A LIFE CYCLE PERSPECTIVE FOR HYDROMETALLURGICAL AND BIOHYDROMETALLURGICAL METAL RECOVERY FROM WEEE

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Submitted to the Institute of Environmental Sciences
in partial fulfillment of the requirements for the degree of
Master of Science
in
Environmental Technology

Boğaziçi University
2019

ACKNOWLEDGEMENTS

This thesis was completed with the kind support and help of many individuals; I would like to extend my sincere gratitude to all of them. First, I would like to thank my family for their support during a troubling time and encouraging me to finish my degree. I would like to thank my thesis advisor, Prof. Dr. Nadim K. COPTY for his constant support and help throughout my time in institute. Assist. Prof. Dr. Mehmet Ali Küçüker also provided constant support and guidance throughout the study; I would like to thank him. I also would like to thank Tubitak project partner and thesis jury Prof. Dr. Burak Demirel.

This study use original experiment data obtained and created by a Tubitak project, “Elektronik Atıklardan Nadir Toprak Elementleri ve Değerli Metallerin Geri Kazanımı için Biyoteknolojik Yaklaşım” (IntenC). Tubitak funded the project (Number 113Y011). I would like to thank IntenC project partners: Prof. Dr. Ata Utku Akçil, Prof. Dr. Turgut T. Onay, Prof. Dr. Orhan Yenigün, Prof. Dr. Hacı Deveci, Assist. Prof. Dr. Hasan Çiftçi, Assist. Prof. Dr. Ersin Yener Yazıcı, Merve Tunalı and Ceren Erüst.

I would like to thank German partners of IntenC project, Prof. Dr. Ing. Kerstin Kuchta, Benedict Buschspies, Dr. Ing. Nils Wieczorek and Dr. Anne Rödl. I would like to specially thank Dr. Anne Rödl for providing support and guidance at a difficult time. Environmental Engineering and Energy Economy (IUE) of Technical University of Hamburg (TUHH) kindly provided commercial LCA database and software.

I would like to thank Marco Villares for sharing his thesis at an early stage of my study. His research was the first study regarding LCA of metal bioleaching at the time and provided guidance.

I would like to thank COST action for reimbursing my two trips to Germany. The author would like to acknowledge the contribution of the COST Action ES1407

ABSTRACT

A LIFE CYCLE PERSPECTIVE FOR HYDROMETALLURGICAL AND BIOHYDROMETALLURGICAL METAL RECOVERY FROM WEEE

Rare earth elements (REEs) are being employed in an increasing number of critical or widely popular consumer/ industrial products leading to increase in their demand particularly in the last few decades. Since almost all of REEs are produced in China, the European Commission and US energy department have identified REEs as critical elements and have directed special efforts to obtain sustainable resources of REE. End of life consumer electrical products contain significant amounts of metals and plastics. Thus the aim of this study is focused on recycling metals from waste electric and electronic equipment (WEEE). WEEE contains high amounts of base metals, precious metals and REEs. The concentration of metals in waste streams is higher than that of natural ores. Current recycling methods consume high amounts of energy and chemicals. Economically feasible industrial facilities (waste incineration) perform poorly for environment. In this study life cycle assessment (LCA) of two metal recovery systems were examined: biohydrometallurgical recovery of copper and hydrometallurgical recovery of neodymium from WEEE. Biohydrometallurgical methods are identified as environmentally friendly and low cost operation methods. An ex-ante scaled-up life cycle assessment (LCA) model was created for copper metal recovery. Results show that recovering only copper metal from WEEE is neither economically feasible nor environmentally friendly. The feasibility and environmental performance of neodymium metal recycling experiment model was investigated with a LCA scenario of neodymium iron boron magnet production model. It was found that neodymium metal recycling economically and environmentally performed better than virgin magnet production.

ÖZET

AEEE’DEN BİYOHİDROMETALURJİK VE HİDROMETALURJİK YÖNTEMLER İLE METAL GERİ KAZANIMI İÇİN YAŞAM DÖNGÜSÜ ANALİZİ YAKLAŞIMI

Nadir toprak elementleri (NTE) birçok kritik önem arz eden veya yaygın olarak kullanılan tüketici/ endüstriyel ürünlerde kullanılmaktadır ve bu durum onlara olan talebin son birkaç on yılda artmasına sebep olmuştur. NTE üretiminin tamamına yakını Çin’de olmaktadır, bu yüzden Avrupa komisyonu ve Birleşik devletler enerji bakanlığı NTE’leri kritik elementler olarak tanımlamakta ve sürdürülebilir kaynaklardan temini için çaba göstermektedir. Kullanım ömürlerinin sonuna gelmiş tüketici ürünleri, yüksek miktarlarda metal ve plastik barındırmaktadır. Bu sebeple araştırma hedefi olarak, atık elektrik ve elektronik cihazların (AEEE) geri dönüşümü belirlenmiştir. AEEE’ler yüksek miktarda adi metaller, kıymetli metaller ve NTE’leri ihtiva etmektedirler. AEEE’deki metal konsantrasyonları, doğal kaynaklardakinden yüksektir. Günümüzdeki geri dönüşüm yöntemleri yüksek miktarlarda enerji ve kimyasal tüketmektedirler. Ekonomik olarak kârlı olan endüstriyel işletmeler (atık yakma) ise çevre dost değillerdir. Bu yaşam döngüsü analizi (YDA) çalışmasında, iki metal geri kazanım sistemi incelenmiştir: AEEE’den bakır metalinin biyohidrometalurjik yöntem ile geri kazanımı ve neodimyum metalinin hidrometalurjik yöntem ile geri kazanımı. Biyohidrometalurjik yöntemler çevre dostu ve düşük operasyon maliyetli olarak tanımlanmaktadırlar. Bakır metalini geri kazanmak için önceden tahmin etme (ex-ante) yöntemi ile ölçeklendirilmiş model oluşturulmuştur. Sonuçlara göre sadece bakır metalini AEEE’den geri kazanmanın ne ekonomik olarak ne de çevresel fayda anlamında yararlı olmadığı ortaya çıkmıştır. Neodimyum metalinin geri dönüşümü deneyi, Neodimyum demir bor mıknatıslarının üretiminin YDA modeli ile ekonomik ve çevresel performans olarak incelenmiştir. Sonuçlara göre geri dönüştürülen metal ile yapılan üretim, birincil kaynaklardan yapılan üretime göre daha ekonomik ve çevreye daha yararlı olarak değerlendirilmiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS/ABBREVIATIONS

Symbol	**Explanation**	**Unit**
A	Area	m^2
C_p	Specific heat capacity	kJ/(kg °C)
D	Diameter of reactor	m
E	Energy	kJ, kWh
ρ	Density of liquid	kg/m^3
k_α	Thermal Conductivity	W/(m K)
L	Liter	
m	Mass	kg
mL	Milliliter	
n	Impeller rotating speed	rpm
Q	Heat energy	kJ, kWh
t	Time	s
T	Temperature	°C
v	Volume	L
w	Weight	kg
η	Efficiency	

Abbreviation	**Explanation**
AEEE	Atık Elektrikli ve Elektronik Eşyalar
AEEEKY	Atık Elektrikli ve Elektronik Eşyaların Kontrolü Yönetmeliği
APOS	Allocation at the point of substitution
BIOX	Biological Oxidation
CRT	Cathode Ray Tube
CFL	Compact Fluorescent Lamps
EEE	Electric and Electronic Equipment
EOL	End of Life
Eq.	Equation
EU	European Union
FAETP	Freshwater Aquatic Ecotoxicity Potential
g	Gram
GWP	Global Warming Potential

HDD	Hard Disk Drive
HRE	Heavy Rare Earth
HREE	Heavy Rare Earth Elements
HTP	Human Toxicity Potential
IntenC	Intensified Cooperation
IOC	Ion Adsorption Clays
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
Kg	Kilogram
Ktons	Kilotons
LCA	Life Cycle Assessment
LCD	Liquid Crystal Display
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LED	Light Emitting Diode Display
LRE	Light Rare Earth
LREE	Light Rare Earth Elements
MAETP	Marine Aquatic Ecotoxicity Potential
MRI	Medical Resonance Imaging
Mt	Million Tons
Nd-Fe-B	Neodymium Iron Boron
NTE	Nadir Toprak Elementleri
ODP	Ozone Layer Depletion Potential
PBS	Pregnant Bioleach Solution
PC	Personal Computers
PCB	Plastic Circuit Board
PDP	Plasma Display Panel
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
REE	Rare Earth Element
REO	Rare Earth Oxide
ROHS	Restriction on Hazardous Substances
ROW	Rest of the World
TETP	Terrestric Ecotoxicity Potential
USD	United States Dollar

USGS	United States Geological Survey
WEEE	Waste Electric and Electronic Equipment

1. INTRODUCTION

Waste Electric and Electronic Equipment (WEEE) streams growing rapidly in the world and is expected to have an annual growth rate of 5% in the coming years, up from 3% per year (Afroz et al., 2013). In 2016, annual WEEE disposal was 44.7 million tons, and it is expected to reach 55.2 million tons by 2021 (Baldé et al., 2017). It is estimated that only 20% of generated WEEE was collected and recycled properly in 2016 (Baldé et al., 2017). In Europe, the amount of WEEE generated was approximately 5 million tons in 2005 (Cebeci et al., 2005) and 12.3 million tons in 2016 (Baldé et al., 2017). In Turkey, the amount of disposed of WEEE in 2016 was about 623 ktons (Baldé et al., 2017) and is expected to reach 894 ktons in 2020 (REC Turkey, 2011). Turkey's WEEE generation rate was 7.9 kg per inhabitant as of 2016 (Baldé et al., 2017). According to the global e-waste monitor (2017), 6% of all WEEE generated in 2017 in the Western Asia region was collected and recycled, mainly by Turkey. Total WEEE generation of region is estimated to be about 2 Mt in 2017 (Baldé et al., 2017).

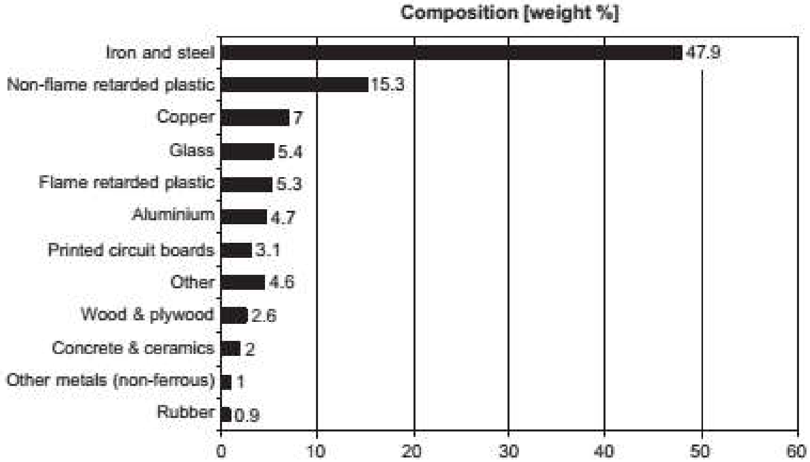

Figure 1.1. Typical WEEE material composition (EIONET, 2013).

An example of typical WEEE material composition is given in Figure 1.1 (EIONET, 2013). WEEE is a significant source of base and precious metals with high economic value. Printed circuit boards (PCB) of personal computers (PC) can contain up to 20% Copper (Cu) and 250 g/ton Gold (Au), which are considered high percentages. These values are 25–250 times higher for gold and 20–40 times higher for copper compared to gold ores (1–10 g/ton Au) and copper ores (0.5–1% Cu), respectively (Tuncuk et al., 2012). These values clearly show that WEEE can potentially be a major secondary resource of metals. Recycle and reuse of metal and non-metal resources from

WEEE can significantly contribute to dampening of environmental impacts of virgin material extraction (Tuncuk et al., 2012).

Rare Earth elements (REEs) have been a focus of interest in recent years for many reasons, especially for the security of supply since they are fundamental for modern high-tech electronics, energy technologies (McLellan et al., 2014) and their ever increasing demand for these metals. These concerns have placed REEs among the list of critical or strategic elements in countries such as the United States of America, the European Union and even China, the top producer and reserve holder country (Chu, S., 2011; European Commission, 2014). Although REE are common in the earth's crust, minable concentrations are located in fewer zones in comparison with most other ores (Reilly II, 2019). At the same time, it is estimated that 55 billion Euros worth of raw materials reside within WEEE as of 2016 (Baldé et al. 2017).

Another important aspect of REE is the environmental impacts of production and political-economic conflict over supply such as 2011 REE crisis (McLellan et al., 2013). However, an extensive evaluation of REE extraction, processing and utilization considering environmental impacts and benefits in a systematic approach and social impacts are largely missing from the literature (McLellan et al., 2014).

As of 2018 China supplies 70.6% of total REE production and has 36.67% of the world's total REE reserves (Reilly II, 2019). However, due to environmental pollution and primitive conditions that Chinese miners and workers are exposed to, the Chinese government has become stricter on its domestic production, adding export quotas and forcing many of the smaller production facilities to close (Sprecher et al., 2014). Recently there has been a decrease of China's share for both global production and reserves of REEs due to increasing production of other nations (Reilly II, 2019). Despite the Chinese government's efforts, illegal and undocumented mining activities exists (Reilly II, 2019). Twenty raw materials were identified as critical from the list of fifty-four candidate materials as of 2013 by the Ad-Hoc Working Group on Defining Critical Raw Materials (European Commission CRM report, 2014). Figure 1.2 shows China's leading production of REE's by percentages for selected elements.

Currently, average global end-of-life recycling rate for REEs are less than 1%. Many technical and economic challenges must be overcome before recycling reaching a commercially feasible scale (Graedel et al., 2011). Research on the recovery of REEs from WEEE gained importance due to these several factors.

There are two main methods are described in the literature for recovery of metals from WEE. The first method is pyrometallurgical processing. Examples of pyrometallurgical processes are incineration, smelting in a plasma arc furnace or blast furnace, drossing, sintering, melting and reactions in the gas phase at high temperatures (Cui et al., 2008). Pyrometallurgy has been vastly used to recover non-ferrous metals and precious metals from WEEE in the past two decades (Cui et al., 2008). However, these processes have significant environmental impacts due to high energy requirements and generation of pollution chemicals.

