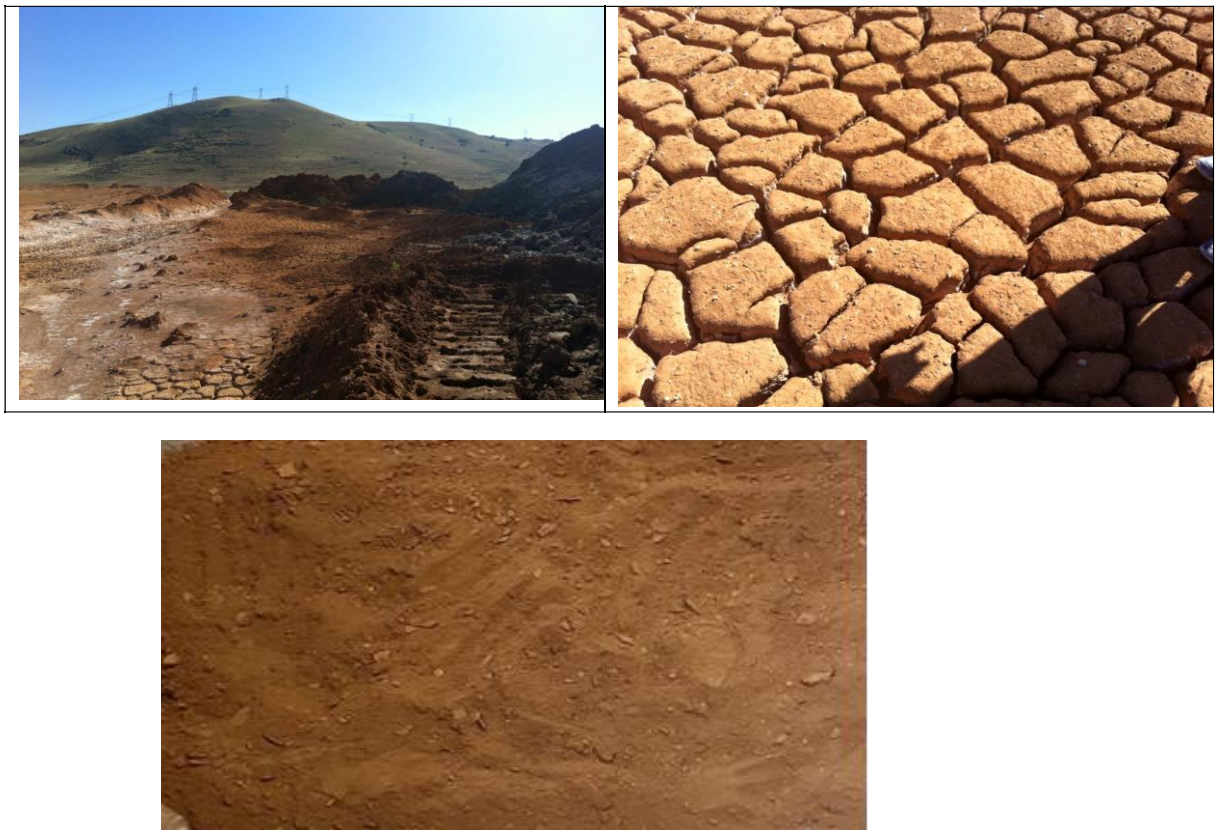


Figure 3. 1. Oreks tailing dam (a) area and (b) surface views and (c) drying of the roll crushed flotation tailing.

3.1.1.2. Characterization of the Pb-Zn oxide flotation tailing sample

a) Particle Size Distribution

Malvern Inst. Mastersizer 2000 at our laboratory was the device used to determine the particle size distribution of the tailing sample. Table 1 summarizes particle size distribution of the sample used. D_{10} is 1 µm; d_{50} is 13 µm; d_{80} is 57 µm; and d_{90} is 100 µm. The diagram on figure 3.2 was generated from this device, and the graph from this result analysis report showed that almost one half of the sample is <10 µm, therefore there was no need for further grinding as the

flotation tailings are very fine. For leaching processes, as the fineness of the particles increases, the leaching efficiency increases, owing to the fact that these fine particles may aggregate and reduce the problem of dispersion during the leaching process. It is difficult to carry out pre-concentration processes on this very fine sample. The particle size distribution is shown in table 3.1.

Table 3. 1. Particle size distribution of the tailing sample

Particle size distribution	
d_{10}	1 µm
d_{50}	13 µm
d_{80}	57 µm
d_{90}	100 µm

MALVERN INSTRUMENTS

MASTERSIZER 2000

Result Analysis Report

Sample Name: ESOGU No:1 - Average	**SOP Name:**	**Measured:** Measurement date and time : 25 Eylül 2018 Salı	
Sample Source & type:	**Measured by:** MasterSizer2000	**Analysed:** 25 Eylül 2018 Salı 15:32:11	
Sample bulk lot ref:	**Result Source:** Edited		
Particle Name: Default	**Accessory Name:** Hydro 2000MU (A)	**Analysis model:** General purpose	**Sensitivity:** Enhanced
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 8.16 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 1.258 %	**Result Emulation:** Off
Concentration: 0.0050 %Vol	**Span :** 7.756	**Uniformity:** 2.45	**Result units:** Volume
Specific Surface Area: 1.9 m²/g	**Surface Weighted Mean D[3,2]:** 3.159 um	**Vol. Weighted Mean D[4,3]:** 35.567 um	

d(0.1): 0.905 um d(0.5): 12.664 um D(0.80) : 56.79 µm d(0.9): 99.123 um

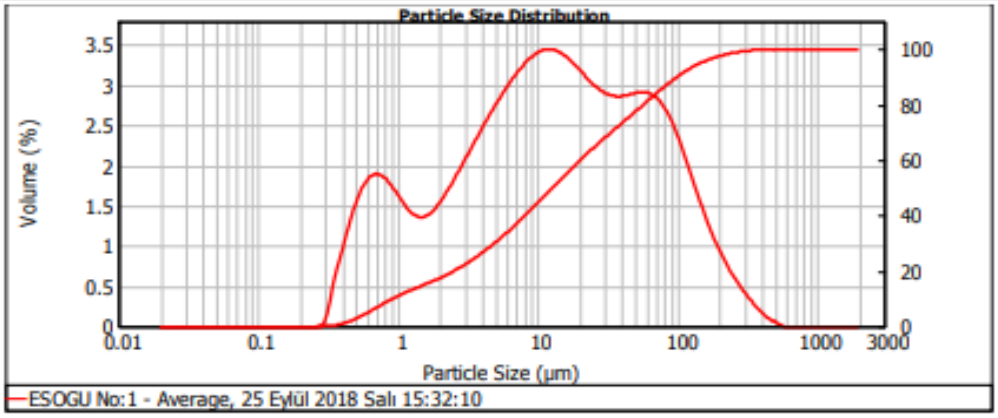


Figure 3. 2. Particle size distribution of flotation tailing sample.

b) XRF, XRD and ICP-AES Chemical and Mineralogical Analysis

The X-Ray Fluorescence (XRF) was carried out using Panalytical Zetium WDXRF. From the results of this analysis, it showed that the tailing sample contains zinc (7.12%), lead (6.77%), arsenic (6.12%), iron (24.39), quartz (12.6%). Traces of cobalt (0.049%) and cerium (0.31%) were also identified. The important and significant base metals from these results were smithsonite and

cerussite. The main impurities were identified as Fe_2O_3, SiO_2, As_2O_3, CaO and Al_2O_3 while the gangue minerals were found to be quartz, goethite, kaolinite, and calcite. Table 3.2 shows the XRF results for the major oxide percentages in the flotation tailing sample.

Table 3.2. XRF results of the tailing sample

Report name	**Result, %**	**Conversion factor**	**% Metal**
CuO	0.057	1.2518	0.046
ZnO	8.859	1.2448	7.12
PbO	7.297	1.0772	6.77
NiO	0.064	1.2725	0.05
As_2O_3	8.074	1.3203	6.12
CeO_2	0.380	1.2284	0.31
MnO	0.035	1.2912	0.026
SrO	0.036	1.1826	0.03
BaO	0.572	1.1165	0.51
Fe_2O_3	34.866	1.4297	24.39
P_2O_5	0.055	2.2916	0.024
SO_3	4.531	2.4972	1.81
Co_3O_4	0.066	1.3469	0.049
SiO_2	12.155	2.1392	5.68
Cl	0.126		0.126

Table 3.2. XRF results of the tailing sample (continued)

Report name	Result (%)	Conversion factor	% Metal
TiO_2	0.246	1.6681	0.15
Al_2O_3	3.873	1.8895	2.05
K_2O	0.657	1.2046	0.55
CaO	5.455	1.3992	3.9
Others	12.596		

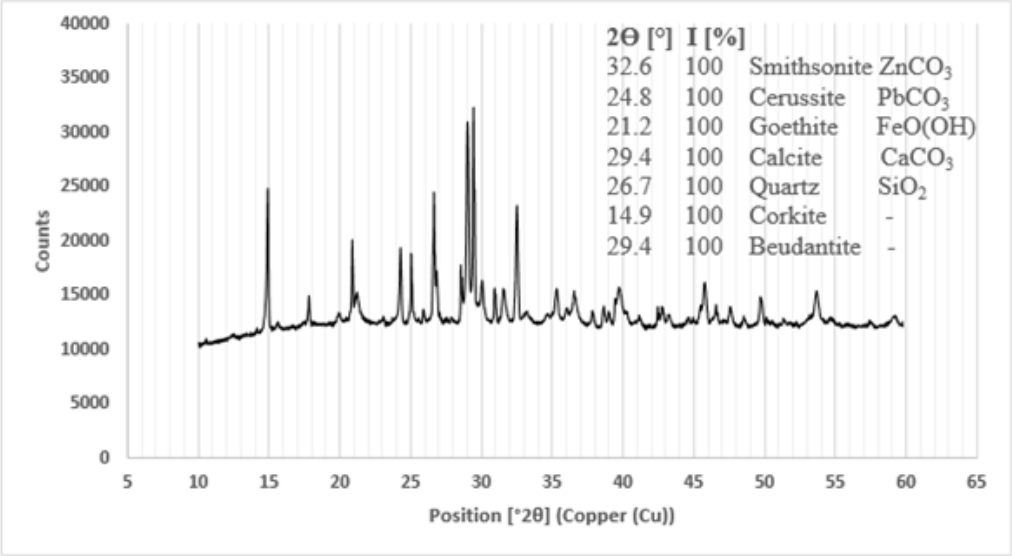


Figure 3. 3. XRD pattern of the Turkish sample

The ICP-AES analysis was carried out to examine the metal concentrations in the tailing sample. These results were considered throughout this research. The analysis showed that the sample is mainly made up of Pb, Zn, Fe and As. The Cu content was seen to be very low, while Ag content was seen to be 101ppm. There are some inconsistencies between the x-ray results and the ICP results. Table 3.3 shows the ICP-AES results of the sample.

Table 3. 3. ICP-AES results of flotation tailing sample

Method	**Analyte**	**Units**	**LOD**	**Results**
WEI-21	Recvd Wt.	Kg	0,02	**<0,02**
ME - ICP61	**Ag**	Ppm	0,5	**>100**
ME - ICP61	**Al**	%	0,01	**1,92**
ME - ICP61	**As**	Ppm	5	**>10000**
ME - ICP61	**Ba**	Ppm	10	**420**
ME - ICP61	**Be**	Ppm	0,5	**0,6**
ME - ICP61	**Bi**	Ppm	2	**<2**
ME - ICP61	**Ca**	%	0,01	**3,91**
ME - ICP61	**Cd**	Ppm	0,5	**245**
ME - ICP61	**Co**	Ppm	1	**<1**
ME - ICP61	**Cr**	Ppm	1	**63**
ME - ICP61	**Cu**	Ppm	1	**306**
ME - ICP61	**Fe**	%	0,01	**21,3**
ME - ICP61	**Ga**	Ppm	10	**10**
ME - ICP61	**K**	%	0,01	**0,66**
ME - ICP61	**La**	Ppm	10	**10**
ME - ICP61	**Mg**	%	0,01	**0,45**
ME - ICP61	**Mn**	Ppm	5	**763**
ME - ICP61	**Mo**	Ppm	1	**9**
ME - ICP61	**Na**	%	0,01	**0,49**

Table 3.3. ICP-AES results of flotation tailing sample (continued)

Method	**Analyte**	**Units**	**LOD**	**Results**
ME - ICP61	**Ni**	Ppm	1	**79**
ME - ICP61	**P**	Ppm	10	**280**
ME - ICP61	**Pb**	Ppm	2	**>10000**
ME - ICP61	**S**	%	0,01	**1,85**
ME - ICP61	**Sb**	Ppm	5	**279**
ME - ICP61	**Sc**	Ppm	1	**4**
ME - ICP61	**Sr**	Ppm	1	**367**
ME - ICP61	**Th**	Ppm	20	**<20**
ME - ICP61	**Ti**	%	0,01	**0,10**
ME - ICP61	**Tl**	Ppm	10	**20**
ME - ICP61	**U**	Ppm	10	**20**
ME - ICP61	**V**	Ppm	1	**43**
ME - ICP61	**W**	Ppm	10	**20**
ME - ICP61	**Zn**	Ppm	2	**>10000**
Ag – AA46	**Ag**	Ppm	1	**101**
Pb – AA46	**Pb**	%	0,001	**7,50**
Zn – AA46	**Zn**	%	0,001	**5,77**

c) TGA Analysis

The thermal characterization of this flotation tailing was determined by Thermogravimetric Analysis (TGA) or Differential Thermogravimetric Analysis (DTA), using Perkin Elmer Simultaneous Thermal Analyzer (STA) 8000 equipment at the ESOGU Central Laboratory. The thermal behaviour of the sample between 30 ^{o}C to 600 ^{o}C was sought and 23 mg of the sample was used at a linear heating rate of 10^{o}C/min in N_2 atmosphere. Figure 3.4. shows the thermogravimetric analysis results.

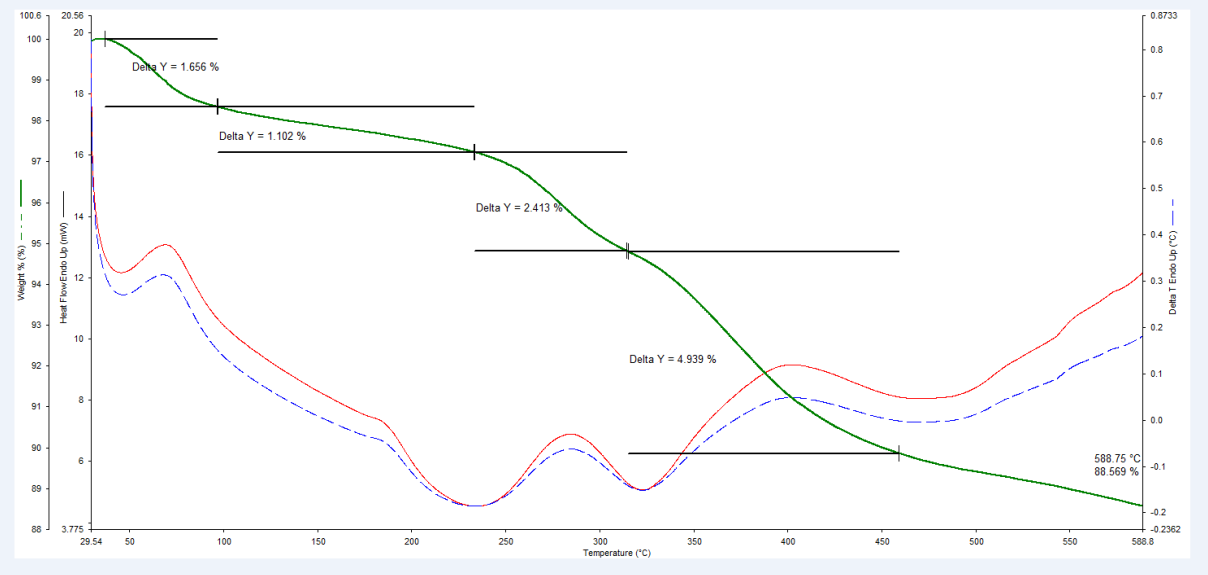
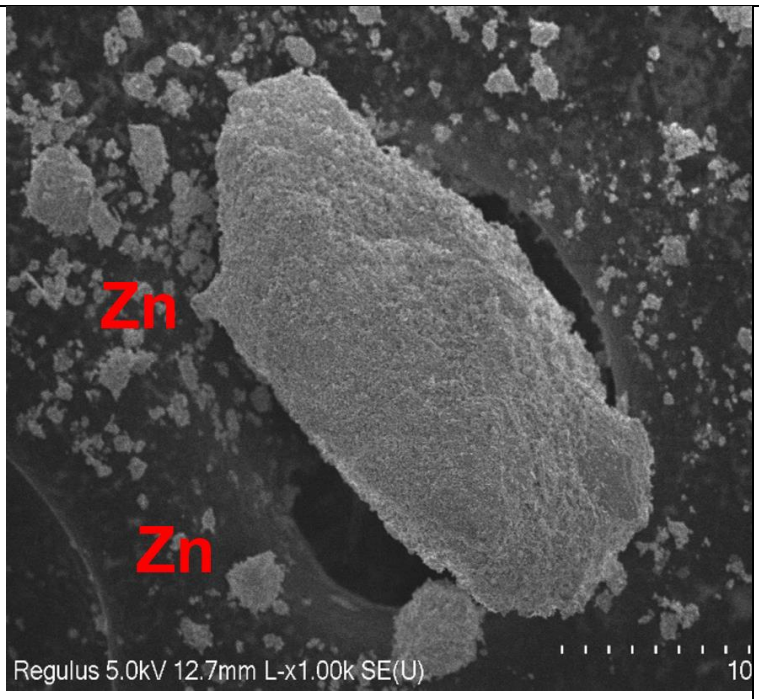


Figure 3. 4. TGA curves for tailing sample

The TGA results show three endothermic peaks. The first occurred between 50 and 100 ^{o}C, the second occurred around 275 ^{o}C, while the third occurred after 400 ^{o}C. Moisture content evaporation occurred until 100 ^{o}C, and the weight loss here was about 1.656%. Crystal water evaporation and dehydration occurs between 100 and 315 ^{o}C. Pb/Zn carbonate decomposition occurs after 400 ^{o}C when water has been lost from the compounds. Carbonate decomposition leads to the release of CO_2 causing oxidation of the metal oxides.