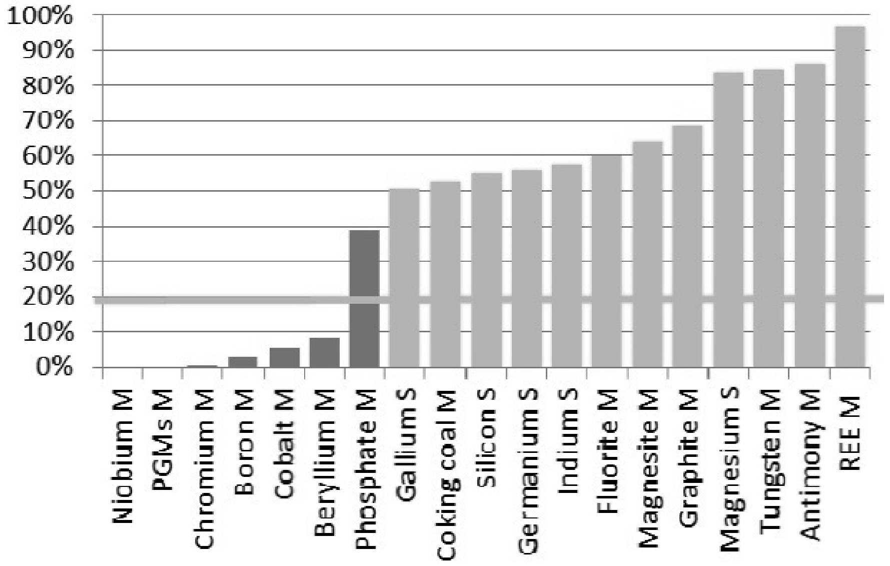

Figure 1.2. China's share of the world Mining or Smelter production (European Commission, 2014).

The second technology for the recovery of metals from WEE is hydrometallurgy. Compared to pyrometallurgical method, the hydrometallurgical method is more exact, predictable and easier to control (Jadhav and Hocheng, 2015). The main steps in hydrometallurgical processing are leaching solid materials with a series of acids or caustics (Cui et al., 2008). Then the solutions are separated and purified by a series of processes such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest (Cui et al., 2008). Finally, the solutions are treated by processes such as electrorefining process, chemical reduction or crystallization for metal recovery (Cui et al., 2008).

In recent years biohydrometallurgical methods for metal recovery has gained attention as a potentially efficient, environmentally friendly technology for precious metals and REEs recovery (Erust, C., et al., 2013). Biohydrometallurgy includes two related microbial processes: bioleaching and biooxidation (Acevedo, 2000). Bioleaching process is the conversion of insoluble metal sulphides (zinc, copper, nickel, cobalt) into water soluble form by means of microorganisms (Erust, C., et al., 2013; Schippers, A., 2014); in contrast, biooxidation is an oxidation process caused by the microorganisms where the metal remains in the solid phase.

Currently only a small fraction of WEEE is treated properly (Baldé et al., 2017). It has been estimated that 23% of global WEEE generated in developed countries, exported to 7 developing countries (Breivik et al., 2014) where improper WEEE recycling is more common. Improper WEEE treatment can cause direct or indirect exposures to a variety of hazardous substances that may affect lung function, thyroid function, hormone expression, birth weight, birth outcomes, childhood growth rates, mental health, cognitive development, cytotoxicity and genotoxicity (Perkins et al., 2014).

In this study a life cycle assessment (LCA) was conducted to evaluate metal recovery from WEEE. The aim of LCA is to evaluate potential environmental effects of novel experimental procedure. LCA is defined as "a technique for assessing the potential environmental aspects and potential aspects associated with a product" (ISO 14040, 2006) a detailed description is given at methodology section. Specifically, this study will focus on two objectives. LCA of rare earth element (REE), neodymium (Nd) recovery from neodymium iron boron magnets (Nd-Fe-B) via hydrometallurgical method and copper metal recovery from mobile phone plastic circuit board (PCB) through Biohydrometallurgical method (Bioleaching). This research work is part of the IntenC project titled "Biotechnological Approach for Recovery of Rare Earth Elements and Precious Metals from E-Waste".

The rest of this thesis is organized as follows. Chapter 2 is a literature review of previous LCA studies conducted for metal recovery from WEEE. Chapter 3 states the purpose of this study and the questions it tries to answer. Chapter 4 describes the methodology, scaling-up procedures, LCA tools and assumptions made in the LCA analysis. Chapter 5 introduces bioleaching method, briefly mentions; PCB, WEEE legislations and WEEE recycling methods and investigates environmental impacts of copper metal recovery from waste PCBs by comparing ex ante LCA model results with a realistic database model. Chapter 6 introduces rare earth element neodymium metal, its current function in applications, demand/ supply balance and investigates potential environmental effects of hydrometallurgical neodymium metal recovery on Nd-Fe-B magnet production via LCA. Chapter 7 discusses LCA study and results in regards to objectives set at the initial stage of research. Chapter 7 also presents final conclusions of this work and recommendations for future studies.

2. LITERATURE REVIEW

This chapter presents a review of the literature on LCA of metal recovery from WEEE. A series of LCA studies was conducted for rare earth oxide (REO) production from basnasite/ monazite ores that are extracted from Bayan Obo mine in Inner Mongolia (Nuss and Eckelman, 2014; Sprecher et al., 2014; Koltun and Tharumarajah, 2014 and Zaimes et al., 2015). Bayan Obo mine in Inner Mongolia is currently the world's largest REE mine (Zaimes et al., 2015). Zaimes et al. (2015) reported that of all the environmental impact categories, the highest contribution comes from mining and extraction & roasting processes. The study showed heavy REO production consumes 20 times more energy than steel production. Highest Green House Gas emission contribution comes from metals respectively, Heavy REOs, Medium REOs, neodymium oxide and other light REOs (Zaimes et al., 2015).

Vahidi et al. (2016) investigated dysprosium metal production from Chinese ion adsorption clays. The study performed a comparison with the above mentioned earlier studies and found out that results are somehow similar with that of Zaimes et al. (2015), except the acidification potential. Zapp et al. (2018) investigated dysprosium metal production for three different production routes and found out hypothetical eudialyte path performed best. The study also pointed out that environmental impacts of dysprosium metal production from IOCs are lower than that of bastnäsite / monazite ores. Vahidi et al. (2017) found out IOCs environmentally doesn't perform better than bastnäsite / monazite ores. However comparisons were made with generic Ecoinvent dataset and it lacks some process information such as solvent extraction (Vahidi et al., 2017). Arshi et al. (2018) investigated potential environmental impacts for production of Nd-Fe-B magnets and rare earth phosphors using data from two companies in China. Two different rare earth production pathways were investigated for magnet and phosphorus production. LCA study showed blue phosphorus production has the lowest life cycle impact for rare earth phosphorus products and magnet production from Bayan Obo mineral ores has lower environmental impacts except for impact categories acidification and eutrophication.

LCA of pyrometallurgically WEEE recovery was carried out by Bigum et al. (2012). The focus of this study was on the recovery of aluminum, copper, gold, iron, nickel, palladium and silver from WEEE. The pre-treatment methods for the WEEE are manual sorting, shredding, magnetic sorting, Eddy-current sorting, air classification and optical sorting. Metallurgical WEEE treatment facility model included a Kaldo plant, a converter aisle, an anode refinery and a precious metal refinery.

Research showed clear advantages of recycling WEEE such as high energy savings but also pointed out to the loss of precious elements during the pretreatment stage. Recovery rates ranged from 12-25% for palladium, gold and silver. Base metals such as iron and aluminum were recovered in much higher quantities (Bigum et al., 2012).

Sprecher et al. (2014) conducted a comparison between 1 kg of neodymium production between virgin material productions and recycling methods was made. 3 scenarios were made for virgin material production: high, baseline (realistic current state) and low. Recycling methods consisted of manually dismantling of hard disk drives (HDD's) using a novel hydrogen method and shredding of HDD's. LCA showed hand dismantling decreases energy consumption by 88% and human toxicity by 98% against baseline scenario while recycling through shredding of HDD's decreased energy consumption by 58% and human toxicity by 81% against the baseline scenario (Sprecher et al., 2014).

Other studies that followed baseline scenario for neodymium magnet production model (Jin et al., 2016; Zakotnik et al., 2016) reported that recycling neodymium metal decreased overall environmental impacts. Modelling neodymium metal recycling was based upon novel hydrogen decrepitation method (Zakotnik et al., 2008; Zakotnik et al., 2009).

Rocchetti et al. (2013) applied LCA to hydrometallurgical treatments using a new portable prototype plant to recover valuable metals from WEEE. Sulfuric acid leaching was followed by metal recovery by selective precipitation. Wastewater treatment with lime was the final step. It has been found that the highest impact was the category of global warming potential, followed by the impact categories of abiotic depletion potential and photochemical ozone creation potential. The data showed that the production of oxalic acid is the highest contributor for the fluorescent powders obtained from fluorescent lamps and CRTs while hydrogen peroxide is the highest contributor for Li-ion accumulators and PCBs (Rocchetti et al., 2013).

An early stage LCA was applied by Villares (2015) for metal recovery from end of life (EOL) PCBs using bioleaching and solvent extraction methods. Using both laboratory scale results and a scaled up commercial model (Shibasaki et al., 2012), comparisons were made with the pyrometallurgical metal recovery plant. The study highlights that, even with the scaled up model, the pyrometallurgical method still has less environmental impacts but there are also opportunities to improve the effectiveness of biohydrometallurgical processes (Villares et al., 2016).

Bioleaching of end-of-life magnets by different bacterial strains were investigated in a recent article (Auerbach, R., Bokelmann, K., et al., 2019). The study has achieved 100% bioleaching efficiency for aluminium, copper and Praseodymium metals and 91% for neodymium metal with bacteria *Leptospirillum ferrooxidans*. *Acidithiobacillus ferrooxidans* had slightly lower bioleaching efficiency for aluminium, boron and neodymium.

Bioleaching experiments conducted for fine fraction of waste incineration slag (industrial and household waste) with different bacteria cultures (Auerbach, R., Ratering, S., et al., 2019). *Leptospirillum ferrooxidans* were more effective for bioleaching rare earth elements (100% Erbium), zinc and cobalt. Co-culture of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* achieved higher bioleaching efficiencies for base metals such aluminium and copper. The study showed that bioleaching of the fine fraction of waste incineration slag is feasible (based on metal bioleaching efficiencies).

3. OBJECTIVE OF THIS STUDY

The main aim of this research is to apply ex-ante approach to a life cycle assessment of the experimental biohydrometallurgical processes for metal recovery from WEEE, which consists of HDD magnets (Nd-Fe-B magnets) and PCB from mobile phones, and determine its environmental impacts. An ex-ante LCA study investigates emerging technologies or techniques before it becomes fully developed and well established at commercial scale. Achieving this aim would provide an early assessment of novel technologies/ techniques and encourage further development of the research itself.

The study will focus on answering these research questions:

- What are the potential environmental impacts of Neodymium metal recycling on the Nd-Fe-B magnet production?
- How can the results of this research further contribute to biohydrometallurgy research and the design of the process?
- What are the potential environmental impacts of bioleaching process from waste printed circuit boards at an industrial scale and how does it compare with the primary production of target metals?
- Is the scaled-up the system provides environmentally friendly and economically feasible scenarios based on laboratory research?
- If the results highlight environmentally friendly and economically feasible design, is this a contribution to research of metal recovery from WEEE?

4. METHODOLOGY

Following the International Standards Association (ISO 14040:2006) methodology, a framework of four independent phases was followed. A Life Cycle Assessment for biohydrometallurgical metal recovery was applied following the steps defined by LCA framework: (i) goal and scope definition, (ii) life cycle inventory (LCI), (iii) life cycle impact analysis (LCIA), and (iv) interpretation. Figure 4.1 shows the relations of the different LCA steps (Guinée, J.B., 2002, ISO 14040, 2006).

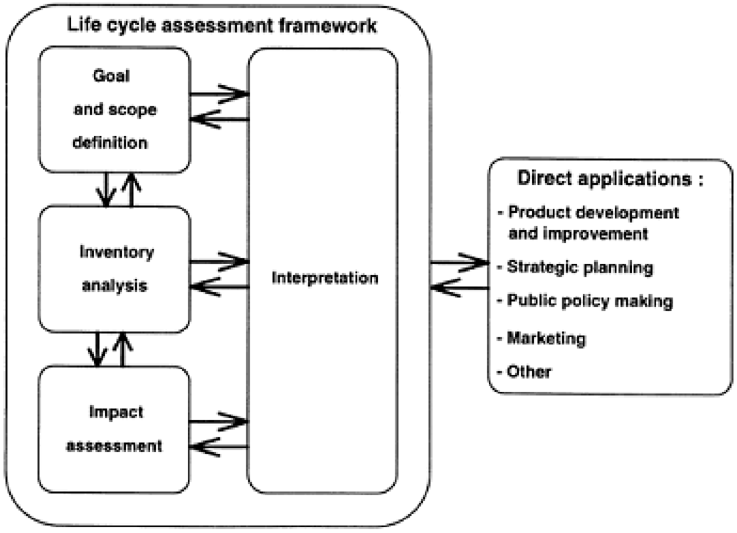

Figure 4.1. LCA framework diagram (ISO 14040, 2006).

4.1. Introduction to Life Cycle Assessment

Life cycle assessment (LCA) is an analytical method that quantifies all the relevant emissions and resources that are consumed, the related environmental and health impacts and resource depletion issues that are associated with any goods or products (JRC-IEA, 2010). A product’s life cycle, from the raw material extraction, material processing, manufacturing, distribution, use, repair, maintenance phases to the disposal or recycling are all accounted to examine environmental impacts. However, LCA is limited to analysis and its interpretation of environmental effects and does not cover all situations. It should be noted that economic and social factors are not considered.

4.1.1. Goal and Scope Definition

The goal and scope definition is the first step of LCA. According to International Reference Life Cycle Data System (ILCD) Handbook, this stage should have covered the reasons for carrying out the LCA study, the intended application(s) of the study, target audience of the results. Also the system boundaries of the study are set during this stage according to the aim (Finnveden et al., 2009). LCAs are iterative studies so initially roughly defined system boundaries get more robust over time (JRC-IEA, 2010). Functional unit, reference flow, technological scope and geographic scope also determined at this stage.