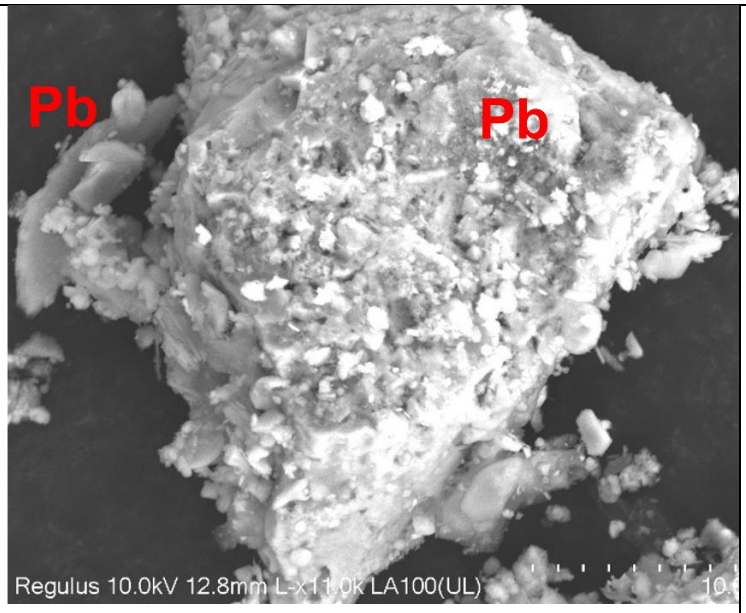
d) SEM-EDX Analyses

The SEM-EDX (Scanning Electron Microscopy and Energy Dispersive Spectrometry) method was used to detect the particle morphology and the surface composition of the flotation tailing. These analyses were performed using the Hitachi-Requlus 8230 SEM and Oxford instrument EDX at 5-10 kV, at ESOGU. These results showed that there were three distinct phases: the bright particles, the grey particles and the dark particles. The bright particles were seen to have Pb and O, identified as cerussite, the grey particles with Zn and O, identified as smithsonite, and the dark particles containing O, Ca, and Si, recognized to be likely calcite and quartz. Figure 3.5 (a) and (b) show the EDX area chemical analysis of the flotation tailing by Rietveld method.



(a)

Spectrum Label	Spectrum 6
C	8.01
O	39.22
Al	4.08
Si	5.10
S	1.66
K	0.90
Ca	2.01
Fe	**20.56**
Zn	**6.14**
As	**3.68**
Pb	**8.65**
Total	100.00



(b)

Spectrum Label	Spectrum 10
C	5.69
O	36.08
Al	1.56
Si	1.26
S	3.70
Fe	**22.75**
As	**7.56**
Pb	**21.40**
Total	100.00

Figure 3. 5. SEM-EDX anaylses of the flotation sample.

3.1.2. For Bioleaching

3.1.2.1. Collection and Preparation of Sulphide Precipitate Sample

The sulphide precipitate sample was collected after the selective precipitation of lead from the Pb-Zn pregnant leach solution (PLS). Filter papers (Whatman 1.70 mm in diameter) were used to collect the precipitates. The precipitate was a very black substance and after filtration, it was kept to stand for some minutes. The precipitate was then dried in an oven for a day and then the dried sample was scraped off the filter paper surfaces with a knife and spatula. This process was not an easy process because most of the dried precipitate remained stuck to the filter paper, resulting in huge sample losses. After the scraping, the sample was ground manually using a ceramic mortar and pestle. Manual grinding was chosen due to the small quantity of the sample and an attempt to limit sample loss as much as possible. A total of about 80 grams of the sample was collected after the scraping and grinding activities and placed in a sample bag, ready for the

subsequent experiments. Figure 3.6 shows the (a) dried precipitate on filter paper, and (b) set-up for grinding.



Figure 3. 6. (a) dried precipitate after filtration, and (b) set-up for manual grinding of the dried precipitate.

3.1.2.2. Characterization of Sulphide Precipitate Sample

a) Particle Size Distribution

The particle size distribution was determined using the Malvern Inst. Mastersizer 2000, at the Mineral Processing Laboratory of ESOGU. The d_{80} was seen to be 15.83 µm, while there was a great disparity in the particle size distribution, as a great chunk of the sample was very fine, which could be explained by the fact that this sample had undergone prior processes such as chemical leaching and precipitation that could have caused major changes in the particle sized and structure. Figure 3.7 shows the diagram generated by the Mastersizer device, while Table 3.4 shows the particle size distribution. Na_2S is used to precipitate PbS from the alkaline leach PLS. The size distribution of precipitate was much finer than the flotation tailings used in this study. d_{10} is about 0.2; d_{50} is 1.7; d_{80} is 15.8, and d_{97} is 34.6 µm.

Table 3. 4. Particle size distribution of the sulfide precipitate sample.

Particle size distribution	
d_{10}	0.199 µm
d_{50}	1.67 µm
d_{80}	15.83 µm
d_{97}	34.59 µm



Figure 3. 7. Particle size distribution of sulphide precipitate.

b) XRD ANALYSIS

Figure 3.8 shows the XRD spectra of the sulphide precipitate. All precipitate is made of PbS.

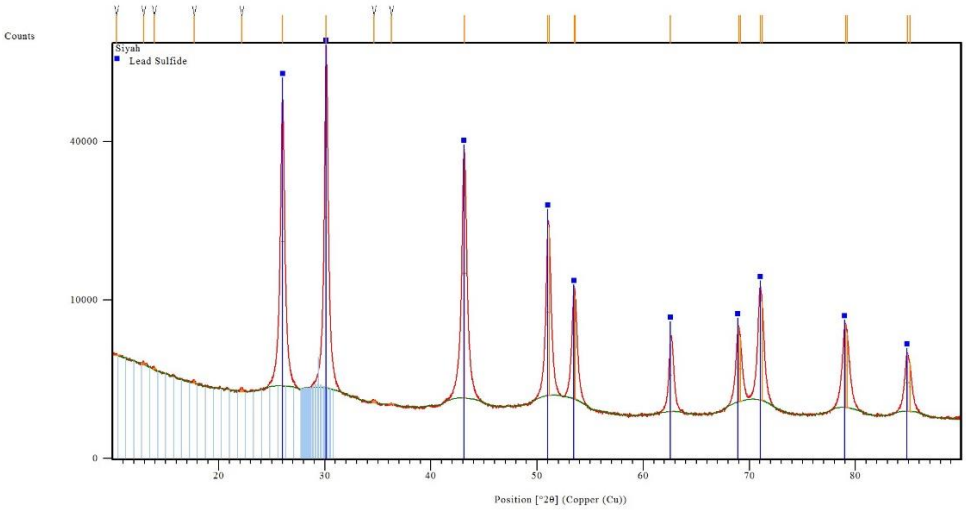


Figure 3. 8. XRD pattern of sulphide precipitate

c) Aqua Regia Dissolution followed by AAS Analysis

Table 3.5 shows the aqua regia analysis with triplicates of the sulphide precipitate. PbS precipitate contains 25.32% Pb and 1.25% Zn in average.

Table 3. 5. Aqua regia analysis with triplicates of the sulphide precipitate

Sample ID	Zn	Pb
Sample 1	1.39	24.80
Sample 2	1.23	25.43
Sample 3	1.15	25.72
Average	**1.25**	**25.32**

3.2. Methods

This study includes mainly the determination of optimum alkaline leaching conditions for the co-leaching of a zinc oxide mineral, smithsonite, and a carbonate-hosted lead mineral, cerussite; followed by the optimum sulphide precipitation conditions for effective Zn-Pb separation, and the optimum bio-leaching conditions for lead recovery from the sulphide precipitate. An optimum flowsheet for the recovery of these metals from the tailings will also be developed.

The principal stages can be divided into:

1) Physical, chemical, mineralogical, and thermal characterization of the flotation tailing sample and the sulphide precipitate, using methods such as X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Atomic Absorption Spectroscopy (AAS), particle size distribution determination, Inductively Coupled Plasma (ICP), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS).

2) Leaching tests to co-extract zinc and lead from the flotation tailing. 49 experiments were conducted in total, and the parameters that were examined during the leaching experiments were:

   i) Reagent type and concentration
   ii) Solid/liquid ratio (S/L ratio)
   iii) Solution temperature
   iv) Leaching time
   v) Enhancer/catalyst effects

3) Sulphide precipitation tests to selectively precipitate lead from the PLS. A total of 10 experiments were conducted, and the parameters examined here were:

   i) Na_2S/Pb weight ratio
   ii) Temperature
   iii) Time

4) Bioleaching tests to recover lead from the sulphide precipitate. 45 experiments were conducted in total, and the parameters examined were:

i) Pulp density
ii) pH
iii) Bioleaching time

The first stage of the experiments which involve physical, chemical, mineralogical, and thermal characterization of the two samples have been detailly reported in the section of "Materials" (Section 3.1) above.

3.2.1. Co-Extraction of Pb and Zn by Alkaline Leaching Method

After the collection, preparation and characterization of the flotation tailing sample, leaching tests were done. All the reagents used in this study were obtained from Merck/Sigma Chemical Company. Deionized/double distilled water was used throughout the experiments. The leaching experiments were conducted at atmospheric pressure. The homogenized particle size was generally below 10 µm. The main objective of these leaching tests was to co-extract lead and zinc from the Oreks flotation tailing sample with maximum grade, as well as efficient non-toxic waste streams, using alkaline solutions and organic acids.

The leaching tests were carried out in a three-necked round bottomed thermostatic Pyrex reactor of 500mL volume. NS 29/32 borosilicate glass spiral reflux vapour condensers (40 cm long) were attached to the reactor's centre neck to prevent water loss by evaporation. Temperature and pH were measured by inserting the thermometer and the pH meter in the side neck of the balloon reactor, as the experiments proceeded. For efficient mixing and temperature control, the glass reactor was placed in an Mtop digital magnetic stirring heated extraction mantle (EAMDS 9603-03), and all the leaching experiments were carried out at 400 rpm. Figure 3.9 shows the

leaching set-up. The lixiviant was placed in the reactor, and let to heat to the desired temperature, after which a weighed amount of the tailing was added to the glass reactor. Approximately 1.25 kilograms of representative samples were used at 1:10 solid/liquid ratio (25g of tailing sample to 250mL of lixiviant) except otherwise stated. Also, a total of 49 leaching tests were done, and in order to obtain the optimum leaching conditions, the reaction parameters were manipulated individually.

In these leaching tests, the two parameters that stayed constant were stirring rate and particle size, except stated otherwise. Since we were working with flotation tailings, the slime size particles had a higher percentage, which made further grinding not feasible, hence only one particle size was used. Concerning the stirring rate, any increase beyond 300-400 rpm causes an increase in the relative motion between the particles and the solution, leading to impeded leaching (Song et al., 2018). Therefore, the optimum stirring speed, as found in previous studies for similar types of ores was employed in these experiments.

Immediately after the leaching process, filtration (using Whatman 1 filter paper, 70 mm in diameter) and washing (using deionized water), which separated the solid phase from the liquid phase were performed. The residue remained on the filter paper and was dried for a couple of hours in a 105 ^{o}C oven. This residue was later tested with XRD, while the filtrate was analysed for Zn, Pb and Fe (three elements) with AAS at ESOGU.

To calculate the leaching efficiency of the metal extraction, equation (3.1) is used:

$$R = \frac{Cm*V}{Co*M} * 100 \tag{3.1}$$

R (%) is the leaching efficiency of the investigated metal,

C_m (g/mL) is the metal ion concentration in the filtrate

C_o (wt. %) is the metal content in feed sample

V (mL) is the volume of the filtrate

M (g) is the mass of the tailing leached

After the AAS analysis, the metal dissolution percentage was calculated using Equation (3.2) below:

$$\text{Dissolution (\%)} = \frac{\text{Metal in the leach solution by AAS (\%)}}{\text{Original metal in the feed sample by AAS (\%)}} * 100 \quad (3.2)$$

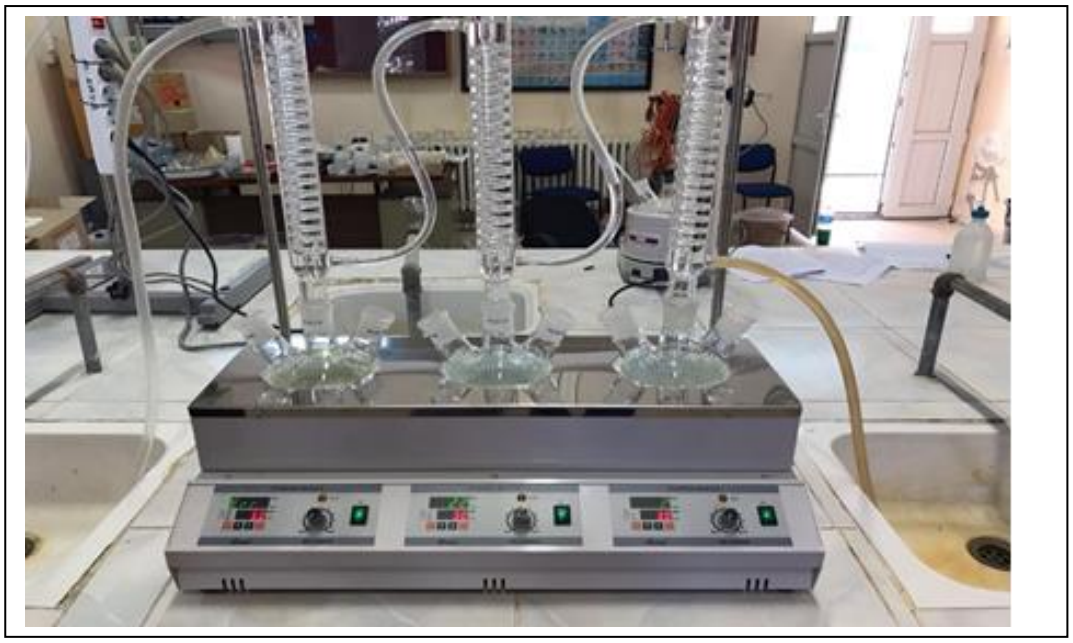


Figure 3. 9. Digital triple experimental leaching set-up

Within the scope of this research, four (4) different leaching lixiviants were used for the co-extraction of Pb and Zn from the flotation tailing. The different conditions were tested for each leaching reagent. Table 3.6 shows the experimental conditions of all the leaching studies.

Table 3. 6. Experimental conditions for leaching tests

Leaching Reagent	**Concentration, mol/L**	**Temperature, ºC**	**Time, mins**	**Other**	**Total number of tests**
NaOH only	(0.5M, 1M, 2.5M, 5M) (4 tests)	25, 75, 85, 95 ºC (4 tests)	30, 60, 120, 180 mins. (4 tests)	Effect of ultrasound (4 experiments)	16
EDTA only	0.2M	85 ºC	30, 60, 120, 180 mins (4 tests)		4
NaOH + NaCl	5M NaOH 0, 1, 2, 3M NaCl (4 tests)	85 ºC	180 mins		4
NaOH + EDTA	0, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, 2.5, and 5.0 M NaOH 0, 0.1, 0.2, 0.3. 0.4 M EDTA (14 tests)	25, 45, 65, 85 ºC (4 tests)	4 experiments (30, 60, 120, 180 mins)	Effect of solid/liquid ratio (1/10, 2/10, 3/10) 3 experiments	25
Total					**49**

In these leaching studies, the metals of interest during testing are Pb, Zn and Fe. Fe is considered an impurity in the tests. The conditions during Co-dissolution of Pb and Zn at maximum percentage and dissolution of Fe at minimum percentage will be considered optimum conditions. The extraction rates will be detailly discussed in the next chapter of results and discussion.

3.2.2. Leaching Enhancement Method with Ultrasound

The objective of these experiments was to improve on the leaching efficiency of the alkaline leaching of the flotation sample. Ultrasound is known to considerably improve on leaching efficiency and has been used over the years to enhance leaching operations (Li et al., 2018; Luque-García and Luque de Castro, 2003; Xin et al., 2013). A device which generates the ultrasound is used, and in our case, the Alex Ultrasonic Cleaner bath was used. The three-necked glass reactor where the lixiviant and a weighed quantity of the flotation tailing were placed, was put into the ultrasonic bath which had already been set at the desired temperature and time. The ultrasonic bath was covered with its lid, but to ensure minimal heat and water loss, the lid was again covered with aluminium foil. The temperature and pH of the leachate were measured using a thermometer and a pH meter. Figure 3.10 shows the set-up of the ultrasonic-assisted leaching before and after covering of the ultrasonic bath respectively.



Figure 3. 10. Ultrasound-assisted leaching set-up

The experiments were carried out in two different ways, with reference to previous research and the literature:

In the first experiment, the leaching conditions were: 5.0 M NaOH; 1hr; S/L=1/10; 400 rpm; 68 ^{o}C, 60 minutes. The experiments took place in the 500 ml three-necked glass reactor, which was placed in an ultrasonic bath, after being set to heat to the desired temperature and time. Without any mixing aid, the ultrasound enhancement took place, for 60 minutes, after which the leachate was filtered and analysed with AAS for lead, zinc and iron.

In the second experiment, the conditions were: 5.0 M NaOH; 1 hr; S/L=1/10; 400 rpm, and there was an alternation between normal leaching with mixing aid, and ultrasound-assisted leaching without mixing aid. The normal leaching was carried out at 85 ^{o}C using the leaching set up of three-necked glass reactor, seated in a mantle, magnetically stirred, and attached to a spiral condenser, while the ultrasound-assisted leaching was carried out at 70 ^{o}C in an ultrasonic bath without any mixing aid. The alternation between normal and ultrasound-assisted was conducted in the space of every 10 mins. The experiment started 10 mins in the heating mantle, magnetically stirred, followed by 10 minutes in the ultrasonic bath, and so on, until it was 60 minutes. The leachate was then filtered and analysed with AAS for lead, zinc and iron.

The major difference between the first and the second experiment is the mixing which was present in the second, but absent in the first experiment. The effect of mixing during ultrasound-assisted leaching was investigated in the second experiment. Alongside, control experiments were done at the same leaching conditions but in the absence of any ultrasound interaction, in order to make a comparison and find out the effect of ultrasound on the leaching efficiency. The results of leaching efficiencies with and without ultrasound, and their comparison are presented in the next chapter.

3.2.3. Purification Method

3.2.3.1. Zinc Recovery through Selective Sulphide Precipitation

After the co-leaching of lead and zinc at optimum conditions using NaOH mixed with an organic acid (EDTA), a process to separate the two metal ions was needed. The objective of this method was to selectively precipitate Pb from a co-leached Pb-Zn PLS in order to separate the Pb ions from the Zn ions.

The precipitation tests were carried out in a 200 mL beaker and covered with aluminium foil to prevent heat and water loss by evaporation. The temperature and pH were measured by inserting the thermometer and pH meter ((Hach HQ40d) equipped with IntelliCAL PHC 28101 probe) into the beaker during reaction. The beaker was placed on a digital magnetic hot plate stirrer which aided with temperature regulation and efficient mixing of the reagents and the PLS. Figure 3.11 shows the set-up for the precipitation reaction.

100 mL of Pb-Zn PLS was poured into a 200 mL beaker which was placed on a magnetic hot plate stirrer and let to heat to the desired temperature. The mixing rate was set at 200 rpm for all experiments, and this was chosen taking into account the volume of the solution used. A weighed amount of ground sodium sulphide red flakes, calculated with respect to Na_2S/Pb ratio, was added to the PLS and a black precipitate was obtained. With the aim of obtaining optimum selective precipitation conditions, the different parameters such as weight ratio, temperature, and time were manipulated leading to the carrying out of a total of 10 experiments. Table 3.7 shows the experimental conditions for all the precipitation experiments.

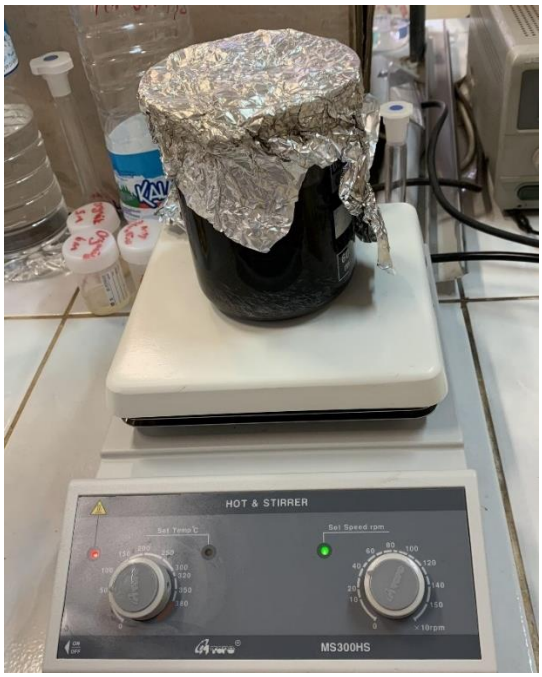


Figure 3. 11. Selective precipitation set-up.

Table 3. 7. Experimental conditions for precipitation tests

Na_2S/Pb weight ratio	**Temperature, ^oC**	**Time, mins**	**Total**
1.2, 1.4, 1.6, 1.8, 2.0, 2.2 (6 experiments)	50 ^oC	60	6
1.4	25, 50 (2 experiments)	10	2
1.4	25, 50 (2 experiments)	30	2
Total			**10**

The shiny golden PLS colour immediately turned black as Na_2S was introduced. Figure 3.12 shows this change in colour, while equation (3.3) shows the reaction of Pb ions with Na_2S to give lead sulphide precipitate.

$$Pb^{2+}{}_{(aq)} + Na_2S_{(s)} \rightarrow PbS_{(s)} + 2Na^{+} \quad (3.\ 3)$$

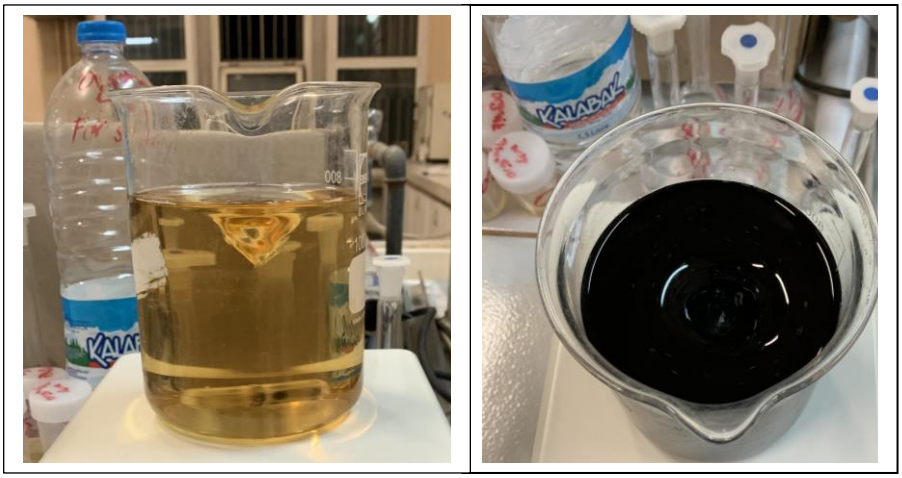


Figure 3. 12. (a) before addition of Na_2S and (b) upon addition of Na_2S

The solutions were filtered after precipitation using the Whatman 1 filter paper, and the volume of the solutions were measured in a measuring cylinder and the difference between the volume before and after the experiment was calculated. The samples were analysed by ThermoScientific AAS at ESOGU to investigate the precipitation percentages of Pb.

The precipitate was left to dry for 24 hours in an oven, and then scraped off the filter paper using a spatula, after which it was manually ground using a ceramic mortar and pestle. This solid precipitate was taken for XRD analysis, at the ARUM centre in ESOGU to determine the mineralogical composition. The calculation of precipitation percentage of the metal ions was based on the difference between metal concentration in the solution before and after the precipitation experiments, according to the equation (3.4):

$$\text{Precipitation (\%)} = \frac{C_1V_1 - C_2V_2}{C_1V_1} \text{ x } 100\% \quad (3.\ 4)$$

C_1 = initial metal concentration in PLS (mg/L)

C_2 = final metal concentration in PLS (mg/L)

V_1 = initial volume of PLS (L)V_2 = final volume of PLS (L)



Figure 3. 13. (a) Solid-liquid separation after selective precipitation, and (b) PLS before and after selective precipitation of lead

3.2.4. Bio-leaching Method

After the separation of Pb and Zn through selective precipitation of Pb by Na_2S, Zn stays in the PLS while Pb is found majorly as PbS in the formed precipitate. The motivation behind this bioleaching method, is to efficiently recover Pb metal ions from this precipitate, with the help of an autotrophic bacterium called *Leptospirillum ferrooxidans.* Even though Pb metal can be produced by direct reduction smelting of PbS, it's not a very attractive process due to issues such as poor recovery, release of SO_2 and high coke requirement. Another option is leaching with NaOH or $PbCO_3$ or Na_2CO_3, but these reactions are exothermic during sintering, so are not suitable for charging into the sinter machines. Also, NaOH and Na_2CO_3 are expensive, which makes the process not cost-effective.

The microorganism, *Leptospirillum ferrooxidans (L. ferrooxidans),* was isolated in the Biotechnology Laboratory at Eskişehir Osmangazi University (Nural Yaman et al., 2020). All the chemicals used for preparing the medium and solution for microbiological studies were provided from Sigma Aldrich (Germany) and Merck (Germany).

3.2.4.1. The medium and culture of Leptospirillum ferrooxidans

The content of the medium was modified from DSMZ 882. The medium was made up of a combination of three solutions: Solution A, Solution B and Solution C. Solution A made up to 950 ml of the medium, and distilled water was used. pH adjustment was done with 10N H_2SO_4. Then the solution was autoclaved at 121 °C for 15 minutes. Solution B made up to 50 ml with 0,25 N H_2SO_4. The pH was adjusted to 1.2, then it was sterilized by syringe filter with 0.22 μm pore diameter. Solution C was composed of a negligible but indispensable amount of trace element. Solution A, B and C were merged after sterilization. Table 3.8 shows the reagents and their respective amounts, used in the preparation of the medium of the bacterium in question.

Table 3. 8. Reagents used in the preparation of the medium of *L. ferrooxidans*

Reagent	Amount
Solution A (g/L)	
$(NH_4)_2SO_4$ (1M)	0,132 g
$MgCl_2$ x $6H_2O$	0,053 g
K_2HPO_4	0.027 g
Solution B (g/L)	
$FeSO_4$ x $7H_2O$	20 g
Solution C (g/L)	
Trace element	1 ml

The bacterium *L. ferrooxidans* was inoculated into the modified DSMZ 882 medium. The culture was statically incubated for approximately 10 days, and the incubation was terminated when the light green medium turned red.

3.2.4.2. Bioleaching experiments

All the experiments were performed in duplicate, and for each experiment, one control experiment was done. The control experiment consisted of only the medium without the bacterium. All experimental setups were performed in 50 ml medium + bacteria. This was quite a small quantity but owing to the fact that there was limited precipitate sample, and pulp density was one of the parameters that were varied, this amount was considered to be reasonable. The temperature chosen for these experiments was 37 °C because previous findings on the bacterium *L. ferrooxidans* confirm that this is the optimum temperature for this bacterium to function (Nural Yaman et al., 2020). The agitation rate was set at 150 rpm. Between 100 and 200 rpm have been found to be appropriate for bioleaching experiments, as higher rates will cause increased loss in solution, taking into consideration that the process will take couple of weeks (Rouchalova et al., 2020).

50 ml of medium and bacteria was placed in a 250 ml sterilized Erlenmeyer flask and then a weighed amount of the sterilized sulphide precipitate was added carefully. Sterilized cotton wool plug was attached to the neck of the Erlenmeyer flask to prevent contamination of the samples. Each of the samples at its own unique conditions was placed on the agitator at 150 rpm and left there for a total of five weeks, while small quantities of the samples were collected weekly in 1ml Eppendorf tubes and analysed for Pb and Zn recovery using the AAS device of ESOGU University. Figure 3.14 shows the bioleaching set-up.

There was another set of experiments that was not touched from the start till the end of six weeks. During collection of samples for analysis, errors like Pb precipitate removal from the solution likely occurs, which changes pulp density of individual experiments as the weeks progress, leading to faulty results at the end. This problem can be avoided by letting the Erlenmeyer flask stand and settle for some minutes before collection of the supernatant fluid at the surface. However, this problem was unavoidable in our experiments due to the small volume (50 ml) we were working with. We decided to conduct another set of experiments with same conditions, except for the fact this new set will not be touched from the start to the end of six weeks. The weekly collection of samples was not performed, in order to do a comparison between that which was being touched on a weekly basis. Alongside were the control experiments that were also not touched till the end of six weeks.

The experiment was set up according to Rouchalova et al. (2020). In the bioleaching experiments, the effects of pH, pulp density and time were investigated on bioleaching. Within this scope, the media of *L. ferrooxidans* were prepared in three different pHs: 1.6, 1.8 and 2.0. The pHs were adjusted with 10N H_2SO_4. The pulp densities of the samples were determined at 1.0 %, 2.5 % and 5.0 %. The amounts of sample according to pulp density were weighed and the samples were autoclaved at 121 °C for 15 minutes, then they were added into the medium. Lastly, the *L. ferrooxidans* was inoculated at 10 %.



Figure 3. 14. Bioleaching set-up

A total of 45 experiments were performed, with each experiment investigating specific parameters. There were 9 test experiments, 9 duplicates, and 9 control experiments making 27 experiments, which were analysed on a weekly basis to find out how much Pb is being extracted progressively over a 5 - week period. Another 9 test experiments and 9 control experiments (making 18 experiments) were prepared under same conditions as the former, but this time, there were no weekly analyses performed on them. They were left to be agitated for 6 straight weeks, and the sample was collected only once, at the end of the 6 weeks for analysis. This makes a total of 45 experiments carried out within a 6-week period, as shown on Table 3.9.

Table 3. 9. The experiments and the different conditions applied in the bioleaching of the sulphide precipitate.

Experiment	**pH**	**Pulp density**	**Time, days**	**For two duplicates and two control experiments:**	**Total number of experiments**
1	1.6	1%	35 and 42	1D, 1C, 1DN and 1CN	5
2		2.5%	35 and 42	2D, 2C, 2DN and 2CN	5
3		5%	35 and 42	3D, 3C, 3DN and 3CN	5
4	1.8	1%	35 and 42	4D, 4C, 4DN and 4CN	5
5		2.5%	35 and 42	5D, 5C, 5DN and 5CN	5
6		5%	35 and 42	6D, 6C, 6DN and 6CN	5
7	2.0	1%	35 and 42	7D, 7C, 7DN and 7CN	5
8		2.5%	35 and 42	8D, 8C, 8DN and 8CN	5
9		5%	35 and 42	9D, 9C, 9DN and 9CN	5
Total					**45**

Heavy metal concentrations in the leaching solutions were determined by atomic absorption spectrometry (Model and Brand). Zinc was considered the impurity in this experiment while lead, the desired metal. The extraction rates as a function of pH, time and pulp density will be discussed in detail in the next chapter.

4. RESULTS AND DISCUSSION

4.1. STEP I: Chemical Leaching for the co-extraction of Pb and Zn

4.1.1. Alkaline Leaching

As indicated in the previous sections, the aim of carrying out these leaching experiments was to co-extract Pb at Zn simultaneously while manipulating parameters such as reagent concentration, time, temperature, solid/liquid ratio, etc. in order to determine the optimum leaching conditions that will yield maximum recovery and grade. Alkaline leaching was considered in the first place due to its unique advantage of not dissolving iron in the solution. Acids do not have this advantage as they dissolve iron into solution. Given that our flotation sample under investigation contains over 20% Fe, it was important to find a reagent that will get rid of this major impurity, to avoid subsequent purification processes for Fe removal. This also reduces the hazardousness of the solid residue (Dutra et al., 2006). In these leaching experiments, NaOH was used as the alkaline reagent, but as the experiments progressed, in search of better results for an optimised co Pb-Zn extraction, the NaOH was mixed with other reagents such as brine NaCl and chelating agent EDTA. These additive reagents have been vastly observed from previous research studies and from the literature review. Firstly, the leaching was done with NaOH only, which didn't yield very good results, especially for Pb extraction. Owing to this, another set of experiments was done with NaOH, and NaCl added to improve on Pb extraction. Zhao and Stanforth (2000) tested the effect of NaCl additive on the alkaline leaching of Zn-Pb ores, and they concluded that NaCl addition enhanced Pb extraction. This enhancement could be explained by the possible formation of soluble Cl-Pb complexes (Zhao and Stanforth, 2000). However, even though this was the case in our experiments, it had a negative effect on zinc which made the results of the experiments unattractive. In search for better Pb-Zn co-extraction, NaOH was now combined with EDTA and the results were considered good and acceptable, as more than 90% Pb was extracted and more

than 80% Zn extracted. At this point, a few experiments with EDTA only (as an organic acid) were done, to compare the difference between NaOH alone, EDTA alone, and a combination of NaOH + EDTA. By the end of the day, the combination with the best results was employed and scaled up, to provide feed for the next step which is purification.

4.1.1.1. Alkaline leaching with NaOH only

The leaching experiments, using NaOH only, as reagent, were carried out and the parameters that were manipulated to determine optimum leaching conditions were NaOH concentration, leaching temperature and leaching time. Also, ultrasound-assisted leaching was performed to investigate whether there would be an improvement in leaching efficiency.

a) Effect of NaOH concentration on dissolution efficiency

These experiments were carried out to find out the effect of NaOH concentration on the extraction efficiencies on both Pb and Zn. While other parameters were kept constant, the NaOH concentrations were varied: at 0.5 M, 1.0 M, 2.5 M, and 5.0 M. At these different concentrations, the Pb, Zn and Fe extraction were tested, and the one with the maximum co-extraction of Pb and Zn was considered optimum. Leaching temperature was set at 85 ^{o}C, leaching time was 180 mins, solid/liquid ratio 1/10, and stirring speed 400 rpm. The results of these experiments are presented in Table 4.1, and the graphical representation is provided in Figure 4.1

Table 4. 1. Recovery efficiency for Pb, Zn, and Fe at varying NaOH concentrations.

NaOH Molarity (mol/L)	Zn Extracted (%)	Fe Extracted (%)	Pb Extracted (%)
0.5	3.42	0	1.06
1.0	9.06	0	9.50
2.5	43.33	0	37.09
5.0	**77.81**	**0**	**40.50**

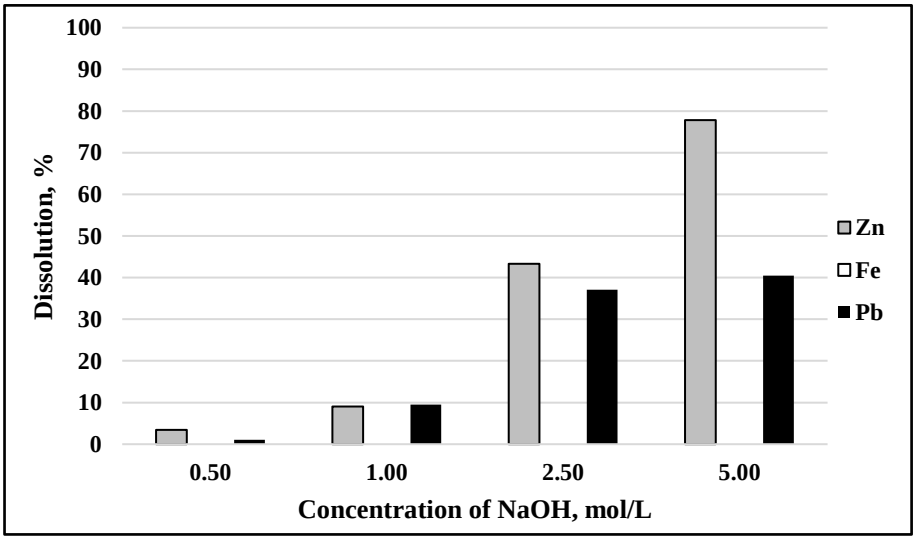


Figure 4. 1. Effect of NaOH concentration on lead, zinc and Fe recovery at 85 ^{o}C, 180 minutes, 1/10 solid/liquid ratio and 400rpm.

As expected, an increase in extraction efficiency was observed as the concentration of NaOH increased progressively. There was no selectivity between Pb and Zn as they were co-extracted at almost the same rate, except for the extraction at 5.0 M NaOH, which was about 2 times more for zinc than lead. Fe did not dissolve in any of the different NaOH concentrations as it was an alkaline solution. With 5.0 M NaOH concentration, 77.81% Zn and 40.50%Pb were extracted. It was also observed that gelation occurred at higher NaOH concentrations, which made filtration difficult. This tendency has also been observed in the literature (Zhao and Stanforth, 2000). Consequently, NaOH concentrations higher than 5.0 M were not used in this experiment.

b) Effect of temperature on dissolution efficiency

The effect of temperature on the extraction of lead, zinc and iron were investigated, as other parameters were kept constant while the temperature was being changed. The temperatures tested were room temperature (25 ^{o}C), 75 ^{o}C, 85 ^{o}C, and 95 ^{o}C. The concentration of NaOH was kept at 5.0 M, leaching time 180 mins, solid/liquid ratio 1/10, and stirring speed 400 rpm. The results of these experiments are presented in Table 4.2, and the graphical representation is provided in Figure 4.2.

Table 4. 2. Recovery efficiency for Pb, Zn, and Fe at varying temperatures

Temperature (^{o}C)	**Zn Extracted (%)**	**Fe Extracted (%)**	**Pb Extracted (%)**
0	0.00	0	0.00
25	69.19	0	24.03
75	75.92	0	38.15
85	77.81	0	40.50
95	**81.14**	**0**	**44.60**

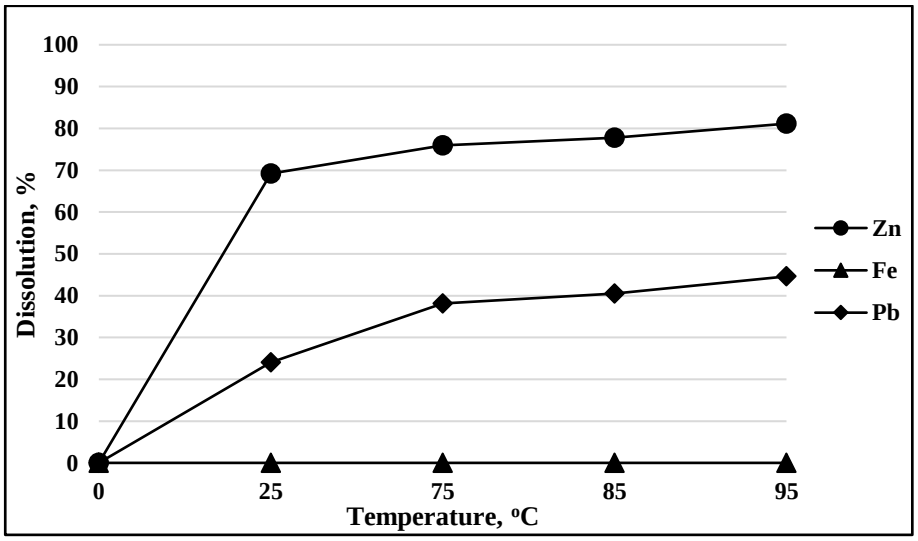


Figure 4. 2. Effect of temperature on lead, zinc and Fe recovery at 5M NaOH concentration, 180 minutes, 1/10 solid/liquid ratio and 400 rpm.