4.1.2. Life Cycle Inventory Analysis (LCI)

Two modelling principles are commonly used for LCA studies; attributional and consequential life cycle model (JRC-IEA, 2010). Attributional modelling accounts for all the potential environmental impacts of the system or product over its life cycle (JRC-IEA, 2010). Consequential modelling aims to describe potential changes in environmentally relevant flows due to decisions making (Finnveden et al., 2009). This step quantifies all the inputs and outputs of the given product system or product. In this study traditional attributional database was used.

4.1.3. Life Cycle Impact Assessment (LCIA)

In the impact assessment phase, data are converted into potential environmental impacts via two-step process: classification and characterization (Villares, 2015). Normalization and weighting steps are optional under ISO 14044:2006. Impact assessment methods characterize results under certain environmental impact categories such as global warming potential (GWP), acidification potential, ozone depletion, fossil fuel depletion etc.

Results of the inventory analysis step are characterized and directed to selected LCIA method. LCIA step aims to understand and evaluate the importance of the potential environmental impacts of the study (ISO 14044, 2006).

4.1.4. Life Cycle Interpretation

In this last phase of LCA study, results are analyzed critically and interpretations are made. Conclusions and recommendations are based upon inventory data and impact assessment results.

Furthermore analyses are made to check system's consistency, completeness and sensitivity in regards to various inputs.

4.2. Small Scale LCA Approach

A laboratory scale system and a flowchart were created to follow-up scale-up procedure given in section 4.4. Experimental procedures completed at laboratory scale and semi-pilot scale, provide a foundation for the large scale operation. The small scale model is the base model for the scaled-up models. It's also useful for finding data gaps and identifying potential problems.

4.3. Large Scale Commercial Model

The goal of modelling a large scale plant is to create a more robust model for comparison of various production models. At the laboratory scale, data gaps create uncertainty and conservative approach even with best available data can lead to overestimation of the process environmental impact. At the early stage development level, LCA studies use experimental data or pilot scale data (Gavankar et al., 2014). An ex-ante approach applied at early stage has data gaps due to development stage of technology. Ex-ante approach was proposed for situations where certain data does not exist due to trade secrets or lack of knowledge at laboratory or pilot scale (Roes et al., 2009).

Höjer et al. (2008) reported that early stage LCA can be used for prediction and explorative purposes and comparisons with different technologies which are useful for evaluating environmental benefits at this level. Hospido et al. (2009) reported that scenarios with scale-up models are useful to evaluate environmental benefits of different technologies.

Comparison of small scale model with maturated technologies can create contradiction at the early stage development level (Tecchio et al., 2014). However they are still encouraged since it can be an early assessment for a developing technology (Tecchio et al., 2014).

4.4. Scaling-up Procedure

A systematic approach for scaling up of plants in LCA was proposed by Shibasaki et al. (2012), which considers different production scales: laboratory scale, mini plant, pilot plant and production plant. LCA of a pilot plant, which is a small scale production plant, results in closest results to production plant, whereas mini plants are still laboratory scale but conditions are set for production plant. The study claims theoretically linear development of all inputs and outputs with the same relation can be expected; however, they are influenced by several factors: yield change, energy supply and efficiency and the amount of waste and emissions generated. Synergy of materials and energy from processes also must be considered due to their economic advantages however the procedure requires sufficient data. Moreover, this method requires a pilot size plant operation (Piccinno et al., 2016) and in-depth understanding of processes at larger scale (e.g. change of materials energy efficiencies).

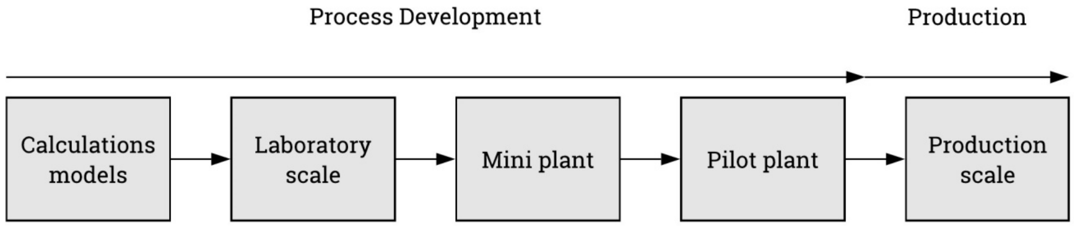

Figure 4.2. Process development scheme (Shibasaki et al., 2012).

A Scale-up framework that follows a five step procedure was proposed to stimulate an industrial scale production with the available data and ignoring the data gap, created by knowledge about the behavior at larger scale (Piccinno et al., 2016). The procedure starts with the experimental data, obtained from direct laboratory experiments of publications. Using this information, a simple plant flow chart is created and then scaled with every materials and equipment involved. In the study, several laboratory scale processes matched with their equivalent scaled-up processes for large scale operations. Relevant processes with this LCA study are given in Table 4.1.

Table 4.1. Proposed scale-up procedure for lab scale processes.

Laboratory scale process	**Scaled-up process according to framework**
Reaction under heating	Insulated batch reactor with heating
Mixing	In tank stirring
Homogenizing (all types)	Rotor-stator type homogenizer
Grinding/ Milling	Grinding
Filtration	Filtration
Centrifugation	Centrifugation
Drying	Oven Drying
Transfer of liquids (Manual)	Pumping
Hazardous waste treatment method	Incineration of hazardous waste

For the next step, every single process step must be scaled-up accordingly. The fourth stage is called linkage of process steps. Each process step is linked through transfer of chemical mixtures. Material recycling and reuse of process heat are also linked. The final step is conducting LCA study using previous steps. An overview of scale-up procedure is given at Figure 4.3.

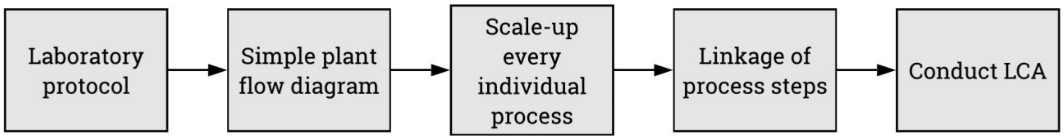

Figure 4.3. Overview of the scale-up procedure (Piccinno et al., 2016).

Hetherington et al. (2014) proposed suggestions for dealing with the early stage LCA studies. Scaling-up issues, challenges and suggestions are detailed in Table 4.2.

Table 4.2. Scaling up issues in using LCA for early research (adapted from Hetherington et al., 2014).

Challenges	**Suggested action for novel LCA**
New technology at the early stage development level will not be as complex as it would be at the industrial scale	Using generated data via process simulations and engineering designs at different scales wherever possible
Laboratory scale results are useful for detecting hot-spots but creates problems when its compared to large scale	Consideration of potential future scenarios using economic input/output models to obtain national average data
New processes at laboratory scale may be less efficient than hypothetical commercial facility	Wherever possible, iterative LCAs should be conducted and the results, generated as new processes, must be published. Therefore understanding about the way scaling-up affecting results can be better

In the current study, two novel metal recovery models were created at commercial scale. The models are based on experimental data from project IntenC. The scale-up procedure was applied following the five step procedure created by Piccinno et al. (2016). Remaining data gaps after scale-up were filled with available data from literature. Adaptations were applied where alternative data were not available.

4.5. Life Cycle Assessment Software and Database

OpenLCA v1.6.3 LCA tool was used in this study. LCA database was Ecoinvent v3.3, modified and licensed by OpenLCA. Selected database was “Allocation at the point of substitution”, APOS default. Database was provided by Technical University of Hamburg Environmental Engineering and Energy Economy (IUE) of TUHH. Selected LCIA method is CML baseline method, which was developed by Institute of Environmental Sciences of Leiden University. Updated version of CML method, v4.4 2015 was used in study.

4.6. System Boundaries

Cradle to gate approach was selected for the study. Cradle here is the end of life WEEE and gate is the metal recovered from WEEE. A schematic representation of the cradle to gate approach is shown in Figure 4.4.

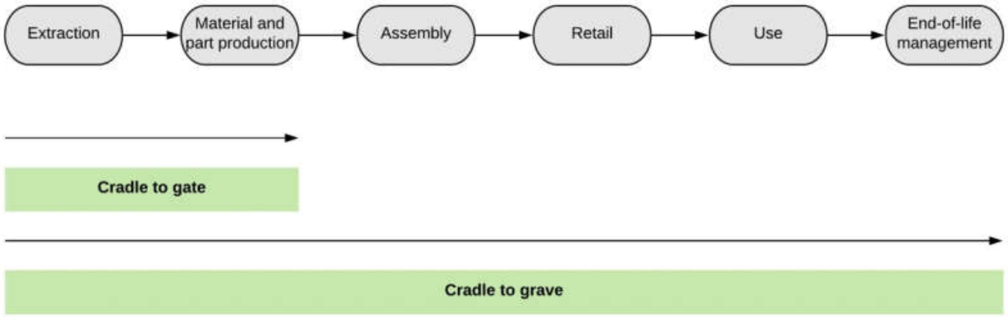

Figure 4.4. Cradle to gate approach (ILCD Handbook, 2010).

Manufacturing, distribution, use and end of life management of WEEE are out of system boundaries. Ecoinvent factory infrastructure dataset primarily used for raw materials and chemicals production and may not reflect specialized bioleaching plant infastructure. So an infrastructure for bioleaching facility was created using Ecoinvent dataset. Maintenance, plant installation, labor, material recycling and energy reuse between processes were not part of the study. Ecoinvent market files are selected for material and service providers. Market files give average transportation distances based on statistical data to reflect real situation (Weidema et al., 2013).

4.7. Data Sources and Uncertainty Issues

The Life cycle assessment study used experimental data provided by the IntenC project (BIOREEs project). Experiments were conducted at both laboratory and semi-pilot scale for bioleaching experiments (IntenC). Other experiments were conducted at laboratory scale using Erlenmeyer flasks (IntenC). Due to nature of this ex-ante study, certain data gaps exist.

4.8. Scale-up Formulations and Assumptions

4.8.1. General Assumptions and Scale-up Framework

Modelling of large scale plant production follows a framework of five steps for chemical processes, given by Piccinno et al. (2016). Proposed scale-up procedures were given in Table 4.3. In this chapter, relevant scale-up formulations and selected values are given.

Table 4.3. Description/ Calculation of scaled-up processes according to framework (Piccinno et al., 2016).

Scaled-up process according to framework	**Description / Calculation**
Insulated batch reactor with heating	$Q_{react}=\frac{C_p * m_{mix} * (T_r-T_0) + A * \frac{k_\alpha}{s} * (T_r-T_{out}) * t}{\eta_{heat}}$
In tank stirring (1000 L tank)	$E_{stir} = 0.0180\ m^5/s^3 * \rho_{mix} * t$
Rotor-stator type homogenizer (1000 L tank)	$E_{hom} = 15.47\ m^5/s^3 * \rho_{mix} * t$
Grinding	8-16 kWh/ton, 16 kWh/ton is selected
Filtration	1-10 kWh/ton dry material, 10 kWh/ton is selected
Centrifugation	Slightly higher than filtration, 11 kWh/ton is selected
Oven Drying	$Q_{dry}=\frac{C_{p,liq} * m_{liq} * (T_{boil}-T_0) + \Delta H_{vap} * m_{vap}}{\eta_{dry}}$
Pumping	$E_{pump}= 55\ J/kg * m$
Waste treatment	Ecoinvent incineration of hazardous waste dataset

It has been assumed that filtration process completely dewater solid fraction to have mass balance. Material losses by leaks, evaporation, spill etc. were neglected. Both bioleaching and hydrometallurgical neodymium metal recovery technologies are not utilized at fully developed commercial scale. Thus for the data selection, data from real life applications of both technologies were given priority over scale-up framework.

Ecoinvent market files represent an accurate picture of current production and transportation state for chemicals and services (Weidema et al., 2013). Thus generic market files were used in the study for almost all chemicals and services. Transportation methods and distances of rare earth elements production are also based on market for neodymium oxides production. Electricity mix is market for medium voltage electricity production in Turkey (industrial mix).

4.8.2. Bioleaching Plant Infrastructure

4.8.2.1. Bioleaching plant material composition. A good of example of a commercial scale biological oxidation (Biox) operation is run by Mintek company at Bogoso gold mine in Ghana. Mintek company runs several commercial biological oxidation plants over a dozen country for metal recovery (Neale et al., 2009). The Bogoso gold mine plant has been operational since 2007 and has the largest reactor tanks by volume at the date (Neale et al., 2009). There are 14 tanks with a 1,500 m^3 volume are running operational with a daily capacity of 820 tpd of a concentrate at a sulphide sulphur grade of 20% (van Niekerk, 2009). A custom infrastructure was created for bioleaching operation based on Bogoso Biox (biological oxidation) plant data. The operation includes 14 stirred tank reactors with a volume of 1,500 m^3 operational capacity. Since some technical information was not shared publicly, assumptions were made following scale-up rules. Specifically, it was assumed that 50 years is total lifespan of bioleaching plant. Reactor tanks along with all the other equipment are assumed to be changed once during its lifespan. Thus total material weight is doubled at the end.

At industrial production scale, bioleaching operations require highly corrosive resistant reactor tanks with a feasible lifespan. Current applications use duplex stainless steel tanks or ceramic lined concrete tanks (Neale et al., 2009). There are three types of steel exist in Ecoinvent database; chromium steel (18/8 stainless steel) low alloyed steel (represent common steel) and unalloyed steel (low carbon steel, mostly used in constructions). It has been assumed that stainless steel (chromium steel) would be used 75% of total steel consumption and low alloyed steel would be 25%. Density of chromium steel is selected as an average of 8,030 kg / m^3 and density of low alloy steel is 7,890 kg / m^3. Average density is 7,995 kg / m^3.