The extraction efficiency was seen to be directly proportional to the increase in temperature, as expected. Again, there was no selectivity between lead and zinc, but zinc was more dissolving in the solution than lead, about 2 times more, for every tested temperature. Fe did not show any sign of dissolution even as temperature increased progressively; it remained undissolved in the solution. At 95 ^{o} C, the highest extraction rates for both zinc and lead were recorded at 81.14% and 44.60% respectively. Most of the Zn dissolved until 25 ^{o}C, then Zn dissolution rates increased slowly. Pb dissolved faster up to 75 ^{o}C, then slows down up to 95 ^{o}C.

c) Effect of time on dissolution efficiency

Time was one of the parameters that was manipulated to find out how lead, zinc and iron extraction are affected by it. As other conditions were kept constant at 5.0 M NaOH, 85 ^{o} C, S/L of 1/10 and mixing speed at 400 rpm, time was varied as follows: 30 mins, 60 mins, 120 mins and 180 mins. The results obtained are presented in Table 4.3, and the graphical representation is provided in Figure 4.3.

Table 4. 3. Recovery efficiency for Pb, Zn, and Fe at varying durations

Time, mins	Zn Extracted (%)	Fe Extracted (%)	Pb Extracted (%)
0	0.00	0.00	0.00
30	73.70	0.00	32.08
60	76.26	0.00	33.12
120	77.52	0.00	37.97
180	**77.81**	**0.00**	**40.50**

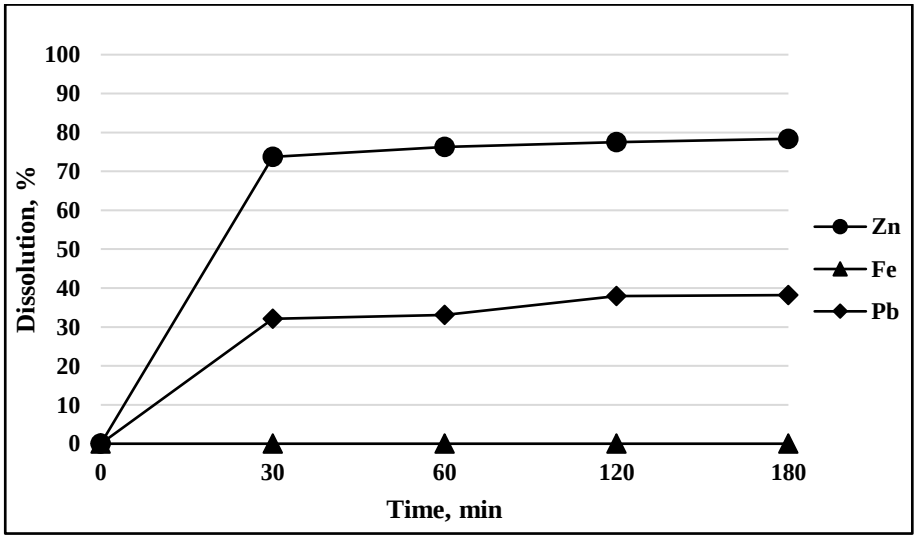


Figure 4. 3. Effect of time on lead, zinc and Fe recovery at 5.0 M NaOH, 85 ^{o}C, 180 minutes, 1/10 solid/liquid ratio and 400 rpm.

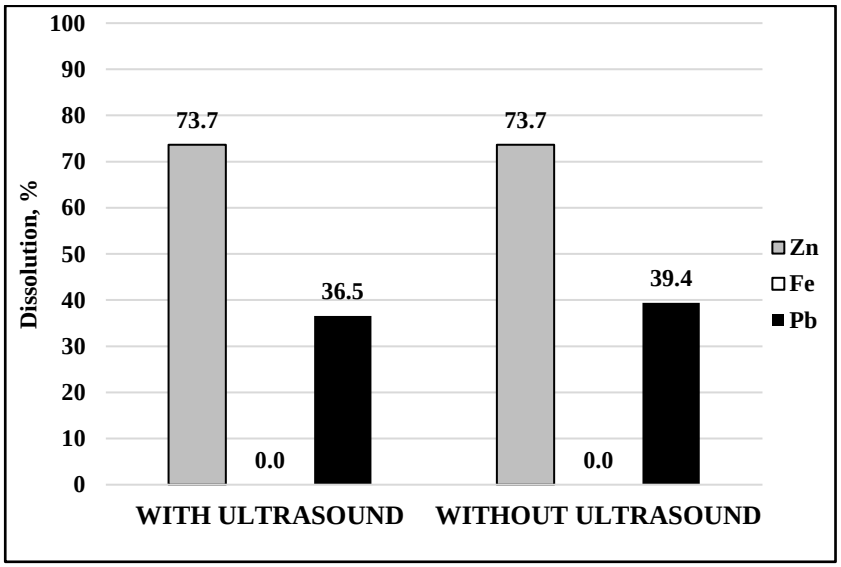
The results showed that time really did not have any significant effect on the extraction of lead, zinc and iron. The extraction of zinc was between 70% and 80% from 30 minutes right till 3 hours, while that of lead was between 30% and 40% with very minor fluctuations within that range. Iron stayed at 0% throughout the durations. The highest extraction was recorded at 180 mins with 77.81% and 40.5% of zinc and lead respectively, even though the difference in extraction at shorter durations was not significant. Most of the Zn and Pb were dissolved in the first 30 minutes.

d) Effect of ultrasound-assisted leaching on dissolution efficiency

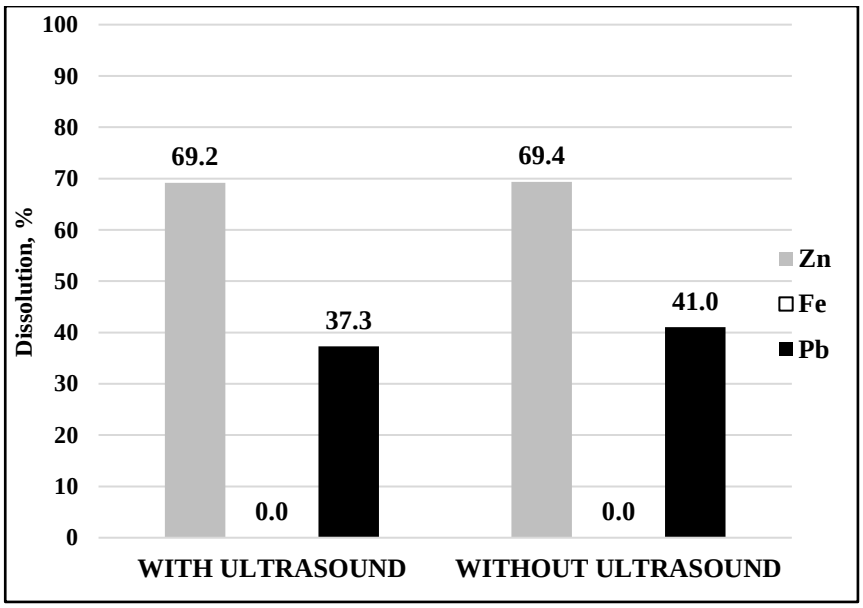
The optimum conditions obtained from the experiments above (alkaline leaching with NaOH only) were 5.0 M NaOH, 85 ^{o} C, 180 minutes, S/L of 1/10 mixing speed at 400 rpm. At these conditions 77.81% zinc, 40.5% lead and 0% Fe was extracted. Because our objective was to co-extract zinc and lead, these extraction percentages were not sufficient to proceed to the next stage of precipitation. In this regard, an enhancement method was used to improve on leaching efficiency. Two test experiments were carried out, one to investigate effect of ultrasound without mixing (conditions: 5.0 M NaOH; 1 hr; S/L=1/10; 400rpm; 68^{o}C, 60 minutes), and the other to investigate the effect of ultrasound with mixing (conditions: 5.0 M NaOH; 1hr; S/L=1/10; 400 rpm, 70 ^{o}C, 60 minutes). Alongside, two control experiments were done, where ultrasound was not applied. The results of these experiments are presented in Table 4.4, and Figure 4.4. (a) and (b).

Table 4. 4. Extraction efficiencies for zinc, lead and iron, with and without ultrasound.

	Zn Extracted (%)	**Fe Extracted (%)**	**Pb Extracted (%)**
a) Fully ultra-sound assisted (no mixing)			
With Ultrasound	73.66	0.00	36.54
Without Ultrasound	73.67	0.00	39.39
b) Ultrasound assisted + normal leach at 10 minutes alternating intervals			
With Ultrasound	69.19	0.00	37.28
Without Ultrasound	69.38	0.00	41.02



(a)



(b)

Figure 4. 4. Effect of ultrasound on extraction efficiencies of zinc, lead, and iron at (a) without mixing and (b) with mixing at 5.0 M NaOH; 1hr; S/L=1/10; 400 rpm, 70 ^{o}C.

From the results, it showed that generally, ultrasound had a negative effect on the leaching efficiencies of zinc and lead, as the results of the pure leaching were higher compared to the results

of the experiments that were introduced to ultrasound. From the graphs, it can be clearly seen that the bar charts are higher when no ultrasound was introduced, but with the application of ultrasound, the bar charts slightly reduced. The reason for a negative effect of ultrasound on these experiments could be explained by the very small particle size. More than 80% of the particle size was below 10 µm, making ultrasound effect almost impossible. The particle size must be no less than -75 µm for a significant ultrasound effect to be perceived. Another possible reason for this negative effect could be because of the high frequency at which the ultrasound operates.

Also, comparing the ultrasound-assisted leaching which had no stirring aid, with that which was stirred at intervals of 10 minutes, it showed that stirring during ultrasound-assisted leaching had a negative effect on the leaching efficiency of zinc, but little or no effect on that of lead. While the former gave 73.66% zinc and 36.54% lead, the latter gave 69.19% zinc and 37.28% lead. Finally, it was concluded that ultrasound did not have a positive effect on the leaching efficiency of this hydrometallurgical process, therefore it was not used again anywhere else further in this work.

4.1.1.2. Alkaline Leaching with NaOH + NaCl

Alkaline leaching of the flotation leaching with NaOH only, at the optimum conditions gave 77.81% zinc, 40.5% lead and 0% Fe extraction. The extraction percentage for zinc is considerably acceptable, but that of lead is quite low, at less than 50%. Since the objective of this study is to co-extract zinc and lead at considerable extraction efficiencies, we will not be able to proceed to the separation step unless the co-extraction of zinc and lead are both above 70% during leaching. In this regard, the leaching efficiency of lead was sought to be improved by the addition of NaCl. According to (Zhao and Stanforth, 2000), the addition of NaCl in alkaline leaching greatly improves on lead extraction.

These experiments were carried out to investigate the effect of NaCl concentration on the extraction efficiencies on both Pb and Zn. While other conditions were kept constant, the NaCl concentrations were varied: at 1.0 M, 2.0 M, and 3.0 M. Leaching temperature was set at 85 ^{o}C, leaching time was 180 mins, solid/liquid ratio 1/10, and stirring speed 400 rpm. The results of these experiments are presented in Table 4.5, and the graphical representation is provided in Figure 4.5

Table 4. 5. Extraction efficiencies of zinc, lead and iron at different NaCl concentrations

NaOH Molarity (mol/L)	**NaCl Molarity (mol/L)**	**Zn Extracted (%)**	**Fe Extracted (%)**	**Pb Extracted (%)**
5	0	77.81	0.00	40.50
5	1	74.51	0.00	51.26
5	2	73.34	0.00	53.67
5	3	72.93	0.00	59.67

It was seen from the results that the addition of NaCl improved on Pb extraction efficiency as expected. The concentration of NaCl in the solution was directly proportional to the dissolution of Pb in the solution. As NaCl concentration was increased from 0 M to 3.0 M, Pb extraction increased by approximately 20%, from 40.50% to 59.67%. On the contrary, this reaction had a negative effect on zinc extraction. NaCl concentration was inversely proportional to zinc extraction, as the zinc extraction efficiency continuously decreased upon progressive addition of NaCl. As NaCl was increased from 0 M to 3.0 M, zinc extraction dropped from 77.81% to 72.93%. Because of these antagonistic reactions between lead and zinc extractions, it was decided that there was no need to continue the experiments at higher NaCl extractions, as it will be favouring Pb extraction but opposing Zn optimum extraction.

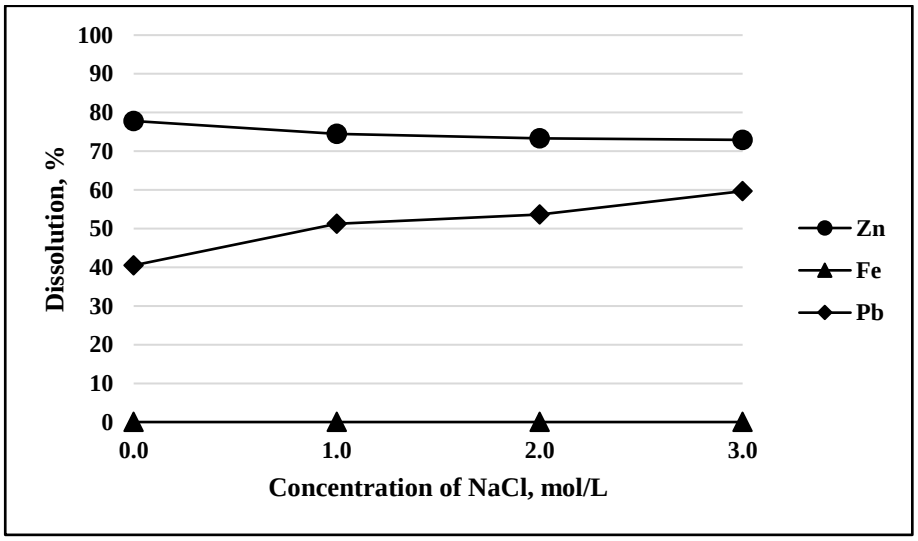


Figure 4. 5. Effect of NaCl concentration on zinc, lead, and iron extraction at 5.0 M NaOH; 180 mins; S/L=1/10; 400 rpm, 85 ^{o}C.

4.1.1.3. Alkaline leaching with NaOH + EDTA

The alkaline leaching experiments, using NaOH mixed with chelating EDTA as lixiviant were conducted with the objective of co-extracting Pb and Zn at considerably acceptable percentages. The other additives and enhancers used in the previous sections were not simultaneously efficient for both Pb and Zn extraction, so more additives were sought with reference to previous findings in the literature. EDTA has been seen to greatly improve on Pb extraction in alkaline leaching (Liu et al., 2014).

The first few experiments carried out with NaOH + EDTA were seen to be highly lucrative, and this influenced the broad investigation of up to 5 parameters and their effect on the maximum extraction of Pb and Zn. The parameters investigated were NaOH concentration, EDTA concentration, solid/liquid ration, leaching temperature and leaching time. These parameters were manipulated in order to determine the optimum leaching conditions for the co-extraction of Pb and Zn.

a) Effect of NaOH concentration on dissolution efficiency

These experiments were conducted to find out how NaOH concentration in the mixture of NaOH + EDTA affects Pb and Zn extraction efficiencies. According to previous works in the literature, NaOH concentration is the most complicated parameter among all the other parameters (Liu et al., 2014). This is because as NaOH concentration is increased progressively, the Pb and Zn extraction trends change at different stages. Because of these varying trends, up to 8 different concentrations were tested, ranging from 0.5M to 5.0 M. Leaching temperature was set at 85 ^{o}C, leaching time was 180 mins, solid/liquid ratio 1/10, and stirring speed 400 rpm, while the NaOH concentrations were 0.5 M, 0.75 M, 1.0 M, 1.25 M, 1.5 M, 2.0 M, 2.5 M, and 5.0 M. The results of these experiments are presented in Table 4.6, and the graphical representation is provided in Figure 4.6

Table 4. 6. Extraction efficiencies of zinc, lead and iron at different NaOH concentrations and 0.2 M EDTA

NaOH Molarity (mol/L)	**EDTA Molarity (mol/L)**	**Zn Extracted (%)**	**Fe Extracted (%)**	**Pb Extracted (%)**
0.00	0.20	84.19	10.73	34.01
0.50	**0.20**	**83.16**	**0.00**	**95.39**
0.75	0.20	60.42	0.00	92.52
1.00	0.20	59.11	0.00	83.06
1.25	0.20	50.51	0.00	71.04
1.50	0.20	50.23	0.00	64.72
2.00	0.20	52.20	0.00	55.13
2.50	0.20	59.67	0.00	49.40
5.00	0.20	67.90	0.00	47.39

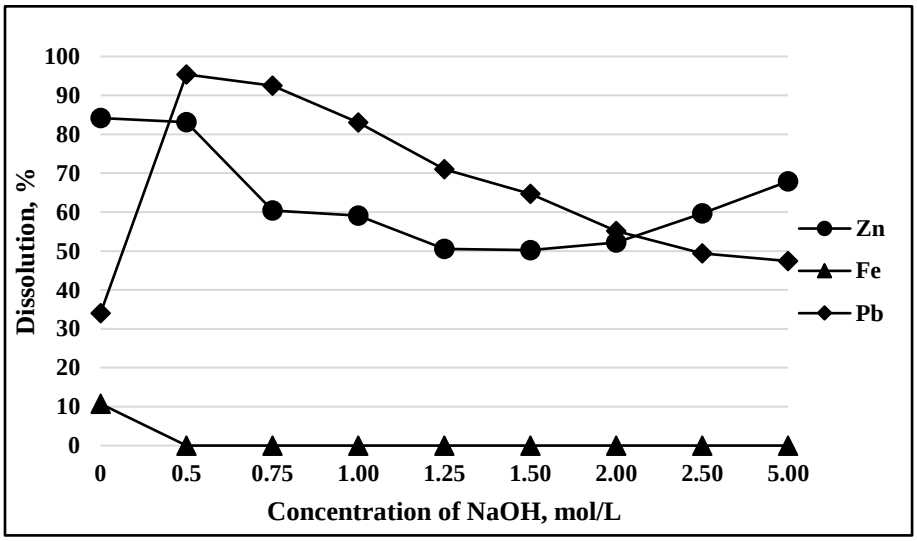


Figure 4. 6. Effect of NaOH concentration on zinc, lead, and iron extraction at 0.2 M EDTA; 180 mins; S/L=1/10; 400 rpm, 85 ^{o}C.

As mentioned above, NaOH concentration is the most complicated parameter, and this can be visibly seen from the graph that the trends for both Pb and Zn are complex. The leaching efficiencies of Pb and Zn can be divided into 3 stages as seen by the graph:

a- When initial concentration of NaOH increases from 0 M to 0.5 M, there is a significant increase in leaching rate of Pb from about 30% to above 90%, while there is little or no effect on zinc leaching rate.

b- When NaOH concentration is increased from 0.5 M to 1.5 M, there is a fall in the leaching rates of both Pb and Zn

c- When the NaOH is increased from 1.5 M to 5.0 M, the leaching rate of Zn starts to increase again, while that of Pb continues decreasing, until they crisscross at a point (between 2.0 M and 2.5 M is the point of intersection between Pb and Zn, where they showed equal leaching rates of about 55%) .

These behaviours may have been caused by oxides and chlorides in the flotation tailing. The NaOH increases the amount of Pb. As soon as NaOH concentration begins to exceed a particular amount, the conditional stability constants for Pb−EDTA and Zn−EDTA complexes will reduce, followed by an increase in zinc, as a result of the formation of $Zn(OH)_2$ complexes (Liu et al., 2014). Since our objective was to co-extract Pb and Zn at maximum leaching efficiencies, 0.5 M NaOH was seen to be appropriate as optimum NaOH concentration in these experiments, as Pb extraction was 95.39% while for Zn was 83.16%.

b) Effect of EDTA concentration on dissolution efficiency

The experiments to investigate the effect of EDTA concentration (in the mixture of NaOH + EDTA) on the leaching efficiencies on both Pb and Zn were conducted. At 0.5 M NaOH (which was the optimum determined for NaOH concentration), four different EDTA concentrations were tested progressively: 1.0 M, 2.0 M, 3.0 M, and 4.0 M EDTA. Leaching time was 180 mins, temperature 85 ^{o}C, stirring speed 400 rpm and solid/liquid ratio 1/10.