Inner diameter and height of tank are selected as 12.22 m and 14 m respectively. Thickness of tank is assumed to be 8 cm; thus, outer diameter is 12.38 m. Liquid level would be 12.63 m. Tank heads would be flat.

$$V_{tank} = (12.38^2-12.22^2) * 14 * \pi / 4] + 12.38^2 * \pi / 4 * 2 = 29.79 \text{ m}^3 \tag{4.1}$$

$$W_{tank} = 7{,}995 * 29.73 = 238 \text{ ton} \tag{4.2}$$

Ecoinvent chemical factory infrastructure dataset was modelled with the data of a single distillation unit in a refinery (Althaus et al., 2007). It has been assumed additional equipment would weigh 50% of total tank steel weight with same steel composition. Thus sum of total steel weight was calculated. It has assumed that total steel weight of bioleaching plant would have same fraction of steel weight that of chemical factory infrastructure dataset. Thus other construction and operational materials would also have the same weight fraction. Material fraction of infrastructure (1 kg) was applied to calculated steel weight and total plant weight obtained. Total weight of all construction materials and their relative fraction in infrastructure file is given in Table 4.4. According to Ecoinvent, total weight of an organic chemical factory would be 12,584 tons (database v3.3). Total weight of bioleaching plant is 17,369 tons (solder added, see Table 4.5). There are more inputs were added into organic chemical factory construction file dataset following the release of Ecoinvent database v3.0. Therefore new inputs (respective to v2.2 dataset) were incorporated into bioleaching plant dataset similarly. Life cycle inventory of bioleaching plant is given in Table 4.4.

Table 4.4. Material composition and weight of copper bioleaching plant construction.

Material Composition	**Ecoinvent material fraction**	**Unit Installations (t)**	**Pipes (t)**	**Support for pipes (t)**	**Control unit (t)**	**Total 25 years lifespan (t)**	**Total 50 years lifespan (t)**
Total weight	1 kg	7,124.24	699.9	112.21	356.21	8,292.62	16,585.23
low-alloyed steel	0.423	1,250.35	466.6	80.15	-	1,797.14	3,594.27
chromium steel	0.249	3,751.05	233.32	8.91	-	3,993.27	7,986.55
rock wool	0.00823	61.25	-	-	-	61.25	122.50
concrete	1.154E-05 (m^3)	2,061.59	-	23.15	-	2,084.74	4,169.49
electronics	0.0430	-	-	-	356.21	356.21	712.42

*concrete amount is different in v2 report and v3.3 database, here old value adapted

Table 4.5. Life cycle inventory of bioleaching plant infrastructure.

Inputs	**Amount**	**Unit**	**Total weight (t)**
Total weight	1	kg	17,369.34
low-alloyed Steel	0.42	kg	3,594.27
Chromium steel	0.24	kg	7,986.55
Rock wool	0.0082	kg	122.50
concrete	9.95E-05	m^3	4,169.49
electronics	0.043	kg	712.42
brazing solder, cadmium free	0.049	kg	784.11
chemical, inorganic	0.057	kg	952
electricity, medium voltage	5.78	kWh	95,862.65
heat, district or industrial, other than natural gas	4.77	MJ	1.38E+08
Water, unspecified natural origin	0.050	m^3	837.55

4.8.2.2. Bioleaching plant construction. As before, inputs are scaled-up for total weight of bioleaching plant. Life cycle inventory of bioleaching plant construction is given in Table 4.6. For 8 days bioleaching operations, only 6.3E-5 fraction of plant would be used. Time fraction is 8 days/

(365 days * 50 years) and spatial fraction is 1/7 (2 tanks of total 14). During steel machining, 18% of material are lost on average (Steiner and Frischknecht, 2007). Recycling of steel material was not modelled.

Table 4.6. Life cycle inventory of bioleaching plant infrastructure.

Input	**Amount**	**Unit**
Bioleaching plant	1.7E+07	kg
building, hall, steel construction	9,459.8	m^2
building, multi-storey	142,303	m^3
decommissioned chemical production facilities	1.7E+07	kg
Occupation, construction site	75,719	m^2*area
Occupation, industrial area, built up	2.4E+06	m^2*area
Transformation, from unknown	49,126	m^2
Transformation, to industrial area, built up	49,126	m^2
low-alloyed Steel (lost to machining)	790.7	t
Chromium steel (lost to machining)	1,757	t
Average steel machining operation	11,580.8	t
Output		
Bioleaching plant construction	1	unit

4.8.2.3. Inoculation tank construction. Duration of both bioleaching and bacterial activation processes are 8 days so infrastructure should be able to produce at least 1050 m^3 of inoculum for 7 bioleaching systems. It is assumed there would be two open pond systems that produce sufficient inoculum for bioleaching operation; one big open pond and a smaller one. Bigger pond would have an internal diameter of 50 m, thickness of 0.5 m and 0.7 m height. Pond is made of concrete and has an agitator with a capacity of 81 kW. An additional small concrete open pond with a volume of 150 m^3 is also added to infrastructure to ensure continuous operations. It is assumed that the open ponds system does not require air supply. Mass loss by evaporation is neglected. Total volume of concrete used is 1150.9 m^3.

The small pond would be constructed with a diameter of 20 m, height of 0.7 m and wall thickness of 0.25 m. Base thickness would be 0.2 m. Main inoculation tank would have a base thickness of 0.5 m. Life cycle inventory of both bacterial enhancement tanks is given in Table 4.7.

Table 4.7. Life cycle inventory of bacterial enhancement tanks (for activation process).

Input	**Amount**	**Unit**
concrete, normal	1075.12	m^3
Occupation, construction site	5154.93	m^2*area
Occupation, industrial area, built up	1.72E+05	m^2*area
Transformation, to industrial area, built up	11,032,681	m^2
Transformation, to unknown	3,436.619	m^2
Waste concrete	2,532	t
Output		
Bacterial enhancement facility	1	unit

4.8.3. Tank Agitations

4.8.3.1. Bioleaching tanks agitations. Biox (Mintek trademark biological oxidation processes) operations use dual hydrofoil impeller (A315 impeller) to increase mass transfer and better energy efficiency (Neale et al., 2009). Typical energy requirements were given as 0.1 kW/m^3 even though an earlier bioleaching operation in Sao Bento required significantly higher energy for stirring as 0.579 kW/m^3 (van Niekerk, 2009). In this study, agitation power capacities are adapted from Neale et al. (2009). Bioleaching operations complete in two reactor tanks consecutively, in 8 days. Agitation pump capacities of tanks are given as 81 kW and 34 kW (Neale et al., 2009) for 1,620 m^3 reactors. Assuming the tanks would have same power/ volume ratio, stirring energy calculated. This is a conservative estimation.

$$E_{stir} = 81\text{ kW} * \frac{1{,}600\text{ m}^3}{1{,}520\text{ m}^3} * 192\text{ h} + 34\text{ kW} * \frac{1{,}600\text{ m}^3}{1{,}520\text{ m}^3} * 192\text{ h} = 20.4\text{ MWh} \tag{4.3}$$

4.8.3.2. Inoculum tanks agitations. 0.05 kW/m^3 power value is selected for bacterial enhancement process (Neale et al., 2009). For 8 days of bacterial cultivation period, energy consumption for both inoculum units are 77.5 kWh.

$$E_{stir} = 0.05\ \frac{\text{kW}}{\text{m}^3} * 1{,}155\text{ m}^3 * 192\text{ h} = 11{,}808\text{ kWh} \tag{4.4}$$

*4.8.3.3. Agitation speed scaling-up for chemical mixing tanks***.** Flask shake speed was set for 170 rpm which is considered as normal speed. Since the largest reactor volume used during experiments was 10 L, base reactor tank for scaling-up is assumed to be a 1000 L tank with a dimension of 1.119 m for both height and diameter. 85 rpm is considered a normal stirring speed for a 1000 L reactor tank. Height to diameter is selected as 1 to reduce shear stress. Following equal tip speed formula (Eq.4.5), stirring rate of 10 m^3 tank is found as 40 rpm. Power consumption is 0.69 kW.

$$D_1 * n_1 = D_2 * n_2 \tag{4.5}$$

For the copper precipitation and neodymium magnet experiments, equal tip speed formulation was assumed. This model provides more reasonable power demand comparing to power/ volume model. The temperature effect on density and viscosity was neglected. Density of bioleach solution was assumed to be 1000 kg/m^3. It has been assumed, pregnant bioleach solution would be transferred to storage tanks temporarily. Ecoinvent liquid chemical tank was used to store pregnant bioleach solutions. There would be one main stirrer that operates at normal speed. Table 4.8 shows power requirements at different speeds for different tanks agitators (impellers). CheCalc web tool was used to calculate agitation speeds with equal tip speed scale-up assumption.

Table 4.8. Details of agitation operation for LCA calculated with web tool CheCalc (Not all power values used in the study).

Tank volume (m^3)	**Diameter (m)**	**Impeller (m)**	**Reactor height (m)**	**Liquid level (m)**	**Shaft speed (rpm)**	**Used tank volume (m^3)**	**Power drawn, (kW)**	**Process**
1.100	1.119	0.447	1.119	1.119	85	1.1	0.69	Neodymium metal recovery
10.193	2.35	0.94	2.35	2.31	40	10	0.30	Copper Precipitation
10.193	2.35	0.94	2.35	2.31	85	10	2.38	
10.193	2.35	0.94	2.35	2.31	120	10	5.87	
10.193	2.35	0.94	2.35	2.31	150	10	15.71	
10.193	2.35	0.94	2.35	2.31	200	10	37.24	
10.193	2.35	0.94	2.35	2.31	300	10	125.68	
1606	12.22	4.888	14	12.79	150	1500	59.73	Bioleaching
4000	17.205	6.882	17.205	-	normal	4000	50.75	Storage
4000	17.205	6.882	17.205	-	higher	4000	99.13	Storage

4.8.4.4. Bioleaching operations cooling/heating energy demand. Bioleaching reactions are exothermic reactions that release high amounts of heat energy (Neale et al., 2009). Energy released from bioleaching reactions vary under set temperature which is defined by selected bioleaching microorganism mix (Mesophilic bacteria, thermophilic bacteria etc.). IntenC bioleaching experiments use mesophilic bacteria mix (section 5.5.2). Oxidation of iron reaction (see Eq. 5.1 in section 5.1) releases the highest amount of energy per mole and starts bioleaching of other metals. A number of metal reactions occur afterwards. Selected metal reactions that occur in stirred tank bioleaching operations are given below. Only iron and copper metal concentrations are significant in bioleach solution; therefore, heat release from other metal reactions are neglected. Eq. (4.8) neglected due to lack of data.

$4Fe^{(+2)} + O_2 + 4H^{(+)} = 4Fe^{(+3)} + 2H_2O$ $\Delta H_{30°C} = -391.1$ kJ (4.6)

$Fe + 2Fe^{(+3)} = 3Fe^{(+2)}$ $\Delta H_{30°C} = -177.5$ kJ (4.7)

$Cu + 2Fe^{(+3)} = 2Fe^{(+2)} + Cu^{(+2)}$ $\Delta H_{30°C} = -20.2$ kJ (4.8)

$Zn + 2Fe^{(+3)} = 2Fe^{(+2)} + Zn^{(+2)}$ $\Delta H_{30°C} = -238.6$ kJ (4.9)

$Ni + 2Fe^{(+3)} = 2Fe^{(+2)} + Ni^{(+2)}$ $\Delta H_{30°C} = = -139.3$ kJ (4.10)

$Pb + 2Fe^{(+3)} = 2Fe^{(+2)} + Pb^{(+2)}$ $\Delta H_{30°C} = -84.4$ kJ (4.11)

Iron(II) concentrations in bioleach solution is 8,096 mg/L (0.141 mol/L) while copper concentration is 8,976 mg/L (0.145 mol/L). Initial iron(II) concentration found from Iron(II) sulfate heptahydrate reagent concentration, which is 0.159 mol/L. Thus 0.014 mol Fe(II) and 0.145 mol Cu oxidized in 1 L of bioleaching solution. Thus cooling energy load from chemical reactions is calculated in Eq. 4.12

$$Q_{generation} = 0.014 * 391.1 + 0.145 * 20.2 = 8.3 \text{ kJ/L} = \text{MJ/m}^3 \quad (4.12)$$

$$Q_{generation} = 8.3587 \text{ MJ/m}^3 = 2.312 \text{ kWh/m}^3 \quad (4.13)$$

Total cooling load is the sum of heat released from reactions and mechanical work inside the tanks minus heat losses from tanks.

$$Q_{reactions} = 2.312 \text{ kWh/m}^3 * 1{,}500 \text{ m}^3 = 34{,}68.9 \text{ kWh} \quad (4.14)$$

$$E_{stir} = (81 \text{ kW} + 34 \text{ kW}) * 192 \text{ h} = 22{,}080 \text{ kWh} \quad (4.15)$$

$$Q_{cooling} = E_{stir} + Q_{reactions} = 25{,}549 \text{ kWh} \quad (4.16)$$

7 mm rock wool insulation material (k=0.045 W/m*K) was chosen to equalize total heat balance. Total surface area of a single reactor tank is 787.25 m^2 and two reactors complete one batch bioleaching operation cycle. Facility temperature is assumed to be 18 °C and operation time is

192 h. Tank steel thermal conductivity assumed to be of SS 304 (14.4 W/m*K). 1D heat loss model of reactor tanks with insulation would be:

$$Q_{loss} = 2 * 787.25 * 6.207 * \left(30\text{-}18\right) * 192 = 22{,}516.81 \text{ kWh} \tag{4.17}$$

Reactors lose almost same amount of heat energy that's generated by chemical reactions thus cooling/ heating energy demands are neglected for the study. Thus its assumed cooling demand would be eliminated by thinner insulation level or would be low.

5. COPPER METAL RECOVERY FROM WASTE PCB BY BIOHYDROMETALLURGICAL METHOD

5.1. Biotic Component of Bioleaching Experiment

Bioleaching is a natural process comprising of microorganisms that have the ability of either oxidizing metal sulfides or oxidizing reduced inorganic sulfur compounds to sulfuric acid, or both of them (Chen et al., 2015; Ilyas et al., 2010). Bioleaching process was developed over more than 60 years ago Biohydrometallurgy is often used in treatment of mine effluents (Salminen et al., 2015), low grade ores (Panda et al., 2012) and metal recovery from secondary resources (Brierley, 2008). Currently industrial copper sulfide bioleaching is practiced mostly as heap or dump bioleaching of secondary sulfides (Panda et al., 2015). Heap and dump bioleaching of copper makes up to 20-25% of world's total copper production (Brierley, 2008). Heap bioleaching of low grade primary sulfide is currently only available for pilot plants and demonstration plants (Panda et al., 2015).

Heap and dump bioleaching of secondary sulfides process is a commercially proven operation and is expected to be utilized more in the future (Panda et al., 2015). Operations are mostly run in South American countries: Chile and Peru (Panda et al., 2012). Their cumulative production accounts for almost 35% of global copper production. Copper production through bioleaching operation accounts for 42% and 33% of total production for both countries, respectively (Panda et al., 2015).

Stirred tank bioleaching operations are widely used for gold production (van Niekerk, 2009). Stirred tank bioleaching operations offer a number of advantages such as better control over operation parameters and extraction of higher concentrated ores. However, bioleach solutions are highly corrosive and require expensive special equipment for operations and operating multi-step metal recovery systems require good grasp of theoretical and operational knowledge. In industrial scale bigger bioreactor volumes and higher slurry densities can be used; however, air supply and dispersion are identified as problematic (Peterson, 2010). Efficiency of gas-liquid mass transfer may be less than laboratory scale or depending on high energy consuming agitators (Peterson, 2010).

Both autotrophic and heterotrophic organisms are used as biotic component for metal recovery from WEEE biotechnologies (Işıldar et al., 2019). Various species of acidophilic prokaryotes are identified in stirred-tank bioleaching/ biooxidation operations (Siezen, J.R., 2009). In the Inten-C project, a mixed culture of mesophilic and chemolithotrophic organisms was used for bioleaching experiments: *Acidithiobacillus thiooxidans*, *Leptosprillum ferrooxidans* and *Acidithiobacillus ferrooxidans*. The leaching mechanism of copper from PCB dust by *A. ferrooxidans* was evaluated as being similar to that of metal sulfides (Choi et al., 2005). *A. ferrooxidans* are capable of bioleaching; zinc (Zn)/ lead (Pb) metals from zinc/ lead pyrite ores around 35 – 40 °C, gold from (arseno) pyrites at 40 °C, Copper (Cu)/ Zn / Iron (Fe) from poly metallic ores (e.g. WEEE) and Cu/ Fe from chalco-pyrite ores around 78 °C (Siezen, J.R., 2009) in stirred tank bioleaching/ biooxidations operations.

There are two mechanisms proposed for the metal bioleaching; a thiosulfate mechanism for the oxidation of acid-insoluble metal sulfides and a polysulfide mechanism for acid-soluble metal sulfides (Siezen, J.R., 2009).

Bioleaching of metals from WEEE (non-sulfide wastes) are subjected to direct and indirect leaching mechanisms by biogenic ferric iron and sulfuric acid (Işıldar et al., 2019). The roles of acidophiles in these processes are catalyzation of the oxidation of ferrous iron (Eq. 5.1) and oxidation of elemental sulfur to sulfuric acid (Eq.5.2) (Işıldar et al., 2016; Işıldar et al., 2019). The biogenic ferric iron (Eq.5.3) and sulfuric acid (Eq.5.4) participate at liberating copper metal from waste material (Işıldar et al., 2019)

$$4Fe^{+2} + 4H^{+} + O_2 \rightarrow 4Fe^{+3} + 2H_2O \text{ (microbial activity)} \qquad (5.1)$$

$$S^{0} + 3/2O_2 + H_2O \rightarrow 2H^{+} + SO_4^{2-} \text{ (microbial activity)} \qquad (5.2)$$

$$Cu^{0} + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \text{ (chemical activity)} \qquad (5.3)$$

$$Cu^{0} + H_sSO_4 + \tfrac{1}{2}\, O_2 \rightarrow Cu^{2+} + So_4^{2-} + H_2O \text{ (chemical activity)} \qquad (5.4)$$

5.2. Abiotic Component of Bioleaching Experiment, Printed circuit boards (PCB)

Printed circuit boards (PCBs) are essential for electronic industry and exists in almost all electronic products (Kaya, 2016). They mechanically support electronic components and electrically connect them by conductive pathways (Li and Zeng, 2012). The PCB is made up of several layers with glass fiber enhanced epoxy and many materials as well as precious metals (Wang et al., 2017). PCBs have a heterogeneous, diverse and variety in composition due to the competitive market they been manufactured in (Hall and Williams, 2007). Technological advances change nature of PCBs even more; for example, modern PCBs use less precious metal then before.

PCBs usually contains epoxy resin, fiber glass, copper, nickel, iron, aluminium, lead, tin and low amounts of precious metals (Li and Zeng, 2012). Modern electronic devices can contain up to 60 different elements including precious metals (Hadi et al., 2015). It has been estimated that 1000 kg of waste mobile phones can yield about 300-350 g of gold along with other metals (Hadi et al., 2015). Since precious metal content of the PCBs is higher than average ore and other WEEE products, metal recycling efforts have focused on them (Tuncuk et al., 2012; Sethurajan et al., 2019). As an average, material composition of PCB is 40% metal, 30% ceramics and 30% plastics (Li and Zeng, 2012). Several studies investigated material composition of PCBs (Table 5.2). Material fractions in PCB are given in Table 5.2.

In general PCB makes up 3% of WEEE stream by weight (Hadi et al., 2015). However, its weight content differs in electronic products. On average, PCBs make up to 22% of mobile phones. Among other electronic devices, mobile phones are one of the fastest growing waste streams due to short lifespan of product. The number of mobile phone users increased to 7.7 billion subscriptions and 4.2 billion of it have active mobile broadband subscriptions (Baldé et al., 2017). Despite these high user numbers, Mobile phones recycling rate is low in both developing countries and developed countries due in part to low public awareness level (Sarath et al., 2015).

Table 5.2. Material fraction of PCB given in several studies, adapted from Li and Zeng (2012).

	a	b	c	d	e	f	g	h	DE-1
Metals	%	%	%	%	%	%	%	%	%
Cu	20	26.8	10	15.6	22	17	23.47	17.67	27.12
Al	2	4.7	7	-	-	4.78	1.33	3.6	1.57
Pb	2	-	1.2	1.35	1.55	4.19	0.99	0.92	1.76
Zn	1	1.5	1.6	0.16	-	2.17	1.51	0.53	0.692
Ni	2	0.47	0.85	0.28	0.32	1.63	2.35	0.27	1.98
Fe	8	5.3	-	1.4	3.6	2	1.22	5.21	1.85
Sn	4	1	-	3.24	2.6	5.28	1.54	-	4.98
Sb	0.4	0.06	-	-	-	-	-	-	-
Au (ppm)	1000	80	280	420	350	350	570	0.021	853
Pt (ppm)	-	-	-	-	-	4.6	30	-	70
Ag (ppm)	2000	3300	110	1240	-	1300	3301	-	5560
Pd (ppm)	50	-	-	10	-	250	294	-	60
Ceramic						-	-	-	-
SiO2	15	15		41.86	30				
Al2O3	6	-	-	6.97	-				
Alkaline and alkaline earth oxides	6	-	-	10.43	-				
Titanates, mita etc.	3	-	-		-				
Plastics		-	-			-	-	-	-
Polyethylene	9.9				16				
Polypropylene	4.8				-				
Polyesters	4.8				-				
Epoxides	4.8				-				
Poly(vinylchloride)	2.4				-				
Poly(tetrafluroethane)	2.4				-				
Nylon	0.9				-				

[a] Shuey et al., (2006); [b] Zhao et al., (2004); [c] Zhang & Forssberg (1997); [d] Kim et al., (2004); [e] Lji & Yokoyama (1997); [f] Kogan. (2006); [g] Ogunniyi et al., (2009), [h] Işıldar et al., (2016)

5.3. PCB Recycling Techniques

Biohydrometallurgical method is an established method for extracting metals such as gold, silver, arsenic, cobalt, copper, manganese, molybdenum, nickel, uranium, vanadium and zinc from primary sources (Işıldar et al., 2019; Morin, 2016). A large group of bacteria as well as fungi can be utilized for bioleaching process (Schippers et al., 2014). Other methods are biosorption, bioelectrochemical and bioprecipitation processes for metal recovery from leachates (Işıldar et al., 2019).

Physical pretreatment is the first step of metal recovery techniques. Dismantling or disassembling relevant parts for selected recovery technique is essential (Sethurajan et al., 2019). Physical separation and size reduction processes typically follow liberation of WEEE components. Aims of physical pretreatment are preparing the metal bearing sample for recycling process and removing hazardous parts of WEEE that would otherwise contaminate metal recycling process. Shredders and hammer mills are typically used for size reduction (Kaya, 2016). Other physical pretreatment processes are magnetics separation, eddy-current separation, electrostatic separation, gravity separation and flotation (Sethurajan et al., 2019).

Hydrometallurgical metal recovery methods require a mechanical treatment process with two steps; dismantling various components and devices and subjecting metal containing components to size reduction (Tuncuk et al., 2012). After pretreatment, hydrometallurgical metal recovery methods are applied by two steps. First step is leaching all metals or selectively leaching metals into leachate and second step is extracting metals from leachate. There are various leaching agents and methods for target metals. Examples of processes are cyanide leaching (precious metals), thiosulfate leaching and thiourea leaching (Akçil et al., 2015) A number of methods can be applied to extract metals from leachate such as precipitation, liquid-liquid extraction, electrowining, cementation and adsorption (Sethurajan et al., 2019).

Incineration is the traditional thermal WEEE treatment process. During incineration treatment process, waste PCBs put into an incinerator under aerobic conditions and organic components decompose and combust at high temperature, leaving incinerator in gaseous form (Wang et al., 2017). After nonmetallic fraction liberation, metals are sorted. However this method is energy intensive and metal recovery rate can be mediocre (Bigum et al., 2012). Another pyrometallurgical method is pyrolysis process where organic resins converted to low molecular weight substances and condensed to pyrolysis oil which is a fuel (Wang et al., 2017). Other pyrometallurgical methods are plasma and molten salt (Wang et al., 2017).

5.4. Bioleaching Copper Metal from PCB, Previous Studies

A number of studies focused bioleaching of metals from PCBs in flasks (Ilyas et al., 2007; Wang et al., 2009; Yang et al., 2009; Liang et al., 2010; Zhu et al., 2011 and Yang et al., 2014). These studies demonstrated metal bioleaching capabilities of various acidophilic bacteria from waste PCB dust and WEEE scrap (Ilyas et al., 2007).

There are fewer experiments conducted for column bioleaching operations. Ilyas et al. (2010), Ilyas et al. (2013) and Chen et al. (2015) investigated column bioleaching of metals. Ilyas et al. (2010) and Ilyas et al. (2013) studies used moderately thermophilic bacteria to bioleach metals from electronic scrap while operation times were 280 days and 165 days respectively. Chen et al. (2015) successfully bioleached metals with *A. ferrooxidans* from waste PCBs by 28 days operation.

Marra et al. (2018) and Işıldar et al. (2016) focused on two step bioleaching processes. The former study showed high success for bioleaching REEs from waste PCB dust (80% to 99%) while the latter study successfully bioleached copper out of waste PCB (98%) at first step. At second step, both studies used cyanide producing bacteria strains to leach out gold and had 48% and 44% gold mobilization efficiency.

5.5. WEEE Legislations

There are three types of regulations in European Union regarding the treatment of WEEE; the WEEE directive, the RoHS (Restriction on Hazardous Substances) directive and the REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) regulations. The objectives of these legislations are reduction of waste preferably by prevention, then reuse and lastly through recycle.

European Union WEEE directive (2012/19/EU) reviewed previous (2002/96/EC) and brought higher standards to WEEE collection objectives to prevent improper management of WEEE (Işıldar et al., 2018). EU directive made manufacturers and distributors financially responsible for covering collection, treatment, recycling and recovery of WEEE costs (Villares, 2015). The new directive also introduced take-back system and set the target of 85% of waste collection from municipal waste by 2020 (Işıldar et al., 2018).

The RoHS directive forces manufacturers to substitute six major toxic substances in any manufactured EEE or spare parts. These substances are lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE). (The RoHS Directive)

REACH regulations aims to protect human health and environment from risks that can be of all chemicals. Manufacturers must identify the risks posed of chemicals they produce and demonstrate the safe use of chemicals (Understanding REACH).

Turkey passed WEEE legislation (Atık Elektrikli ve Elektronik Eşyaların Kontrolü Yönetmeliği) in 2012 (22.05.2012). The legislation is very similar with EU WEEE directive. It aims to limit use of hazardous substances in manufacturing, identifying exceptions for the legislative and creates a framework that regulates legal and technical principals to decrease WEEE generation and disposal (AEEEKY, 2012).

5.6. Copper Recovery via Bioleaching and Precipitation Experiments

Experiment data for copper recovery from WEEE system is from IntenC project. There are four steps for the copper metal recovery experiments (IntenC): WEEE sample treatment (pretreatment), bacteria culture activation, bioleaching and copper metal precipitation (IntenC). Experiment flowchart is given in Figure 5.1 (IntenC).

5.6.1. WEEE Sample Treatment

A number of end-of-life (EOL) mobile phones and PC mainboards were collected to provide WEEE samples (IntenC). After characterization of each sample and some initial bioleaching experiment, a PCB from mobile phones sample, labeled DE-1, was chosen for bioleaching experiments due to its high metal content (IntenC). Metal content of Sample DE-1 is given in Table 5.4 (section 5.6.3).

WEEE samples were manually dismantled and PCBs were separated from devices (IntenC). After dismantling each device, PCB sample size was reduced down to 2 cm to 2 cm by cutting PCB to pieces (IntenC). PCB sample size was further reduced to 250 micron by a ground mill (IntenC). Feedback ratio of material is about 10% (Retsch ZM 200).

5.6.2. Bacterial Culture Activation

A mixed culture of mesophilic bacteria (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans, Leptosprillum ferrooxidans*) were used in the bioleaching studies (IntenC). High metal content has toxic effect on bacteria (Liang et al., 2010) so bacteria culture has been grown on and adapted to bioleaching process conditions without WEEE sample first (IntenC).

Mixed culture was actively grown on 9K medium for 8 days (IntenC). Initial conditions for Fe (II) were 9 g/L and pH 1.8 (IntenC). An orbital shaker kept culture at 30 °C and agitated at 150 rpm (IntenC). After 8 days of activation period, bacterial culture grown to 10^7 cell/mL (IntenC). Details of the 9K medium are given in Table 5.3 (IntenC).