The results of these experiments are presented in Table 4.7, and the graphical representation is provided in Figure 4.7

Table 4. 7. Extraction efficiencies of zinc, lead and iron at different EDTA concentrations and 0.5 M NaOH

NaOH Molarity (mol/L)	**EDTA Molarity (mol/L)**	**Zn Extracted (%)**	**Fe Extracted (%)**	**Pb Extracted (%)**
0.50	0.00	3.42	0.00	1.06
0.50	0.10	57.06	0.00	64.74
0.50	**0.20**	**83.16**	**0.00**	**95.39**
0.50	0.30	86.00	5.03	49.10
0.50	0.40	90.06	7.78	42.64

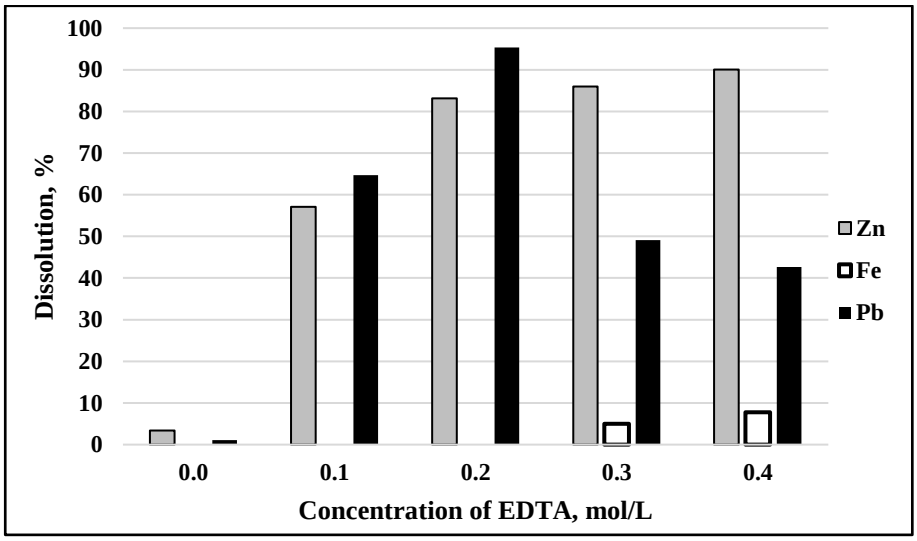


Figure 4. 7. Effect of EDTA concentration on zinc, lead, and iron extraction at 0.5 M NaOH; 180 mins; S/L=1/10; 400 rpm, 85 ^{o}C.

It was seen from the results that at 0 M EDTA, 0.5 M NaOH gave less than 5% for both lead and zinc, which was an extremely low leaching efficiency. Upon the addition of 0.1 M EDTA, a significant increase to above 50% in the leaching rate of both lead and zinc was observed. It was seen that the addition of EDTA is directly proportional to the leaching rate of zinc, as zinc extraction increased progressively as EDTA concentration was increased. Also Pb increased significantly when EDTA was increased from 0 M to 0.2 M EDTA, where it obtained its peak at 95.39%. After this, further addition of EDTA above 0.2 M led to the leaching and dissolution of Fe in the solution, which was probably the reason for the abrupt drop in Pb extraction rate from 95.39 % to about half at 49.10%. The more the EDTA concentration was increased, the more Fe was being dissolved in the solution, and the less Pb extraction was being recorded, while the Zn extraction rate continuously increased. Therefore, the optimum co-leaching efficiencies was selected to be 0.2 M EDTA, because at this point was maximum Pb leaching rate and 0% Fe dissolution, as the dissolution of Fe (which is an impurity) in the solution was not desirable.

Also, higher leaching rates of Pb are experienced first, before it drops, and then higher leaching rates for the other metal ions. The explanation for this could be that $EDTA^{2-}$ ions bind with lead ions to form stable complexes in an alkaline Na_2EDTA solution, in a 1:1 molar ratio. $EDTA^{2-}$ ions will always bind first with lead oxide before zinc oxide, due to its higher affinity for Pb^{2+} than Zn^{2+}. The equation (1.4) below shows it. When the EDTA has exceeded a level, this excess EDTA will bind with zinc and cause continual increase in zinc concentration, and then subsequently Fe concentration.

$$Zn{-}EDTA + PbO + H_2O = Pb{-}EDTA + Zn(OH)_2 \quad (4.1)$$

c) Effect of solid-liquid ratio on dissolution efficiency

Experiments were also carried out to investigate the effect of solid-liquid ratio on lead, zinc and iron leaching rates. Three solid-liquid ratios were tested: 1/10, 2/10 and 3/10, and as this parameter was being manipulated, the other parameters were set at: 0.5 M NaOH, 0.2 M EDTA, 85 ^{o} C, 180 mins, and mixing speed at 400 rpm. The results are presented in Table 4.8, and the graphical representation is given in Figure 4.8.

Table 4. 8. Extraction efficiencies of zinc, lead and iron at different solid-liquid ratios

S/L ratio	Zn Extracted (%)	Fe Extracted (%)	Pb Extracted (%)
1\10	**83.16**	**0.00**	**95.39**
2\10	54.06	0.00	68.87
3\10	46.04	0.00	50.66

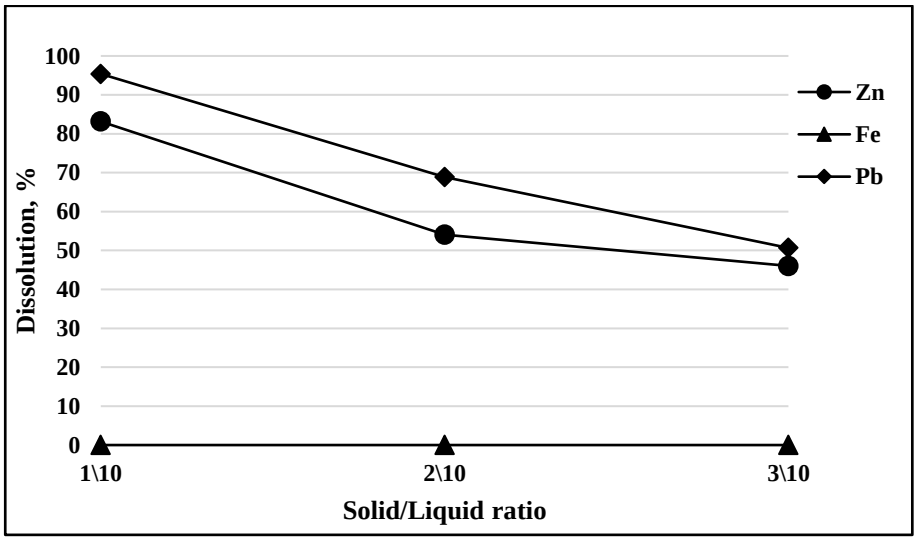


Figure 4. 8. Effect of solid-liquid ratio on zinc, lead, and iron extraction at 0.5 M NaOH; 0.2 M EDTA; 180 mins; 400 rpm, 85 ^{o}C.

The results demonstrated that solid-liquid ratio was inversely proportional to the leaching rates of both Pb and Zn, as expected, because this is the same observation in previous works and in the literature As solid-liquid was increased from 1/10 to 3/10, the leaching rates for Pb and Zn reduced accordingly and progressively. The highest leaching rates were observed at the solid-liquid ratio of 1/10 where 95.39% Pb and 83.16% Zn were achieved, and this was chosen as the optimum condition for these experiments.

d) Effect of temperature on dissolution efficiency

With NaOH +EDTA as lixiviant, the effect of temperature on the leaching efficiency of Pb, Zn, and Fe from the Oreks flotation tailing was tested. The temperatures tested were: 25 ^{o} C (room temperature), 45 ^{o} C, 65 ^{o} C, and 85 ^{o} C. The other parameters were kept constant at 180 minutes, solid/liquid ratio 1/10, and stirring speed 400 rpm. The results of these experiments are shown in Table 4.9, and the graphical representation in Figure 4.9.

Table 4. 9. Extraction efficiencies of zinc, lead and iron at different temperatures

Temperature (°C)	Zn (%)	Fe (%)	Pb (%)
0	0.00	0.00	0.00
25	70.34	0.00	52.10
45	73.57	0.00	67.13
65	77.02	0.00	81.93
85	**83.16**	**0.00**	**95.39**

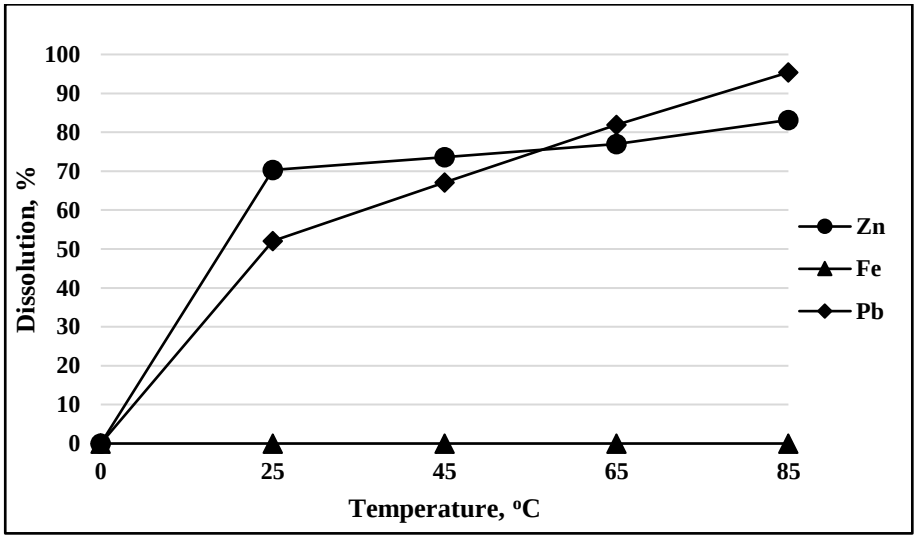


Figure 4. 9. Effect of temperature on zinc, lead, and iron extraction at 0.5 M NaOH; 0.2 M EDTA; 180 mins; S/L=1/10; 400 rpm.

The results, as expected, showed that temperature was directly proportional to the leaching rates of Pb and Zn. According to graph, the upward slope for Pb was steeper than that of Zn, which was an indication that the leaching rate for Pb was faster than that of Zn. At room temperature, Zn extraction was seen to be higher than that of Pb as it was around 70% while Pb was around 50%; but as the temperature was increased progressively, Pb extraction subsequently overtook that of Zn. The highest co-extraction of Zn and Pb were recorded at 85 °C with Pb at 95.39% and Zn at 83.16%. This was selected as the optimum temperature for this work.

e) Effect of time on dissolution efficiency

With NaOH +EDTA as lixiviant, time was varied in a short range in order to study its effect on the leaching efficiency of Pb, Zn, and Fe from the flotation tailing. Also, Fe stayed undissolved as temperature was increased. While the other parameters were kept constant, the leaching time was varied at: 30 mins, 60 mins, 120 mins, and 180 mins. Conditions for the experiments were: 0.5 M NaOH, 0.2 M EDTA, 85 ^{o}C, solid/liquid ratio 1/10, and stirring speed 400 rpm. The results of these experiments are shown in Table 4.10, and the graphical representation in Figure 4.10.

Table 4. 10. Extraction efficiencies of zinc, lead and iron at different durations.

Time (mins.)	**Zn Extracted (%)**	**Fe Extracted (%)**	**Pb Extracted (%)**
0	0.00	0.00	0.00
30	75.78	0.00	83.35
60	74.99	0.00	91.55
120	77.87	0.00	92.01
180	**83.16**	**0.00**	**95.39**

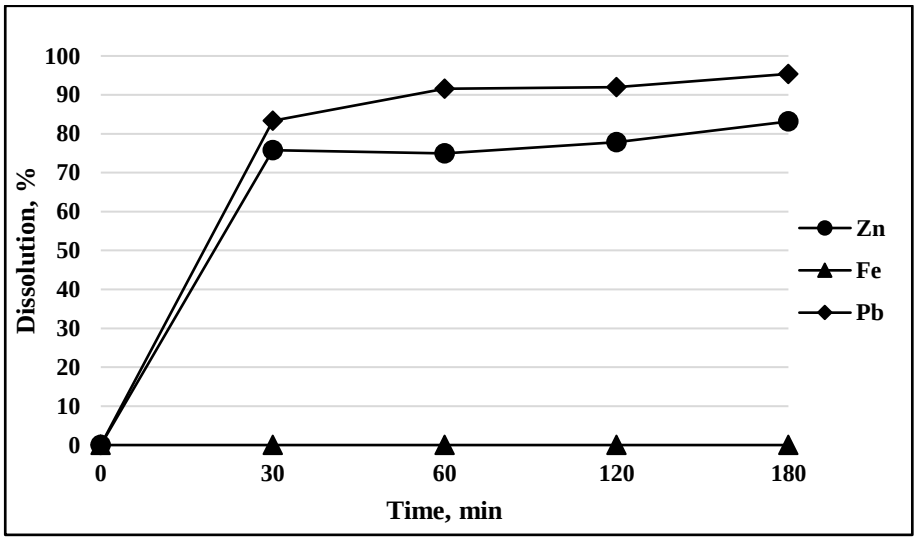


Figure 4. 10. Effect of time on zinc, lead, and iron extraction at 0.5M NaOH; 0.2M EDTA; 85^{o}C mins; S/L=1/10; 400rpm

According to the results, time did not have a considerable effect on the extraction of lead, zinc and iron, as expected. The graphs were almost linear, with just very minor fluctuations as time progressed. The highest Pb and Zn extraction were seen at 180 minutes with 95.39% and 83.16% respectively, therefore 180 mins was taken as the optimum leaching time for this work.

4.1.2. Organic Acid Leaching with EDTA only

Ethylenediaminetetraacetic acid (EDTA), an organic acid and a chelating agent which is biodegradable, was used as lixiviant to test its effect on the dissolution of Pb, Zn, and Fe. While time was varied, the other parameters were kept constant at 180 mins, 85 ^{o} C, solid/liquid ratio 1/10, and stirring speed 400 rpm. The results are shown in Table 4.11, and the graphical representation in Figure 4.11

Table 4. 11. Extraction efficiencies of zinc, lead and iron at different durations, at 0.2 M EDTA

EDTA Molarity (mol/L)	**Time (mins.)**	**Zn Extracted (%)**	**Fe Extracted (%)**	**Pb Extracted (%)**
0.2	0	0.00	0.00	0.00
0.2	30	76.65	7.37	27.68
0.2	60	77.51	9.35	28.04
0.2	120	80.69	10.03	28.75
0.2	**180**	**84.19**	**10.73**	**34.01**

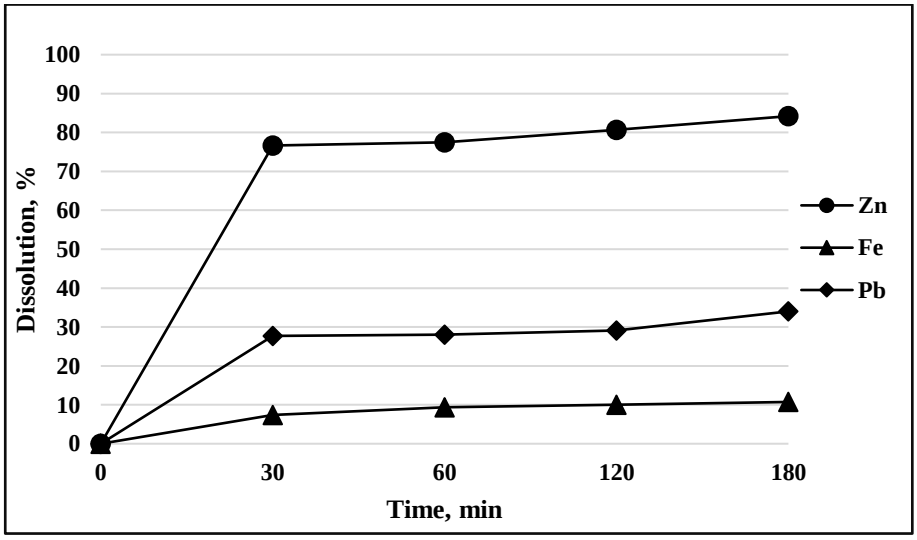


Figure 4. 11. Effect of time on zinc, lead, and iron extraction at 0.2 M EDTA; 85 ^{o}C mins; S/L=1/10; 400 rpm

The results indicated that co-dissolution of zinc, lead and iron occurs when EDTA is used. Compared to all the other metal dissolutions, zinc dissolved considerably, with 84.19% extraction achieved in 180 minutes. As for lead, the leaching rate was not as efficient as that of zinc, with 34.01% extraction achieved in 180 minutes, which was less than half of what zinc achieved in the same duration. Iron, unlike in the other alkaline experiments, was able to be dissolved by this

organic acid EDTA, but owing to EDTA's weak acidity, just 10.7% of iron was dissolved in 180 minutes. There was no selectivity at all in this experiment, and the order of metal dissolution was in this order: Zn > Pb > Fe. These results were consistent with the findings of (Hussaini et al., 2021a) and the reason all the parameters were not studied extensively using EDTA in this research, was because they have been studied by Hussaini et al., 2021 using the same sample, except for minor differences in temperature and the reagent concentrations. The reason why the experiment was carried out in the first place was for the sake of consistency, because the experimental conditions for this research determined above was 0.2 M EDTA and 85 ^{o}C.

STEP 1 CONCLUSION:

After all the chemical leaching tests were carried out using NaOH together with other additives and enhancers, as well as using the organic acid EDTA, taking into account the objective of this research which was to co-extract lead and zinc at their maximum leaching rates, the optimum conditions determined were: 0.5 M NaOH, 0.2 M EDTA, 85 ^{o}C temperature, S/L: 1/10, stirring rate: 400 rpm, time: 180 minutes. At these optimum conditions, the desired metals, lead and zinc were co-leached at 95.4% and 83.2% respectively, while the main impurity Fe was 0% leached in the solution, and this undissolved Fe remained in the residue after filtration. This residue was dried in the oven and sent for XRD analysis which confirmed the presence of goethite (FeO(OH)) as well as calcite ($CaCO_3$) in the residue.

At these optimum conditions, the experiments were scaled up to provide sufficient feed for the next step (step 2) which is the precipitation step. Figure 4.12 shows the proposed flowsheet of the alkaline leaching with NaOH and EDTA.