Table 5.3. 9K medium details (IntenC).

Reagents	**Amount of consumption**
Iron(II) sulfate heptahydrate-$FeSO_4.7H_2O$	44.2 g/L
Ammonium sulfate-$(NH_4)_2SO_4$	3.0 g/L
Magnesium sulfate heptahydrate-$MgSO_4.7H_2O$	0.5 g/L
Di-Potassium hydrogen phosphate-K_2HPO_4	0.5 g/L
Calcium nitrate-$Ca(NO_3)_2$	0.1 g/L
Deionized water	990 g/L
Sulfur (S)	1 g/L
Sulfuric acid (1M)	2.72 mL/L

5.6.3. Bioleaching Experiment

A number of experiments were conducted to optimize bacterial bioleaching parameters (IntenC). It has been found that 10% (v/v) inoculum ratio and 10% (w/v) pulp density conditions are optimal for copper bioleaching at 30 °C (IntenC). Initial pH was set to 1.8 by adding 1M sulfuric acid. 100 g WEEE sample and 100 mL inoculum added into 900 mL 9K medium (IntenC). The temperature was kept at 30 °C and flasks were stirred at 150 rpm (IntenC). After 8 days, it has been found that base metals have been bioleached more efficiently by bacteria than rare earth elements (IntenC). Pregnant bioleach solution was filtered under centrifuge and liquid fraction send for copper precipitation (IntenC). Gold rich solid solution was chemically leached (85%) during

IntenC experiments but was not extracted thus gold recovery is cut-off. Initial solid metal fractions (DE-1), bioleached metal concentrations (DE1RL) and remaining metals (DE1RS) are given in Table 5.4 (IntenC).

Table 5.4. Metal content of sample DE-1 during experiment steps (IntenC).

Metal	**DE-1 (g/kg)**	**DE1RL (mg/L)**	**DE1RS (g/kg)**
Cr	0.326	0.21	0.145
Mn	2.560	255.8	0.395
Fe	18.500	89,760	34.055
Ni	19.800	1,267.8	19.500
Cu	271.200	8,976	8.096
Zn	6.925	483	2.380
Al	15.700	NA*	19.380
Cd	0.005	ND**	<0.0001
Pb	17.600	ND**	10.085
Si	20.800	103.4	NA**
Co	0.544	70.6	0.110
Mo	0.253	0.1	<0.0001
Ag	5.560	ND*	5.580
Au	0.853	0.21	0.880
Sn	41.975	NA**	21.645
Nd	8.290	33.05	6.400
La	0.248	0.29	0.155
Ce	ND*	0.22	0.055
Pd	0.060	ND**	0.175
Pt	0.070	0.2	0.075
Pr	1.010	3.59	0.425
Dy	0.174	5.08	0.075

NA* denotes not analyzed and ND** denotes not detected

5.6.4. Copper Precipitation as Copper Hydroxide

After bioleaching experiments, pregnant bioleaching solution (PBS) had copper concentration of 8,960 mg/L and iron concentration of 8,090 mg/L (IntenC). Iron and copper precipitated as hydroxides at this step (IntenC). 250 mL Hydrogen peroxide solution (30%) added into 500 mL PBS (volume ratio 1:2), then 14 g sodium hydroxide (50%) added into mix to increase pH to 2.8 (IntenC). The mix was constantly stirred for 5 minutes at 300 rpm and room temperature (IntenC) and 87% of iron precipitated as iron hydroxide ($Fe(OH)_3$) (IntenC). Filtration removed iron hydroxide from solution. pH was set to 5.6 with the addition of 14 g sodium hydroxide and 97% of copper precipitated as copper hydroxide ($Cu(OH)_2$) (IntenC). Finally copper hydroxide filtrated from solution (IntenC). Remaining copper concentration is 46.7 mg/L while iron concentration is 0.122 mg/L (IntenC). Further experiment such as biosorption were considered unnecessary due to low metal concentration thus wasn't included into the LCA study.

5.6.5. Small Scale Model for Life Cycle Assessment

The 9K medium was used for bacterial enhancement and bioleaching processes. Ecoinvent database modelled all chemicals as 100% pure. A custom 9K medium solution was created and all solid reagents were added into dataset. A conversion was made for all acids used for experiments. 2.72 mL sulfuric acid is added into 1 L 9K medium. 0.153 mL stock sulfuric acid solution (95%) would be slowly added to 0.68 mL deionized water then diluted to 2.72 mL. 1M 2.72 mL sulfuric acid requires 0.145 mL 100% sulfuric acid (0.267 g) and 2.575 mL distilled water. Density of 100% sulfuric acid is 1.84 g/cm^3 and weight of pure sulfuric acid consumption is 0.471 g. Total groundwater consumption is 997.28 mL. Groundwater extraction process was neglected.

Life cycle inventory of the 1 L 9K medium is given below in Table 5.5. Deionized water was replaced with ground water due to high consumption of water. It was assumed that the mineral content of groundwater would not affect bioleaching experiments in any way. Groundwater consumption is an estimate. Following IntenC experiment data, a framework of small-scale copper recovery method was created (Figure 5.1).

Table 5.5. Life cycle inventory of 1 L 9K medium (IntenC).

Inputs	**Concentration**	**Amount of consumption (1 L)**
Iron(II) sulfate heptahydrate-$FeSO_4.7H_2O$	44.2 g/L	44.2 g
Ammonium sulfate-$(NH_4)_2SO_4$	3.0 g/L	3.0 g
Magnesium sulfate heptahydrate-$MgSO_4.7H_2O$	0.5 g/L	0.5 g
Di-Potassium hydrogen phosphate-K_2HPO_4	0.5 g/L	0.5 g
Calcium nitrate-$Ca(NO_3)_2$	0.1 g/L	0.1 g
Water, ground water consumption	997.28 g/L	0.9973 g
Sulfur (S)	1 g/L	1 g
Sulfuric acid	2.72 ml/L	0.2674 g

5.6.5.1. Dipotassium phosphate production dataset. Dipotassium hydrogen phosphate production dataset does not exist in the Ecoinvent database. According to Phospharic acid and Phosphates chapter of Ullman’s Encyclopedia of Industrial Chemistry, production of potassium phosphate salts from phosphoric acid and potassium hydroxide are similar with sodium phosphate salts production from phosphoric acid and sodium hydroxide (Schroedter et. al, 2015). Thus Ecoinvent sodium phosphate production dataset input sodium hydroxide was replaced with potassium hydroxide. Phosphoric acid quantity was adjusted as described below:

Original reaction for dataset: $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$ (5.5)

Adapted reaction for study: $H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O$ (5.6)

Output 1 kg of sodium monophosphate is 1kg/ 142 kg/kmol = 0.00704 kmol (5.7)

Phosphoric acid: 0.00704 kmol x 98 kg/kmol = 0.69 kg (5.8)

Dataset original value = 0.737 kg, Ecoinvent activity conversion rate = 0.737/ 0.69 = 1.07 (5.9)

Sodium hydroxide: 0.00704 kmol x 80 kg/kmol = 0.5632 kg (5.10)

Dataset original value: 0.990 kg, Ecoinvent activity conversion rate= 0.990/ 0.5632 = 1.76 (5.11)

Now we use these conversion factors (Eq. 5.9, Eq. 5.11) for dipotassium hydrogen production:

Adapted reaction for study: $H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O$ (5.12)

1kg/ 136 kg/kmol = 0.0075253 kmol (5.13)

Phosphoric acid: 0.007353 kmol x 98 kg/kmol = 0.7206 kg (5.14)

Ecoinvent activity conversion rate = 0.7206 x 1.07 = 0.77 kg H_3PO_4 (5.15)

Potassium hydroxide: 0.007353 kmol x 56 kg/kmol = 0.412 kg (5.16)

Ecoinvent activity conversion rate = 0.412 x 1.76 = 0.72512 kg (5.17)

Input H_3PO_4 amount 0.737 kg would be 0.77 kg and Input KOH amount 0.990 kg to would be 0.725 kg.

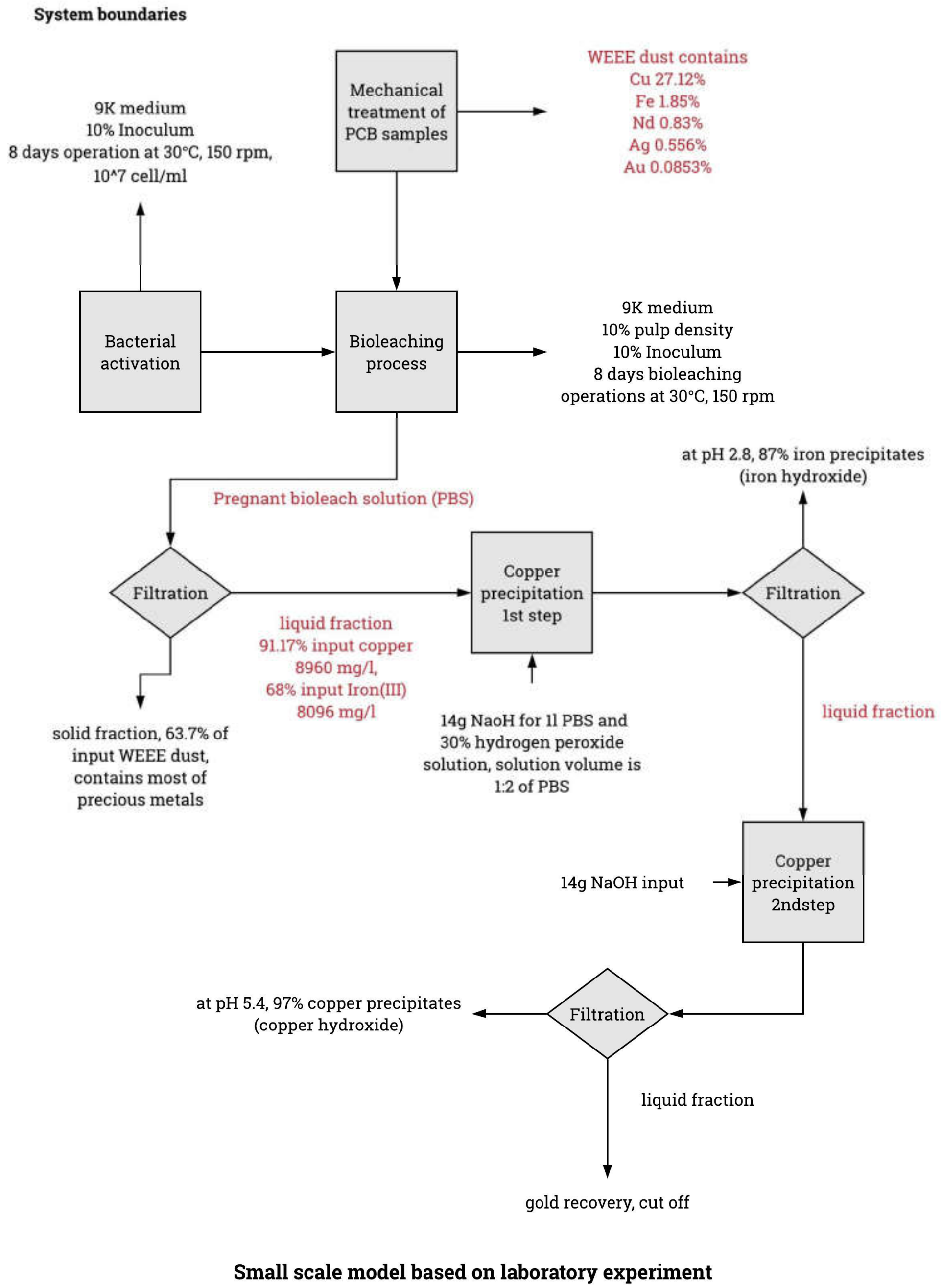

Figure 5.1. Flowchart of small scale copper metal recovery model (IntenC).

5.7. Life Cycle Assessment for Scaled –up Copper Metal Recovery Model from Waste PCBs

5.7.1. Goal and Scope of the System

The goal of the LCA is to calculate possible environmental impacts of metal recovery with bioleaching processes from WEEE, gathered from mobile phone PCBs. The scope of the study is biohydrometallurgical metal recovery from WEEE. Functional unit is the recovery of 1 kg elemental copper from mobile phone PCB. Institute of Environmental Sciences of Boğaziçi University in Istanbul, Türkiye was selected as geographical scope. Regional priorities for dataset selection are respectively Turkey, Rest-of-world (ROW), and Global. Technological Scope is the technology used at laboratory experiments. Reference flow is the 1 kg of recovered metal from WEEE sample using biohydrometallurgical and hydrometallurgical techniques at the plant gate. Reference flow for comparison is dataset from Ecoinvent database v3.3, 1 kg of elemental copper was modelled for global copper market scenario which reflects current situation, both primary production (mining) and recycling.

5.7.2. Life Cycle Inventory for Scaled –up Copper Metal Recovery Model from Waste PCBs

5.7.2.1. Industrial WEEE shredding operations. Ecoinvent database has a WEEE treatment facility dataset based on literature data and assumptions. Facility modelling is based on a modern shredder facility with 2 shredder, 2 magnetic separation & 2 Eddy-current separation steps. 7% material loss is also considered for WEEE dust treatment. It was assumed that output WEEE dust would have the same metal fraction with PCB sample DE-1 given in section 5.6.3. Life cycle inventory of PCB dust treatment is given in Table 5.6.

Table 5.6. Life cycle inventory for scaled-up WEEE pretreatment process.

Input	**Amount**	**Unit**
Waste electric and electronic equipment	-1.0756	item(s)
Output		
Shredded PCB dust	-1	kg

5.7.2.2. Bacterial enhancement process. Bacterial activation process has two fold purposes: Enhancement of bacterial culture for bioleaching operations (Işıldar et al., 2016) and limit bacterial growth inhibition caused by hazardous compounds of PCB (Liang et al., 2010). Bacterial activation process that uses the infrastructure is explained in section 4.8.2.3. Only a temporal fraction of 8 days operation for 50 years of lifespan is applied to infrastructure. It was assumed open pond bacterial growth operations would not need additional air supply, and evaporation of water is neglected. Agitation power value of 0.05 kWh/m^3 would be sufficient to stir both ponds. Life cycle inventory of bacterial activation process for 8 days of operation is given in Table 5.7. Heating energy requirement is neglected.

Table 5.7. Life cycle inventory for scaled-up bacterial enhancement process.

Input	**Amount**	**Unit**
Bacterial enhancement infrastructure	4.3E-4	item(s)
9K medium	1,150	m^3
Electricity, medium voltage, TR mix (pumping 9K medium)	63.5	MJ
Electricity, medium voltage, TR mix (agitation)	57.7	kWh
Output		
Inoculation for bioleaching	1,150	m^3

<u>5.7.2.3. Bioleaching process.</u> Bioleaching operation parameters are given in section 5.5.3. Plant infrastructure was used as an input with spatial fraction (1/7) and temporal fraction (section 5.6.2.2). High pulp densities in industrial scale bioreactors would increase volumetric oxygen demand and gas-liquid mass transfer may be less than that of laboratory scale experiments (Peterson, 2010). In stirred reactors, air supplied by blowers enters tank and disperses just under the dual hydrofoil impellers (van Niekerk, 2009; Brierley, 2008). In Ecoinvent database only the compressors supply air. Air volume required from bioleaching operation is scaled from a Biox project (52,000 Nm^3/h) operation in Spain (Neale et al., 2009). Total air volume requirement for 8-day batch operation is 1,533,518.8 Nm^3 air (for 2 reactors with a volume of 1,500 m^3).

Table 5.8. Life cycle inventory for scaled-up bioleaching process.

Input	**Amount**	**Unit**
Bacterial enhancement infrastructure	6.2E-5	item(s)
9K medium	1,350	m^3
Electricity, medium voltage, TR mix (pumping 1500 m^3 solution)	86.05	MJ
Electricity, medium voltage, TR mix (agitation)	22,080	kWh
Electricity, medium voltage, TR mix (filtration after bioleaching process)	1,500	kWh
Shredded PCB dust	-150	kg
Compressed air, 600 kPa gauge	1,533,518.8	m^3
Liquid storage tank	0.0038	item(s)
Inoculation for bioleaching	150	m^3
Output		
Pregnant bioleach solution	1,500	m^3

After bioleaching, copper concentration is 8,960 mg/L. It has been assumed that all the copper would come from bioleached PCB dust thus 1 L solution would be diluted to 2.760 L. Therefore, 1.76 L deionized water is added to every liter of PBS. 2,640 m^3 deionized water is required to dilute 1,500 m^3 pregnant bioleach solution. It has been assumed that dilution would be done with groundwater and solution would be stored in dataset liquid organic chemical storage tanks. Scaled-up volume after dilution is 4,140 m^3. 2,040 m^3 hydrogen peroxide (30%) solution would be also stored simultaneously. Thus a fraction of [(6,210 m^3/ 1,600 m^3) * 18/ (365 * 50)] = 0.00383 units would be used for each bioleaching operations. Its assumed stirring speed in storage tanks would be quite low thus power demand would be 0.005 kW/m^3.

<u>5.7.2.4. Copper precipitation process.</u> 2,070 (750) m^3 hydrogen peroxide (30%) solution was added into pregnant bioleach solution (4,140 m^3). 2,070 (750) m^3 hydrogen peroxide (30%) solution would require 621 (325.462) tons of hydrogen peroxide (100%) and 1,449 m^3 deionized water. It has been assumed that copper precipitation processes would be completed in 6 times in an hour for each of six tanks with a 10 m^3 volume. Thus in 18h (per batch cycle) all bioleached copper and iron would be separated from solution. LCI for copper precipitation from PBS given in Table 5.9.

Table 5.9. Life cycle inventory for copper precipitation process.

Input	**Amount**	**Unit**
Pregnant bioleach solution (PBS) after dilution, deionized water volume added to total deionize water amount	1,500	m^3
Electricity, medium voltage, TR mix (pumping 4,710 m^3 solution, weights 5,103.22 t, deionized water + hydrogen peroxide)	280.6	MJ
Electricity, medium voltage, TR mix (agitation for both precipitation operations)	7.2	kWh
Electricity, medium voltage, TR mix (1st filtration after bioleaching, removing solid iron hydroxide)	553.4	kWh
Electricity, medium voltage, TR mix (2nd filtration after bioleaching, removing copper hydroxide)	580.1	kWh
Sodium hydroxide	115.9	t
Liquid storage tank agitation energy	559	kWh
Hydrogen peroxide	325.4	t
Deionized water	4,089	m^3
Output		
Copper hydroxide (s)	58,136.1	kg

5.7.2.5. Proxy process; Reduction of copper hydroxide to copper metal. Copper metal precipitates as copper hydroxide with the addition of 0.5M sodium hydroxide to pregnant bioleach solution with a volume ratio of 1:2. In order to compare potential environmental impacts of copper recovery via biohydrometallurgy, a two-step custom process was created.

Copper hydroxide has low solubility in water and decompose to copper (II) oxide Cu(II)O at 100 °C (Wayne, H., 2002). Copper (II) oxide reduces to copper metal at 250 °C with the presence of carbon, carbon monoxide or hydrogen (Wayne, H., 2002). A similar process that exists in database is the reduction of cobalt oxide dusts (grey and black) to cobalt metal (Donaldson and Beyersmann, 2000) with carbon monoxide and hydrogen. Decomposition of Cobalt(II,III) oxide (Co_3O_4) to Cobalt oxide (CoO) occurs at temperatures above 900 °C (Donaldson and Beyersmann, 2000)

Cobalt(II,III) oxide (black cobalt) reduces to cobalt metal by two step process. First, cobalt(II,III) oxide reduces to cobalt oxide (gray cobalt) then cobalt oxide reduces to the cobalt metal. It has been stated that both cobalt oxides reduce to cobalt metal powder under conditions well below the melting point of the either oxides or metal (Donaldson and Beyersmann, 2000). Both reactions occur at higher temperature than copper oxide reduction, thus heating energy demand for cobalt reduction accepted as conservative estimate and adapted for molar ratio.

1 kg of cobalt metal is 16.97 moles and 1 kg of copper is 15.737 mol. 2 MJ heating value is adjusted by 15.737/ 16.97 factor. It has been assumed that half of copper hydroxide would be reduced by carbon monoxide and other half would be reduced by hydrogen. 95% yield efficiency was assumed for both reactions. Life cycle inventory for copper reduction process is given in Table 5.10.

$$Cu(OH)_2 + heat = Cu(II)O + H_2O \tag{5.18}$$

$$Cu(II)O + CO_{(g)} = Cu + CO_2 \tag{5.19}$$

$$Cu(II)O + H_{2(l)} = Cu + H_2O \tag{5.20}$$

Table 5.10. Life cycle inventory of copper hydroxide reduction for 1kg copper metal.

Input	**Amount**	**Unit**
Copper hydroxide	1.616	kg
Carbon monoxide	0.23	kg
Hydrogen (liquid)	0.016	kg
heat	1.86	MJ
Aluminium hydroxide facility	9E-10	unit(s)
Output		
Copper metal	1	kg

5.7.2.6. System boundaries and scaled-up model flowchart. A scaled-up model was created following scale-up framework (Piccinno et al., 2016) and assumptions made for this system using experiment data (IntenC). System boundaries of large scale system are given in Figure 5.2. Gold recovery was cut-off.

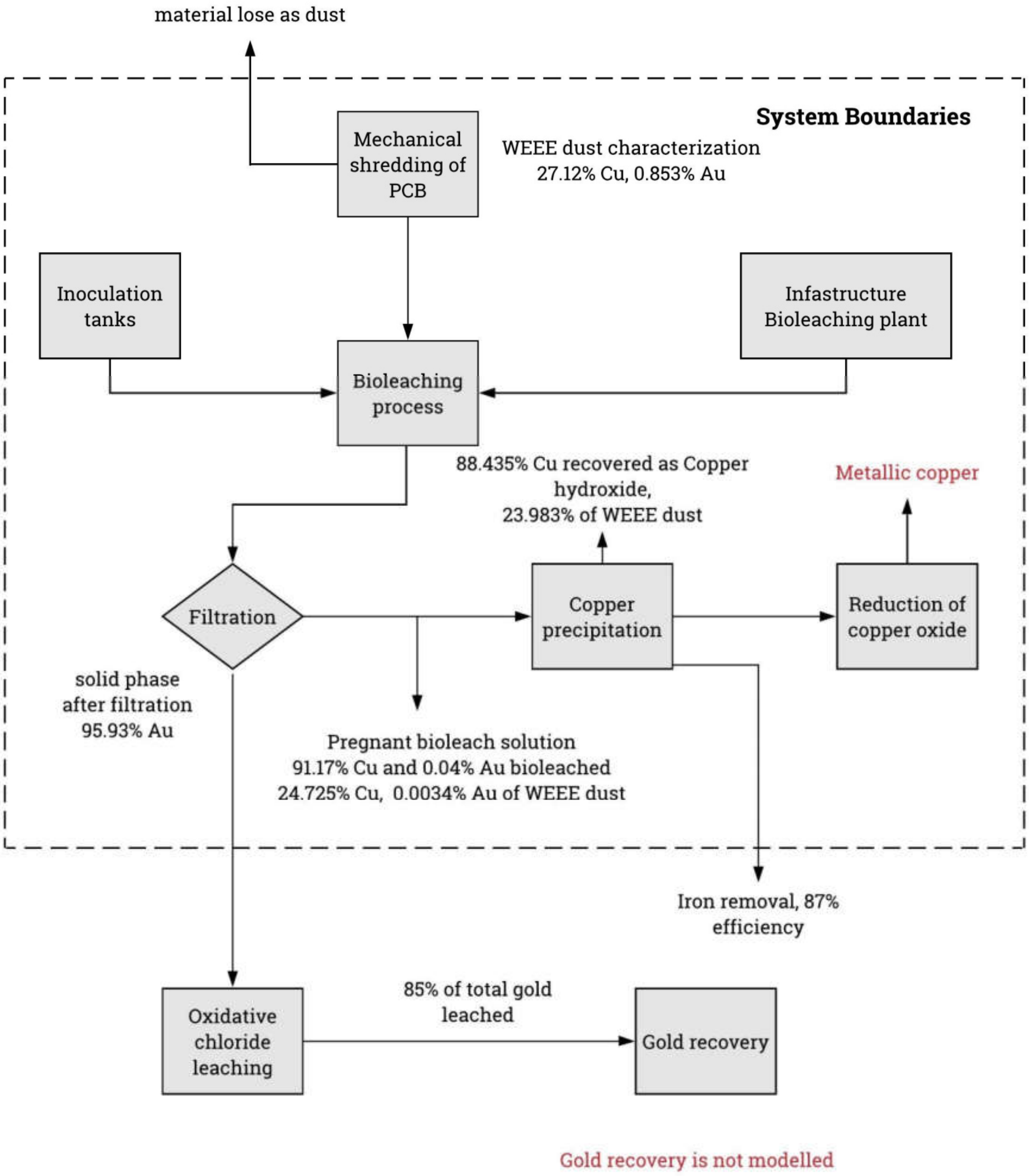

Figure 5.2. System boundaries for biohydrometallurgical copper metal recovery system (IntenC).

5.7.3. Life Cycle Impact Assessment of Copper Metal Recovery from Waste PCB Dust

It has been calculated that a total of 35,975 kg copper would be recovered theoretically after 8 days of bioleaching batch operation and following processes. Thus process values are scaled down by 2.78E-5 to recover 1 kg of copper. A comparison was made with 1 kg of virgin copper production in Rest of the world and 1 kg of copper recycled with bioleaching and copper precipitation processes. Results of LCIA are given in Table 5.11. Comparison of 1 kg copper price is given in Table 5.12.

Table 5.11. Comparison of copper metal recycling with virgin copper production.

Environmental Impact Categories	**Virgin copper production (ROW)**	**Recycled copper metal**
Acidification potential - average Europe	0.55	0.12
Climate change - GWP100	5.08	23.4
Terrestrial ecotoxicity - TETP inf	2.07	0.25
Photochemical oxidation - high Nox	0.021	0.005
Eutrophication - generic	0.45	0.045
Freshwater aquatic ecotoxicity - FAETP inf	119.93	25.79
Marine aquatic ecotoxicity - MAETP inf	3.4E+05	1.17E+05
Ozone layer depletion - ODP steady state	3.2E-07	4.09E-06
Human toxicity - HTP inf	610.49	48.53
Depletion of abiotic resources - elements, ultimate reserves	0.0017	0.00017
Depletion of abiotic resources - fossil fuels	50.59	288.65

Table 5.12. Comparison of 1 kg copper recycling cost to 1 kg copper market price.

Copper metal source	**Virgin copper production**	**Recycled copper metal**
Cost (USD/kg copper)	6.14	7.37

5.7.4. Interpretation

LCIA of scaled-up model indicated that copper recovery through bioleaching and copper precipitation using hydrogen peroxide does not offer clear environmental advantage and at the same time is not cost effective. This is mostly due to the high compressed air consumption and chemicals consumption such as hydrogen peroxide and sodium hydroxide. Eight of eleven environmental impact categories favored the recycling system. It should be noted recycling system performed better for acidification potential. However, huge energy consumption for recycling system is a problem.

Sensitivity analysis was conducted for the entire copper metal recycling system for three parameters: air consumption, hydrogen peroxide consumption and electricity consumption. Results of the air consumption sensitivity analysis are given in Table 5.13. Sensitivity analysis for hydrogen peroxide consumption parameter are given in Table 5.14 and Sensitivity analysis for the electricity consumption parameter are given in Table 5.15.

Table 5.13. Sensitivity analysis results with air production parameter.

	Percentage change				
Environmental Impact Category	-20	-10	0	10	20
Acidification	-4.7	-2.3	0	2.3	4.7
Climate change	-4.4	-2.2	0	2.2	4.4
Ultimate reserves, fossil fuels	-3.8	-1.9	0	1.9	3.8
Cost	-2.9	-1.4	0	1.4	2.9

Table 5.14. Sensitivity analysis results for hydrogen peroxide parameter.

	Percentage change				
Environmental Impact Category	-20	-10	0	10	20
Acidification	-8.3	-4.1	0	4.1	8.3
Climate change	-9.4	-4.7	0	4.7	9.4
Ultimate reserves, fossil fuels	-10.3	-5.1	0	5.1	10.3
Cost	-13.0	-6.5	0	6.5	13.0

Table 5.15. Sensitivity analysis results for electricity parameter.