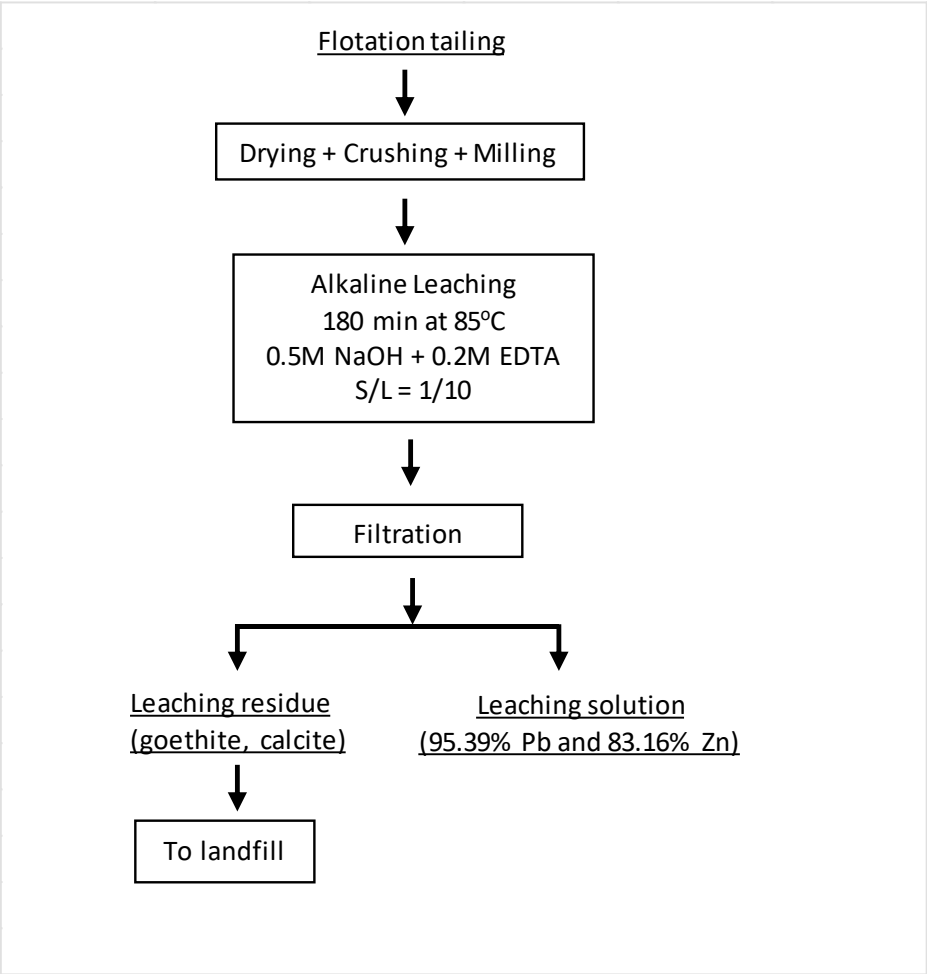


Figure 4. 12. Schematic flowsheet for the co-dissolution of Pb and Zn from oxidized Pb-Zn flotation tailing by one-step alkaline leaching.

4.2. STEP II: Lead and Zinc separation through selective precipitation of lead

After the objective of the first step (which was to co-leach Zn and Pb at maximum co-dissolution) was achieved and scaled up, the next objective of step 2 was to selectively separate Pb from Zn through a precipitation process. Usually, cementation of Pb by the addition of zinc powder is employed, but this method is most effective in acidic medium. On the contrary it is ineffective in alkaline medium, therefore precipitation is mostly employed. (Zhao and Stanforth,

2000). For the precipitation process, there exists a range of potential precipitants that can be used for the selective precipitation of Pb from alkaline Zn solution. The popular ones include sodium carbonate, sodium phosphate, sodium sulfate, and sodium sulfide (Youcai and Stanforth, 2001). Youcai and Stanforth (2001) did research to find out which among these precipitants were the most effective and they concluded that sodium sulphide was the most effective precipitant in the selective precipitation of Pb from alkaline Zn solution, since the other precipitants were unable to form significant precipitates. Other findings from the literature are also consistent with this, making the use of sodium sulphide for Pb -Zn separation through selective precipitation very applicable. This was also a basis for the selection of sodium sulphide as the precipitant for the precipitation experiments. From the precipitation using Na_2S, the following Eq 4.2 can be used:

$$Pb^{2+}_{(aq)} + Na_2S_{(s)} \rightarrow PbS_{(s)} + 2Na^{+} \qquad (4.\ 2)$$

Other researchers say that the probable components of the precipitate could be largely PbS with some minor phases of Na_2PbS_2, but the precipitate of our experiments after an XRD analysis showed only numerous high peaks of PbS.

The results of the experiments carried out to investigate the effect of Na_2S/Pb weight ratio, effect of time and temperature have been given in this section.

4.2.1. Effect of Na_2S/Pb weight ratio on selective precipitation of lead

The experiments to find out the effect of Na_2S/Pb weight ratio on the precipitation of lead and zinc were carried out. This is the most important parameter to investigate when attempting to selectively precipitate lead from zinc. Due to the similar chemical behaviour of Pb and Zn in alkaline environment, both Pb and Zn will precipitate upon the addition of Na_2S, but this happens

consecutively, beginning with Pb. When Pb precipitation has been completed, then Zn precipitation starts at once. One of the reasons why Pb precipitates first could be owing to the relative insolubility of PbS compared to ZnS (Zhao and Stanforth, 2000).

Our objective was to selectively precipitate lead at its maximum, without the concomitant loss of Zn. To determine at what point this can be realised, the weight ratio experiments come in handy. From the literature, the weight ratio of 1.8 has been seen to be the ratio at which there is maximum Pb precipitation and minimum concomitant Zn loss. (Liu et al., 2011; Youcai and Stanforth, 2001; Zhao and Stanforth, 2000), so we used 1.8 as and our reference, and tested values that were around 1.8. Six different weight ratios tested were: 1.2, 1.4, 1.6, 1.8, 2.0, and 2.2 under the conditions of 60 minutes and 50 ^{o}C. The results are shown in Table 4.12 and the graphical representation in Figure 4.13.

Table 4. 12. Percentage of Zn and Pb precipitations at different weight ratios.

Na_2S/Pb weight ratio	**Precipitation of Zn (%)**	**Precipitation of Pb (%)**
1.2	15.34	91.52
1.4	**18.05**	**99.92**
1.6	22.82	99.95
1.8	38.59	99.93
2.0	43.39	99.93
2.2	52.02	99.93

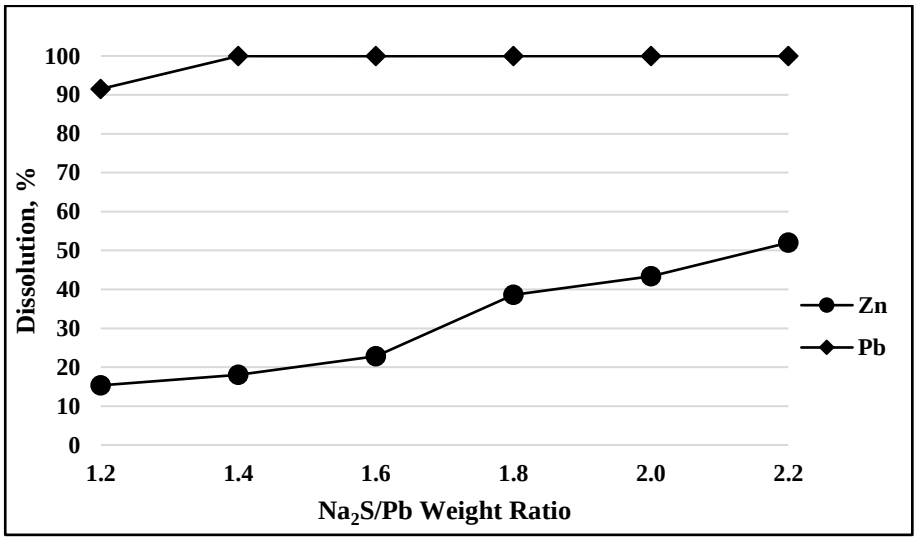


Figure 4: 13. Effect of Na_2S/Pb weight ratio on the precipitation rates of Pb and Zn (Conditions: 60 mins, 50 ^oC).

The results showed that at a weight ratio of 1.2, more than 90% Pb had already precipitated, and further increase in this ratio led to almost 100% Pb precipitation. On the other hand, Zn progressively precipitated as the weight ratio was increased in the range of 1.2 and 2.2 weight ratio. From the results, Na_2S/Pb weight ratio of 1.4 was selected as optimum, since at this point, almost 100% Pb and less than 20% Zn precipitation was attained.

4.2.2. Effect of temperature and time on selective precipitation of lead

After the determination of the weight ratio, different temperatures and durations were tested to find out which of them is most appropriate for these experiments. Since it was observed that the colour change of the PLS from gold to black was immediate, testing shorter time periods for these experiments was considered. The durations tested were 10 mins, 30 mins, and 60 mins, while the temperatures tested were 25 ^oC (room temperature) and 50 ^oC. The results are shown in Table 4.13 and the graphical representation in Figure 4.14.

Table 4. 13 Percentage of Zn and Pb precipitations at different durations and temperatures.

Time, mins	Temperature(ºC)	Zn precipitation(%)	Pb Precipitation(%)
10	**25**	**18.15**	**99.99**
	50	24.03	99.97
30	25	20.82	99.98
	50	25.86	99.85
60	50	18.05	99.92

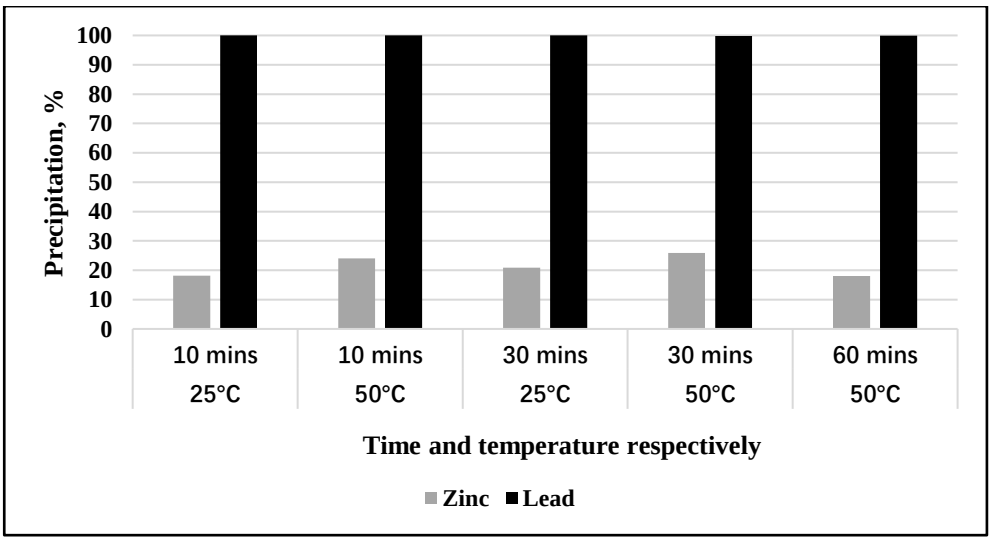


Figure 4. 14: Effect of time and temperature on the precipitation rates of Pb and Zn, at Na_2S/Pb weight ratio of 1.4

From the results, it was seen that higher temperatures favoured Zn precipitation, while it had a negative effect on Pb precipitation. In the same time frame, when temperature was increased from room temperature to 50 ºC, Zn precipitation increased while Pb precipitation decreased. Also it was seen that longer durations favoured Zn precipitation while it had a negative effect on Pb precipitation. At the same temperature, when time was increased from 10 minutes to 30 minutes, Zn precipitation increased while Pb precipitation decreased. This implied that in order to obtain maximum Pb and minimum Zn precipitation, minimal time and temperature are required. This also serves as an economical advantage when less time and lower temperature are employed. The

optimum time selected was 10 minutes while the optimum temperature was room temperature (25^{o}C) where 99.99% Pb and 18.15% Zn precipitation were obtained.

STEP 2 CONCLUSION:

After all the experiments carried out in this precipitation step, the optimum conditions decided were: Na_2S/Pb weight ratio of 1.4, duration of 10 minutes and temperature of 25 ^{o}C; and under these conditions, 99.99% Pb and 18.15% Zn precipitation were obtained. The precipitate was dried and sent for XRD, and the analysis confirmed that most of the precipitate was made up of galena (PbS), as all the peaks indicated galena. Also the solution was analysed with AAS and less than 1% Pb was identified. The precipitation experiments under these conditions were then scaled up to provide sufficient feed for the next step which is the bioleaching step (Step 3). Figure 4.15 shows the proposed flowsheet for the selective precipitation of lead using Na_2S.

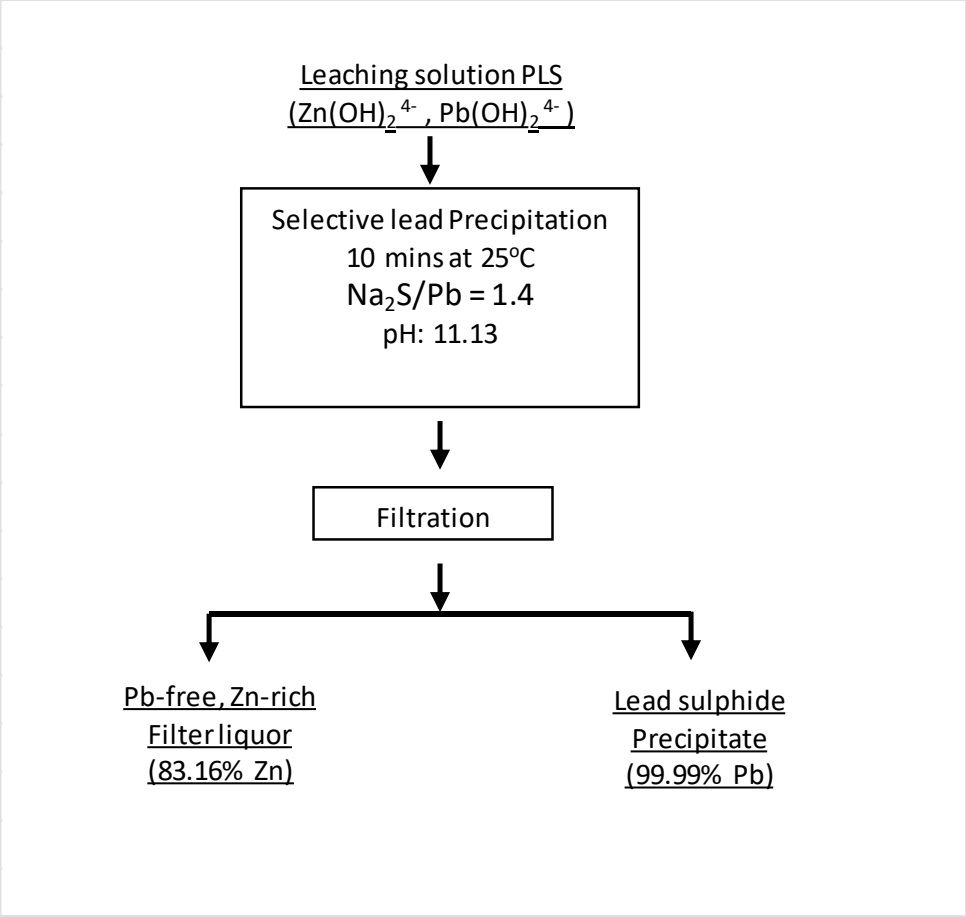


Figure 4. 15. Schematic flowsheet for the separation of lead from zinc by selective precipitation of Pb using Na_2S,

4.3. STEP III: Bio-Leaching Experiments for Lead Recovery from Sulphide Precipitate

In this step, bioleaching experiments were carried out to extract Pb from the sulphide precipitate that was obtained in step 2 (precipitation step). This precipitate as we saw earlier in the characterization section, contains about 25% Pb, with about 1% Zn. Pyrometallurgical methods are usually the way out for these kinds of precipitates, as they could be sent for smelting, but these methods are not cost-effective and they are not environmentally friendly. For this reason, bioleaching was adopted as the method to extract Pb from this sulphide precipitate. Using the

bacterium *Leptospirillum ferrooxidans,* experiments were carried out and the effect of parameters such as pulp density, pH and time, on the extraction efficiencies were investigated.

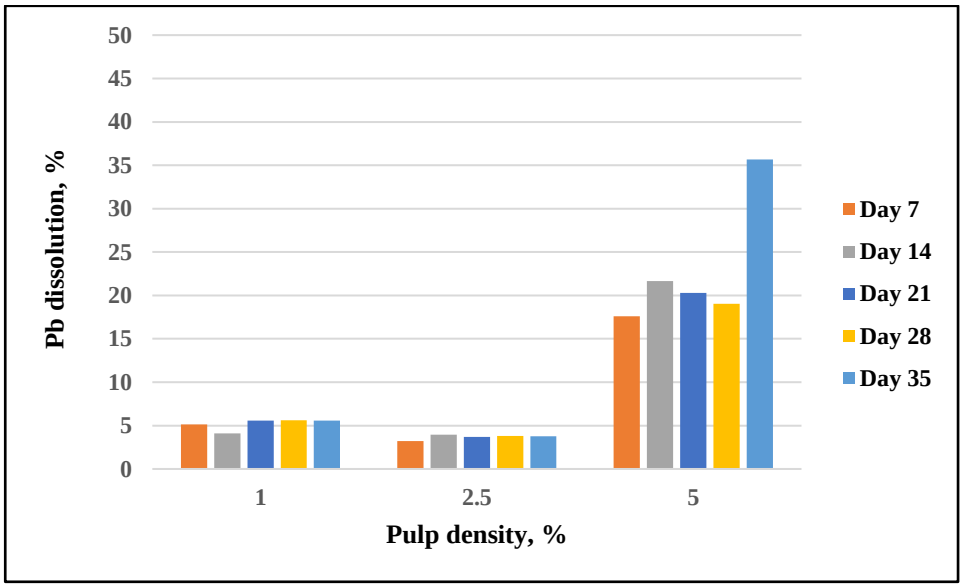
4.3.1. Lead extraction

4.3.1.1. Effect of pulp density on Pb extraction

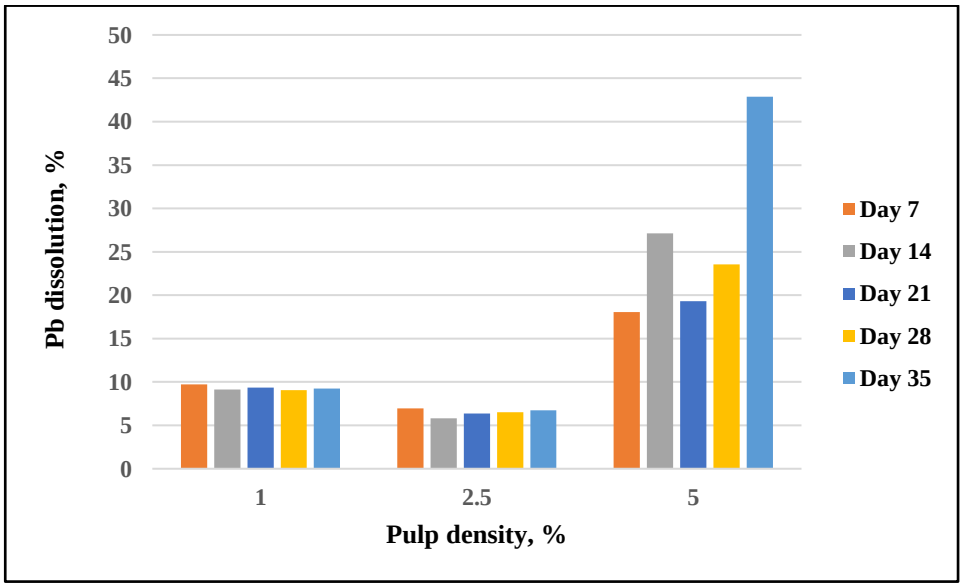
The experiments to find out the effect of pulp density on Pb dissolution were carried out over a 35-day period, at three different pHs: 1.6, 1.8, and 2.0. At each of these pHs, 3 pulp densities were tested which were 1%, 2.5% and 5%. The results are presented in Table 4.14 and the graphical representation in Figure 4.16 (a), (b) and (c).

Table 4. 14. Lead extraction efficiencies at different pHs and pulp densities over a 35-day period

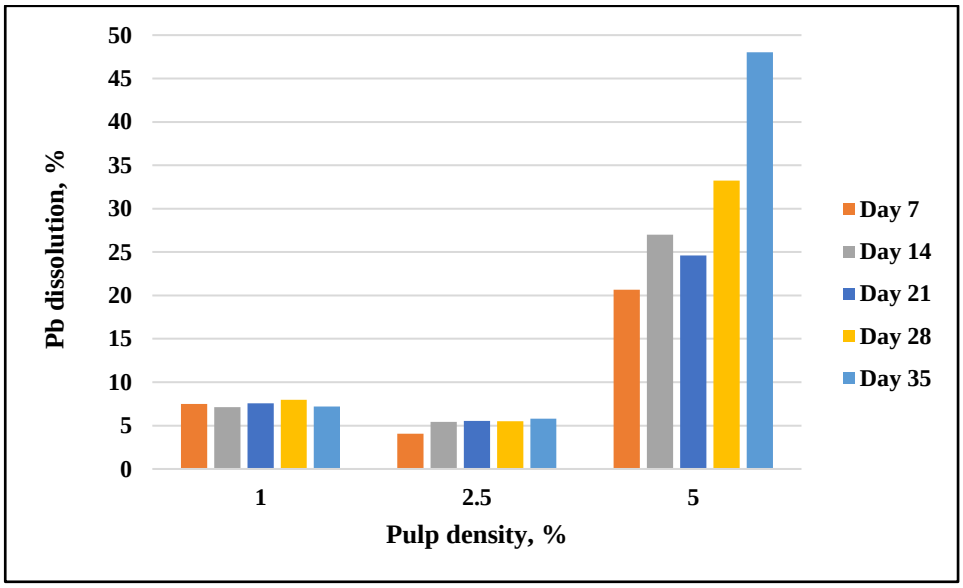
pH	Pulp density (%)	Day 0	Day 7	Day 14	Day 21	Day 28	Day 35
		Pb (%)	Pb (%)	Pb (%)	Pb (%)	Pb (%)	Pb (%)
1.6	1	0	5.15	4.09	5.59	5.61	5.58
	2.5	0	3.22	3.96	3.68	3.81	3.76
	5	0	17.58	21.66	20.3	19.05	35.66
1.8	1	0	9.72	9.12	9.36	9.05	9.24
	2.5	0	6.94	5.82	6.35	6.5	6.74
	5	0	18.05	27.13	19.3	23.56	42.86
2.0	1	0	7.48	7.14	7.56	7.98	7.2
	2.5	0	4.08	5.42	5.53	5.49	5.8
	5	0	20.67	27.01	24.6	33.24	48.03


Pb dissolution, %
50
45
40
35
30
25
20
15
10
5
0
1
2.5
5
Pulp density, %
Day 7
Day 14
Day 21
Day 28
Day 35

(a) pH 1.6


Pb dissolution, %
50
45
40
35
30
25
20
15
10
5
0
1
2.5
5
Pulp density, %
Day 7
Day 14
Day 21
Day 28
Day 35

(b) pH 1.8



(c) pH 2

Figure 4.16. Effect of pulp density on Pb extraction rate at pH (a)1.6 (b)1.8 and (c)2.0 over a 35-day period.

From the results, it can be seen that the trends of pulp densities from 1% to 5% across all the three pHs are quite very similar. The pulp density at 1% and 2.5% across all the pHs (pH 1.6, 1.8 and 2) were seen to yield very poor Pb extraction results. Over a 35-day period, the results for 1% and 2.5% pulp density never exceeded 10% Pb extraction. The probable reason could be due to the very low mass of sample in the solution (0.5 g for 1% and 1.25 g for 2.5%) which could have been mistakenly taken out of solution in bits during weekly collection for analysis, maybe due to insufficient settlement of the solution before collection of the supernatant.

However, the case was a bit different for the pulp density of 5% across all the three pHs. At pH 1.6, the weekly pulp densities of 5% were found to yield Pb extractions between 15% and 25% within a 28-day period. However, on the 35th day, the Pb extraction rose to over 35%. Similarly, at pH 1.8, the weekly pulp densities of 5% yielded Pb extractions between 15% and 30% within a 28-day period, and on the 35th day, the Pb extraction significantly increased, and

almost attained 45%. At pH 2.0, pulp density 5%, Pb extractions were between 20% and 35% within a 28-day period, with a noticeable increase on the 35th day to almost 50% Pb extraction.

It can be concluded from these results that higher pulp densities favour Pb extraction, as 5% showed better results compared to 1% and 2.5%. But in contrast, many researchers have found that higher pulp densities led to lower extraction yields (Abhilash et al., 2013; Makita et al., 2004; Olubambi et al., 2008), and they explained that this could be as a result of increase in friction between particles as pulp density increases which could cause mechanical damage to the bacterial cell. From the study of Olubambi et al., 2008, the pulp densities tested were %, 10%, 15%, and 20% (w/v) on the bioleaching of sulphide ores. 5% pulp density gave the maximum extraction yield while 20% gave the least, which led to their conclusion that increase in pulp density leads to decrease in extraction yields. While their pulp densities ranged from 5% to 20%, ours ranged from 1% to 5%, so we are assuming that the mass of operation was very small in our case to make a strong conclusion. Testing higher pulp densities in this work could change the narrative.

4.3.1.2. Effect of pH on Pb extraction

The experiments to find out the effect of pulp density on Pb dissolution were carried out over a 35-day period, at three different pHs: 1.6, 1.8, and 2.0. At each of these pHs, three pulp densities were tested which were 1%, 2.5% and 5%. The results are presented in Table 4.14 and the graphical representation in Figure 4.14 (a), (b) and (c).

In order to find out the effect of pH on the extraction of Pb, experiments were carried out over a 35-day period, with weekly collection of the sample over this period. The pHs tested were 1.6, 1.8, and 2.0, while only the pulp density of 5% was considered in these experiments, as the other pulp densities had demonstrated very poor Pb extraction.

The weekly collection of small quantities for analysis caused fluctuations in pH in the experiments, which led to the establishment of new experiments that were conducted and let to stay for the period of 42 days without any weekly collection or touching. At the end of the 42 days, there was a clearer analysis and more reliable results obtained. The result is shown in table 4.15 and the graphical representation in Figure 4.17.

Table 4.15. Pb extraction efficiencies at different pHs, at 5% pulp density, after a 42-day period

pH	Pulp density(%)	Pb extraction(%)
1.6	5	78.69
1.8	5	100.00
2	5	95.65

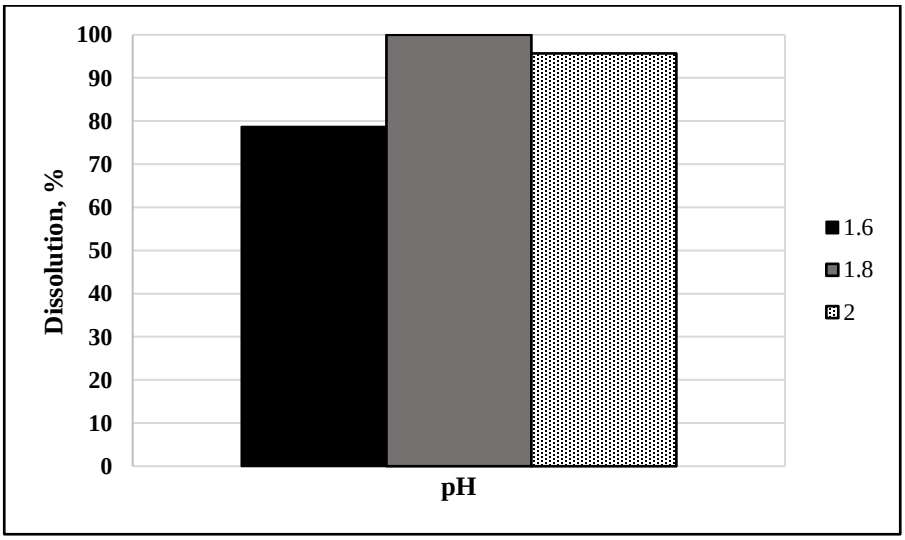


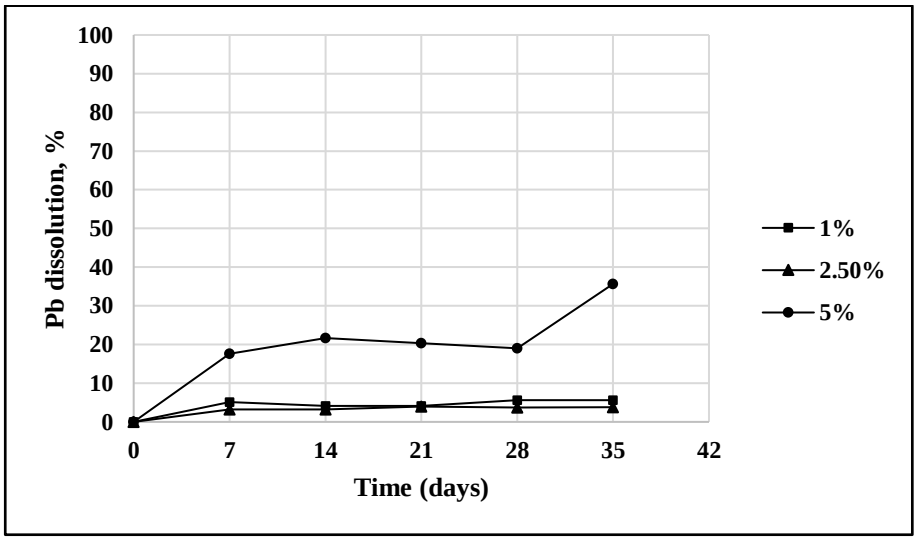
Figure 4.17. Effect of pH on Pb extraction at 5% pulp density, after a 42-day period

The results showed that the highest Pb extraction occurred at pH 1.8, over a 42-day period. At this pH, 100% Pb was extracted in 42 days, while at pH 1.6, 78.69% and pH 2.0, 95.65% Pb was extracted. These results were very consistent with the results of previous works in the

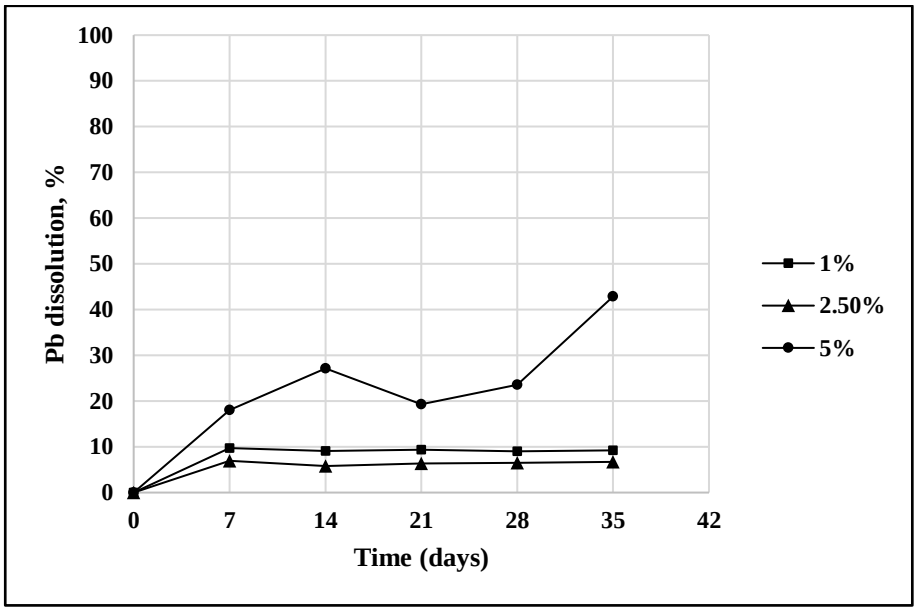
literature, as pH 1.8 has been seen to be the most appropriate pH of operation of *Leptospirillum ferrooxidans* (Nural Yaman et al., 2020)

4.3.1.3. Effect of time on Pb extraction

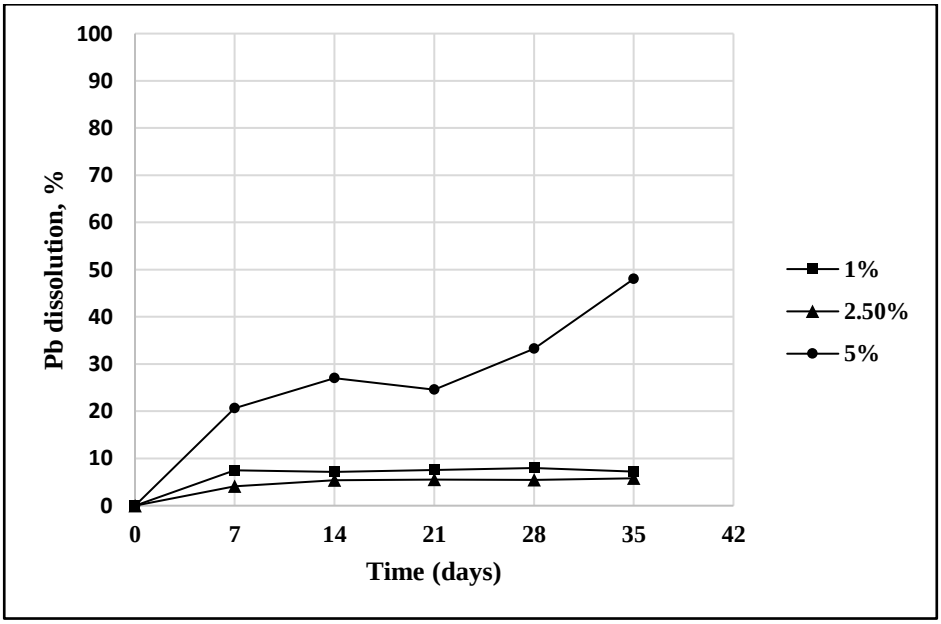
The effect of time on Pb extraction was investigated at three different pHs (pH 1.6, 1.8, and 2.0) and three different pulp densities (1%, 2.5%, and 5%). The experiments were progressive, from day 1 to day 35, and small quantities of the samples were collected on a weekly basis to follow-up the behaviour and trend of extraction. The results are in Table 4.14 and the graphical representation in Figures 4.18 (a), (b) and (c).



(a) pH 1.6



(b) pH 1.8



(c) pH 2.0

Figure 4.18. Effect of time on Pb extraction rate at pH (a)1.6 (b)1.8 and (c)2.0 over a 35-day period.

According to the results, it showed that time had little or no effect on the Pb extraction of samples with 1% and 2.5% pulp density at all the three different pHs, The Pb extractions at these said pulp densities were always between 0% and 10% from day 1 right till the 35th day, and their graph representations were plateaued from day 7 till the last day. Just as explained before, the very low mass in these said pulp densities could have influenced these poor results (0.5 g for 1% and 1.25 g for 2.5%), and over time, bits of the sulphide precipitate could have been removed during weekly collection of supposed supernatant for analysis, making progressive improvement of the bioleaching experiments very difficult

However, time had a significant effect on the Pb extraction of samples with pulp density of 5% at all the three pHs. At 5% pulp density, the trend and behaviour of the graphs as time progresses is similar for all three pHs. A significant observation was the dip on day-21 across all the pHs, followed by a significant rise in Pb extraction on day-35. The trend is not very predictable, as it is a biological experiment, and many things can happen in-between. The highest Pb extraction was recorded on day-35 at pH 2.0, accounting for almost 50% Pb extraction.

4.3.2. Zinc Impurity extraction

From the aqua regia analysis of the sulphide precipitate, 1.25% Zn impurity was identified, therefore during the bioleaching experiments and the weekly AAS analyses, Zn extraction was checked as well. Figure 4.19 shows the Zn extraction over a 35-day period.

From the result, it was seen that as early as the first week, all (100%) of the zinc in the sulphide precipitate had been extracted. This was probably due to the fact that the amount of zinc in the precipitate was only 1%, and so the extraction was almost immediate. The effect of pH, pulp density, and time did not change for both the test and the control experiments; this is why there

was no need treating the parameters differently, because the graph produced was the same for all conditions.

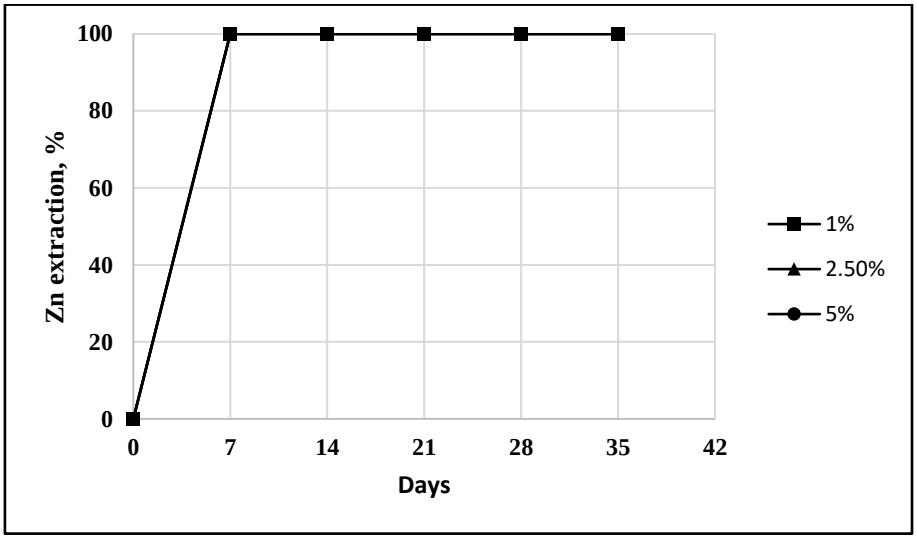


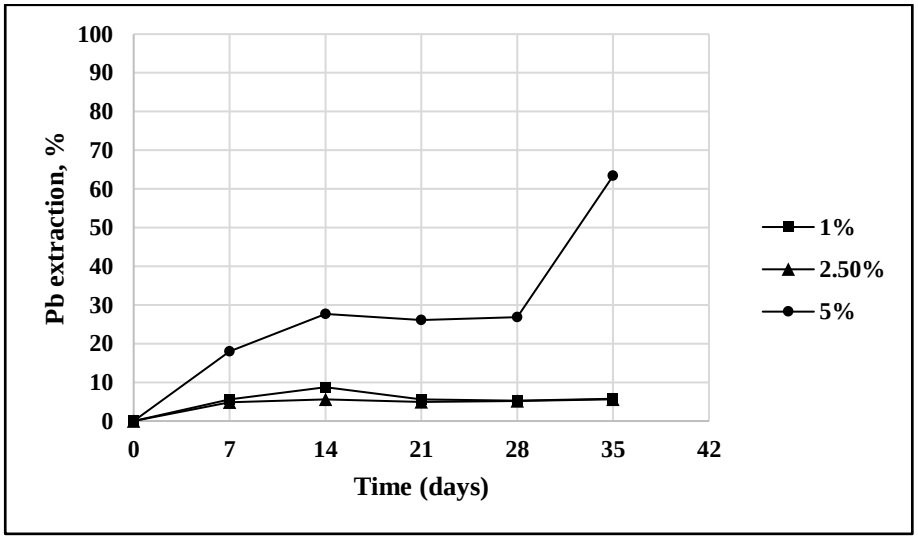
Figure 4.19. Effect of time on the extraction of Zn impurity (Same graph at all pHs, and all pulp densities. Same graph too for control experiment)

4.3.3. Control Experiments

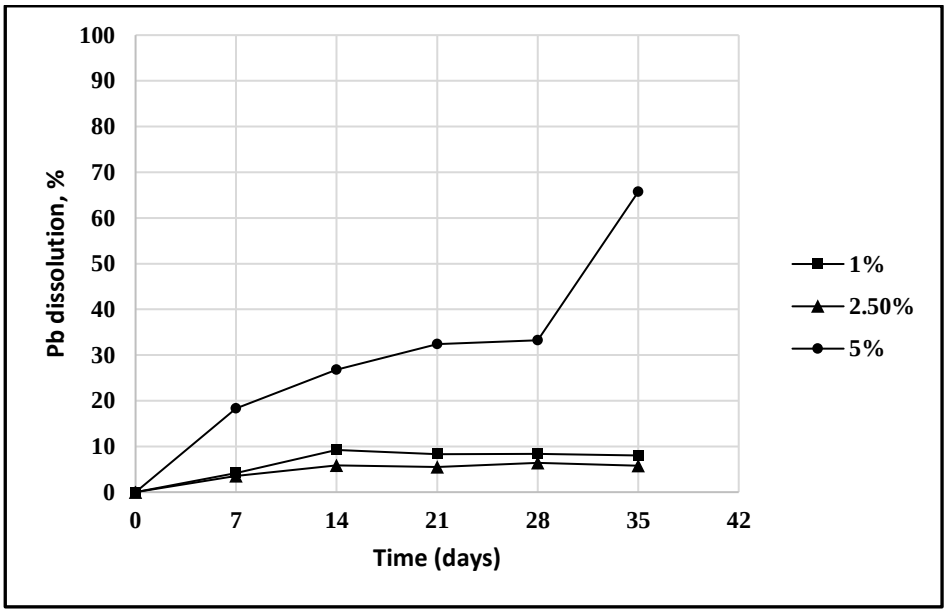
For each of the experiments that were carried out, a control experiment was done, to be able to evaluate the activity of the bacterium during the bioleaching time. The control experiments had everything set up just as the test experiments, but the difference was that the control experiments did not contain the bacterium *Leptospirillum ferrooxidans.* The results of these control experiments are provided in Table 4.16 and the graphical representations, as a function of time, on Figures 4.20 (a), (b) and (c).

Table 4. 16. Lead extraction efficiencies for control experiments at different pHs and pulp densities over a 35-day period.

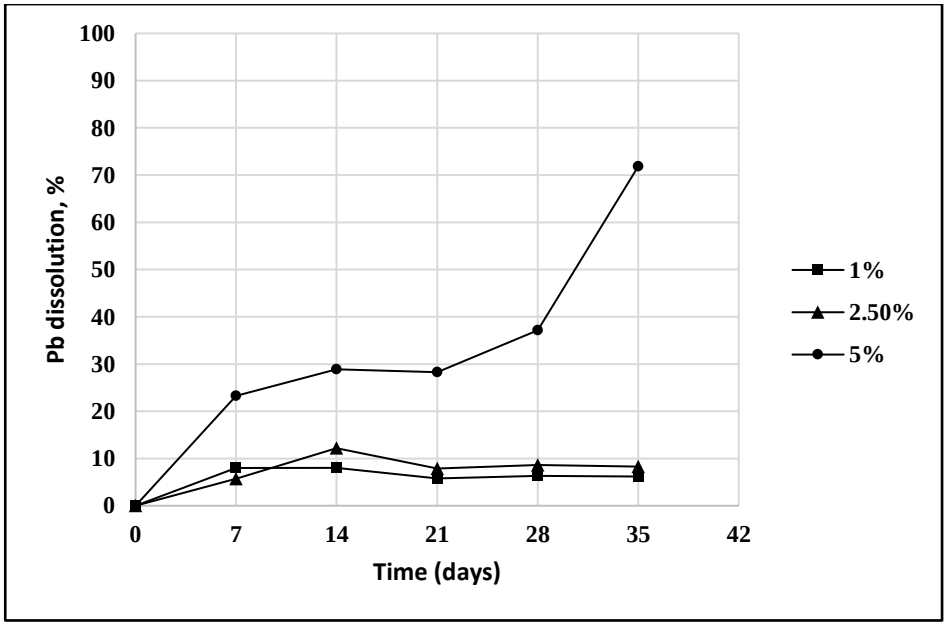
pH	Pulp density (%)	Day 0	Day 7	Day 14	Day 21	Day 28	Day 35
		Pb (%)	Pb (%)	Pb (%)	Pb (%)	Pb (%)	Pb (%)
1.6	1	0	5.59	8.74	5.6	5.3	5.74
	2.5	0	4.84	5.57	4.9	5.2	5.61
	5	0	17.98	27.65	26.1	26.83	63.37
1.8	1	0	4.19	9.23	8.33	8.41	8
	2.5	0	3.55	5.84	5.47	6.41	5.79
	5	0	18.29	26.78	32.41	33.26	65.7
2.0	1	0	8.00	7.99	5.81	6.34	6.19
	2.5	0	5.69	12.19	7.89	8.64	8.27
	5	0	23.25	28.91	28.24	37.18	71.83



(a) pH 1.6



(b) pH 1.8



(c) pH 2.0

Figure 4.20. Effect of time on Pb extraction rate of control experiment at pH (a)1.6 (b)1.8 and (c) 2.0 over a 35-day period.

From the results, it shows clearly that the control experiments had a better Pb extraction yield than the test experiments. This was unexpected, as the highest Pb extraction was recorded at 71.83%, at 5% pulp density, in 35 days in the absence of bacteria, while on the other hand under the same conditions, but in the presence of bacteria, 48.03% Pb extraction was obtained.

These results implied that the presence of bacteria instead inhibited the extraction of Pb, rather than enhancing it. Issues related to inhibited Pb extraction during bioleaching processes have also been observed severally in the literature. Some researchers say it is owing to the fact that precipitates are formed during the bioleaching process, and these precipitates coat the particles so much so that bacterial access to the particle is hindered, leading to a slow-down in the extractability (Rouchalova et al., 2020). Another issue in this type of bioleaching is that the bacterium is not receiving enough oxygen supply for its proper functioning. Auerbach et al., (2019) suggested that the low Pb extraction was due to Pb precipitation as insoluble lead sulphate, in the presence of sulphate ions (Auerbach et al., 2019). This shows from our experiments that it could be likely the same case, as insoluble lead sulphate is precipitated, inhibiting Pb extraction.

STEP 3 CONCLUSION:

All the experiments and their control experiments demonstrated the inefficiency of the bacterium *Leptospirillum ferrooxidans* on the extraction of Pb from the sulphide precipitate. To improve on this situation, a mixed culture could be employed, that is, another bacterium combined with *Leptospirillum ferrooxidans* to achieve a better extraction yield (Conić et al., 2014), or rather a completely different bacterium could be employed to investigate its effect on Pb extraction. Figure 4.21 shows the proposed flowsheet for the bioleaching of the lead sulphide precipitate.

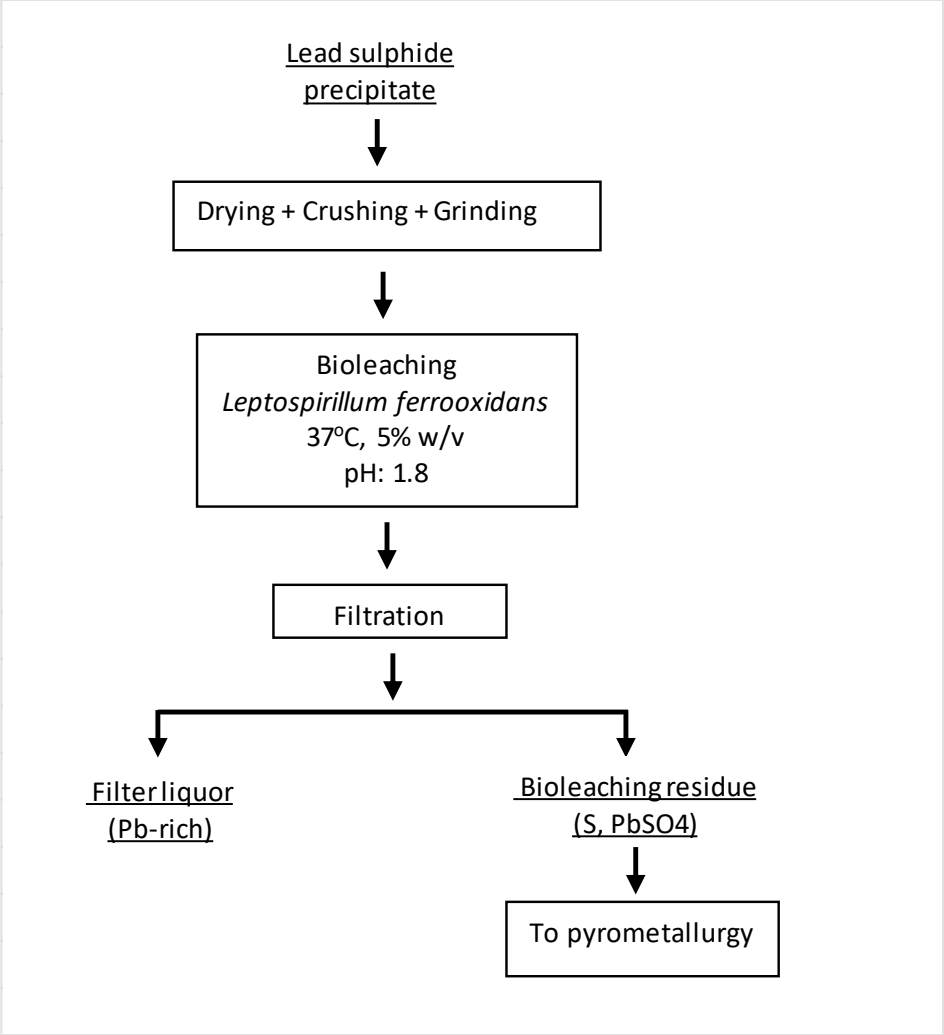


Figure 4. 21. Schematic flowsheet for the bioleaching of lead sulphide precipitate using *L. ferrooxidans*.

5. FINAL ASSESSMENT

5.1. Flowsheet Generation

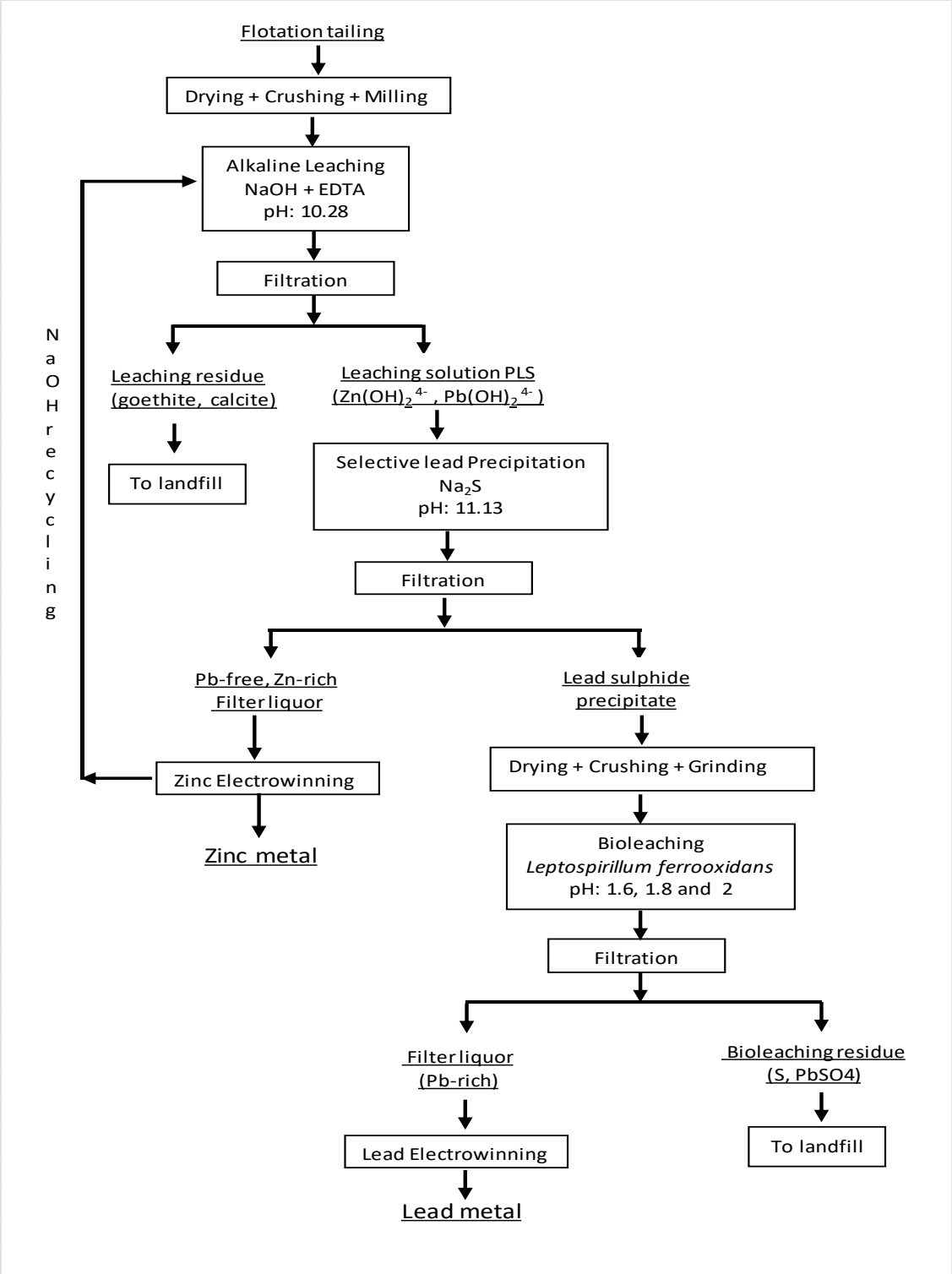


Figure 5. 1. Final schematic flowsheet for the preparation of Zn and Pb concentrates from oxidized Pb-Zn flotation tailing by one-step alkaline leaching, one-step precipitation and bioleaching.

5.2. Cost Analysis and Metallurgical Performance

Table 5. 1. Hydrometallurgical steps, their reagent consumptions, and metallurgical performance.

	Reagent(s)	Reagent Consumption at Optimum conditions	Metallurgical Performance
STEP 1 (Leaching)	NaOH + EDTA	0.5 M NaOH, 0.2 M EDTA, 1/10 S/L, 85 ^{o}C, 180 mins	- Tailing grade: 5.77% Zn, 7.5% Pb, 21.3% Fe
		NaOH Consumption: 200 kg/t tailing	- Recovery: 95.4% Pb, 83.2% Zn, 0% Fe
		EDTA Consumption: 744.48 kg/t tailing	- 71.55 kg/t Pb, 48.006 kg/t Zn, 0 kg/t Fe
			- 4.6908 g/L Zn, 8.6691 g/L Pb
STEP 2 (Precipitation)	Na_2S	1.4 Na_2S/Pb weight ratio, 10 mins, 25 ^{o}C	- PLS content : 4.6908 g/L Zn, 8.6691 g/L Pb
		Na_2S Consumption: 5 g Na_2S/L PLS 5g Na_2S/100 g tailing, which is 50 kg Na_2S/t tailing	- Recovery: 99.99% Pb precipitation - 71.54 kg/t Pb (solid)

Table 5. 2. Prices of reagents, and consumption/ tonne of tailing

Reagents	Reagent consumption	Prices (www.alibaba.com)	How much will be spent on one tonne of tailing
NaOH	0.2 t NaOH/t tailing	233 – 400 $/t	**46.6 – 80 $**
Na_2S	0.05 t Na_2S/t tailing	300 – 400 $/t	**15 – 20 $/t**

Table 5. 3. Prices of metals

Prices of metals	www.lme.com (2022)	Revenue with 100% recovery
Zn metal	2970 $/t	1 t * 0.0577% Zn * 2.97$/t
Pb metal	2435$/t	1t * 0.075% Pb * 2.435

In an ideal situation where 100% recovery was attained, 57.7 kg and 75 kg of zinc and lead respectively will be recovered from 1 ton of the treated flotation tailing. According to the London Metal exchange pricing, 1 tonne of waste is valued at $ 437. A couple of mining companies in the Kayseri region sell their waste at $ 30 – 50/t to China and Iran. This is an indication that the hydrometallurgical recycling of the wastes by the companies themselves will be far more profitable for the company. These recycling technologies are also necessary for protecting the environment, for secondary metal production and for job creation. If the flotation tailing contains gold, it will even be of higher value.

6. CONCLUSION AND RECOMMENDATIONS

Within the scope of this study, the flotation tailing obtained from OREKS Mine tailing dam in Kayseri, containing 5.77% zinc and 7.50% lead and 21.3% iron, was leached and purified, and from the experiments, the following conclusions were obtained:

An efficient Zn and Pb extraction hydrometallurgical (alkaline leaching) route has been developed, using NaOH and EDTA as leaching agents, under the optimum conditions: 0.5 M NaOH, 0.2 M EDTA, 85 ^{o}C temperature, S/L: 1/10, stirring rate: 400 rpm, time: 180 minutes, yielding 95.39% Pb and 83.16% Zn. It was seen that an increase in temperature will improve on Pb and Zn extraction while an increase in EDTA above 0.2 M will increase Zn extraction but greatly reduce Pb extraction. Fe extraction too starts which is not favourable for the experiments. This route is seen to be technically feasible for the co-extraction of Pb and Zn

A purification step was carried out to separate lead from zinc using selective precipitation. After selective precipitation with Na_2S, 99.9% Pb is removed from the PLS as PbS, and the Pb-free solution containing about 80% Zn can be taken for electrowinning, where more than 99.5% Zn metallic powder could be obtained. The weight ratio parameter played a very important role in the precipitation experiments, since both Pb and Zn have similar chemical properties in alkaline medium and will both be precipitated by Na_2S. However, it happens consecutively, starting with Pb, and as soon as Pb's precipitation has been exhausted, Zn precipitation begins. Therefore, it is important to take note of the weight ratio which gives maximum Pb precipitation and minimum Zn precipitation. The optimum weight ratio for the experiments was a Na_2S/Pb weight ratio of 1.4. The other optimum conditions were: duration of 10 minutes and temperature of 25 ^{o}C. This step was also concluded to be both technically and economically beneficial with 15–20 $ worth Na_2S spent for 1 tonne of tailing.

The lead sulphide precipitate obtained from the precipitation experiment after being dried, crushed and ground, was introduced into the bioleaching stage with the objective of obtaining high Pb extractions using the mesophilic bacterium *L. ferrooxidans.* After variating the parameters of pH, pulp density and time, not up to 50% Pb was extracted in all the experiments. In contrast, the corresponding control experiment gave 78.13%, which was far higher than the test experiments. It was concluded that the bacterium *L. ferrooxidans* was not an appropriate microorganism for the bioleaching of galena precipitate, reasons why a cost analysis was not made in this step. For future investigations, a mixed culture of *L. ferrooxidans,* together with another microorganism is being proposed.

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