	Percentage change				
Environmental Impact Category	-20	-10	0	10	20
Acidification	-0.3	-0.1	0	0.1	0.3
Climate change	-0.3	-0.1	0	0.1	0.3
Ultimate reserves, fossil fuels	-0.3	-0.1	0	0.1	0.3
Cost	-0.2	-0.1	0	0.1	0.2

In conclusion, results of all three sensitivity analyses indicate that the system is most sensitive to changes of hydrogen peroxide consumption for environmental impacts and economical performance.

6. NEODYMIUM METAL RECOVERY FROM NEODYMIUM IRON BORON MAGNETS BY HYDROMETALLURGICAL METHODS

6.1. Rare Earth Elements

Rare earth elements (REE) are defined as the 15 lanthanide elements, Scandium (Sc) and Yitrium (Y) by International Union of Pure and Applied Chemistry (IUPAC). Rare earth elements are usually divided into two groups; light rare earth elements (LREEs) and heavy rare earth elements (HREEs). However there is an argument about the definitions of LREEs and HREEs (Binnemans et al., 2018). IUPAC classified elements from lanthanum (La) to europium Eu as light rare elements (Connely et al., 2005) and elements from gadolinium (Gd) to lutetium (Lu) and Y as heavy rare earth elements (Binnemans et al., 2018). Rare earth elements are present in over 200 known mineral species (Koltun and Tharumarajah, 2014) but only some of them are found feasible due to their high REEs concentrations, such as monazite, bastnäsite, xenothymiun and ionic clays (Lima et al., 2016). It is impossible to operate a mine for a single REE since all ores have different content of various LREEs and HREEs (Binnemans et al., 2018).

The occurrence of REE in nature is not so rare but mining zones with sufficient concentrations are more uncommon than most other ores (Reilly II, 2019, Lide, 2004). REE production in 2018 and countries with discovered reserves are given in Table 6.1. It has been stated that illegal and undocumented mining operations continue in China, the leading country for both mine production and reserves, despite government efforts.

China specializes in REEs production including the mining of rare earth elements, separating rare earth oxides from mineral ores and reducing rare earth oxides into rare earth metals (Binnemans et al., 2013). It is also the leading country for both the production of permanent magnets and lamp phosphors (Binnemans et al., 2013). China's dominance in rare earth market for all production stages raises concerns about supply dependency, especially regarding critical military and industrial applications (Hurst, 2010).

Table 6.1. World's annual mine production and reserves for REE in 2018 (Reilly II, 2019).

Country	**Annual Production (tons)**	**Reserves (tons)**
United States	15,000	1,400,000
Australia	20,000	3,400,000
Brazil	1,000	22,000,000
Burma (Myanmar)	5,000	-
Burundi	1,000	-
China	112,000	44,000,000
India	1,800	6,900,000
Malaysia	200	30,000
Russia	2,600	12,000,000
Thailand	1,000	-
Vietnam	400	22,000,000
Other countries	0	4,400,000
World total (rounded)	170,000	120,000,000

In recent years REE have gained significant importance due to their use in critical technologies such as permanent magnet production, being a catalyst for petroleum industry, lamp phosphorus, many electronics consumer products (screens) and critical military industries (Hurst, 2010). According to USGS mineral commodity summaries 2019, estimated distribution of rare earths by end use are respectively: catalysts, 60%; ceramics and glass, 15%; metallurgical applications and alloys, 10%; polishing, 10% and other, 5%. Examples of REE containing applications and demand drivers for applications are given in Table 6.2.

Open-pit mining and leaching of ion adsorption clays are two commonly used extraction methods for rare earth mining (Jha et al., 2016). Open-pit mining primarily extracts bastnäsite, monazite and xenotime minerals that are rich in light rare earth (LRE) oxides (Jha et al., 2016). Ion adsorption clays have higher (60%) heavy rare earth (HRE) oxides content than mineral ores (Jha et al., 2016).

Table 6.2. Applications that use REE and their respective usage in products (adapted from Binnemans et al., 2013, www.rainbowsrare-earth.com).

Application	**Rare earth elements**	**Product examples**
Permanent magnets	Nd, Pr, Tb, Dy	Automotive industry, Wind turbines, industrial engines, computers and auxiliary devices, HDDs, mobile phones, mp3 players, cameras, Voice coil motors. Hybrid and Electric vehicles, Cordless power tools, Sensors, Medical imaging (MRIs)
Lanthanum Nickel metal hybrid batteries	La, Ce, Pr, Nd	Electrical vehicle and hybrid car batteries. Hydrogen absorption alloys for re-chargeable batteries
Phosphors	Eu, Y, Tb, La, Ce, Gd	LCDs, PDPs, LEDs. Energy efficient fluorescent lights/lamps, CRTs, CFLs
Fluid cracking catalysts (FCC)	La, Ce, Pr, Nd	Petroleum products, especially by heavy oils and tar sands
Polishing powders	Ce, La, Nd	TVs, monitors, tablets, mirrors and silicon chips
Auto catalysts	Ce, La, Nd	Combustion engine vehicles, demand driven by strict air pollution standards
Glass additive	Ce, La, Nd, Er	Decoloring agent for glasses (Ce), Digital camera lenses (La increases glass refractive index)
Fiber optics	Er, Y, Tb, Eu	Rare earth doped optical fibers (Signal amplification)

Bastnäsite (La, Ce)FCO_3 and monazite (Ce, La, Y, Th)PO_4 minerals are extracted with open-pit mining mainly in the Bayan Obo region in Inner Mongolia region of North China while leaching of ion adsorption clays mostly in Southern China (Jha et al., 2017; Vahidi et al., 2016). Bastnäsite mineral contains approximately 70% of rare earth oxides (mostly LREE). Monazite mineral's LREE content is similar with Bastnäsite mineral but HREE content is higher and contains naturally occurring Thorium (Th) element. Xenotime is a rare earth phosphate mineral which is rich in yitrium (Y) and HRE elements (Jha et al., 2016). Ion adsorption clays contain more high-value heavy RE oxides while in general reserves RE oxides concentrations are lower (Vahidi et al., 2016; Vahidi et al., 2017).

6.2. Rare Earth Element Neodymium

Neodymium is a light rare earth element with an atomic number of 60 and part of lanthanide element group. Neodymium abundance in earth's crust is 41.5 ppm while abundance in oceans is 2.8×10^{-6} mg/L (Lide, 2004). Neodymium oxide (Nd_2O_3) production was estimated by 22,391 tons/year on average between 2010 and 2014 (Binnemans et. al, 2018). Neodymium concentration in mines varies significantly (McGill, 2000). Neodymium oxides concentrations in several ores are given in Table 6.3.

Although neodymium has been widely used for high strength Nd-Fe-B permanent magnet production, it has also been found in a number of other applications. General uses of neodymium metal are in: Nd-Fe-B high strength permanent magnets, lasers, Metal halide lamps, Nd stabilized ZrO_2 synthetic gems, coloring agent, glass blower and welder googles (Lucas, J., 2015).

Nd-Fe-B magnet production is estimated to increase 7% (Rollat et al., 2016) each year and will continue to increase due to ever increase in demand for clean tech applications (Schulze et al., 2016). The majority of REE demand is for magnet elements such as neodymium and dysprosium (Jowitt et al., 2018). In order to supply neodymium demand, large number of other light REEs such as lanthanum and cerium are also generated (Binnemans et al., 2018). Thus an excess supply of light REEs is generated and this affects the prices. This is called the balance problem (Binnemans et al., 2014).

Neodymium has been evaluated as most critical element in terms of supply risk and economic importance recently (Europe Commission, 2017), replacing dysprosium (Europe Commission, 2014). Applications that use neodymium and its respective share in total consumption are given in Table 6.4.

Table 6.3. Composition of neodymium and dysprosium as REO in mineral ores/ IOCs by weight %, (adapted from Deng, H., et al. 2019; McGill, 2000; Vahidi et al., 2016).

Source	**Mineral ore/ IOCs**	**Location**	**Nd2O3, %**	**Dy2O3,%**
(Mcgill, 2000)	Bastnäsite	United states	12	0.031
		China	18.5	0.1
	Monasite	Australia	17.38	0.69
		China	15.74	1.02
	Xenotime	Malaysia	2.2	8.7
	Apatite	CIS	14	1
Qi, D., 2018	Bastnäsite	Inner Mongolia, China	17.41	<0.3
		Mountain Pass (USA)	13.5	0.03
	Monasite	Taiwan	19.14	0.54
		Inner Mongolia, China	28.38	0.1
		Australia	18.35	0.56
	Xenotime	Guangdong, China	1.86	8.83
	Hingganite concentrate	Inner Mongolia, China	15.58	4.63
	IOCs, rich La Nd LRE ore	China	30.18	1.77
adapted from Vahidi et al., 2016. Original source is Shi, F. 2009.	IOCS, site A	Southern China, 130 million metric tons; 0.05-0.2 wt. %, REO	5.1	7.5
	IOCS, site B		26	4.1
	IOCS, site C		7.4	8.6
	IOCS, site D		30.2	1.8
	IOCS, site E		18.7	4
	IOCS, site F		13.4	7.1

Table 6.4. Neodymium metal usage by applications in percentages, adapted from Curtis, (2010).

	Application						
	Magnets	Battery alloys	Metallurgy	Auto catalyst	Glass additives	Ceramics	Others
Usage ,in %	69.4%	10%	16.5%	3%	3%	12%	15%

6.3. Neodymium Iron Boron Magnets

Permanent magnets are the most significant application of rare earth elements. Permanent magnets production consumed 20-23% of total rare earth oxides by volume, representing 53% of total value (Gutfleisch et al., 2011). There are two main types of permanent magnets commonly used: samarium-cobalt (Sm-Co) magnets and neodymium-iron-boron (Nd-Fe-B) magnets (Lucas, J., 2015). Currently Nd-Fe-B magnets makes up to 95% of total permanent magnet market (Binnemans et al., 2018). Nd-Fe-B magnets are cheaper and have higher magnetic field strength (Binnemans et al., 2018). Neodymium iron boron magnets are represented by $Nd_2Fe_{14}B$ matrix phase. Nd-Fe-B magnets have the highest energy product (200-440 kJ/m^3) of all permanent magnets (Binnemans et al., 2013). Currently sintered-magnet production dominates the market by great margin (Yang et al., 2017). Annual bonded magnet production rose up to 10,000 tons (Binnemans et al., 2018).

REEs content of neodymium-iron-boron (Nd-Fe-B) magnets can be up to 31 to 32 % by weight (Yang et al., 2017). Magnet weight ranges from less than 1 g to 2000 kg (Yang et al., 2017). Rare earths elements composition in magnets varies significantly depending on the application. Several studies investigated elemental composition of magnets; Table 6.5 below gives elemental composition of neodymium magnets from respective studies.

Table 6.5. Elemental composition of several Nd-Fe-B magnets from selected studies.

Magnet application	HDDs	HDDs	HDDs	Uncoated EV motor
Elements	IntenC project	Küçüker et al., 2017	Sprecher et al., 2014	Jin et al., 2016
Iron (Fe)	53.36	67.4	72	66.88
Neodymium (Nd)	21.84	24.3	27	18
Praseodymium (Pr)	NA*	ND*	-	4.60
Boron (B)	NA*	1.2	1.28	1.02
Dysprosium (Dy)	NA*	1.1	-	6.15
Cobalt (Co)	NA*	ND*	-	2.84
Nickel (Ni)	NA*	0.8	-	
Aluminium (Al)	NA*	0.8	-	0.12
Copper (Cu)	NA*	ND*	-	0.18
Gallium (Ga)	NA*	ND*	-	0.21

NA* denotes not analyzed and ND** denotes not detected

6.4. Neodymium Iron Boron Magnet Production Methods

There are two main production routes for Nd-Fe-B magnets. The traditional route, sintered magnet route and bonded magnet route (Yang et al., 2017). Classical powder manufacturing route (sintered magnet route) is used for Nd-Fe-B magnet production process (baseline scenario) in this LCA study as defined by Sprecher et al. (2014) and Jin et al. (2016). Magnet alloy elements such as rare earth elements, iron and boron are combined in a crucible (Jin et al., 2016). First process is strip casting where magnet alloy is melted by an industrial crucible (Jin et al., 2016). Then melted alloy is slowly poured over a fast spinning, water-cooled copper wheel to produce alloy flakes with a few millimeters thick and several centimeters long (Sprecher et al., 2014; Jin et al., 2016). Second process is called hydrogen decrepitation where Nd-rich grain boundaries expands by hydrogen then falls apart in coarse powder with an average particle size of 4 - 7 µm (Sprecher et al., 2014; Jin et al., 2016). Third process jet milling to further reduce particle size to further 3 – 4 µm (Sprecher et al., 2014). The fine powders are subsequently put in a mold and mixed with lubricants (Jin et al., 2016). Under intense pressure with the addition of magnetic field presence, magnet blocks are formed (Sprecher et al., 2014). This process is called aligning and pressing. The fifth process is vacuum sintering where magnet blocks from previous step are vacuum sintered at pressures of 2 – 10 mbar (Sprecher et al., 2014). The sixth process is called grinding and slicing where sintered magnet blocks were sliced into rough shapes then ground and polished into its final form (Sprecher et al., 2014). Electroplating is the seventh process where magnets are coated with nickel to be protected from moisture (Sprecher et al., 2014). Last process step is pulse magnetizing and testing process where magnets are subjected to a strong magnetic field and gone through quality control (Sprecher et al., 2014). In LCA work environmental impacts of this last step is neglected.

Bonded magnets are also called polymer based magnets (Lucas, J., 2015). Magnet powder are mixed with polymers to gain material flexibility which allows complex shaping for magnets (Lucas, J., 2015). During production jet milled alloy flakes are mixed with polymer then pressed or injected into a shaped magnet (Yang et al., 2017).

6.5. Neodymium Iron boron Magnets Recycling Techniques

Neodymium iron boron magnets are widely used by several industries due to its high magnetic properties (Binnemans et al., 2013). It has been estimated that annual production reached up to 79,500 tons by year 2014 (Binnemans et al., 2013). Thus recycling of neodymium metal gained importance; however only 1% of REEs from end-of-life products recycled in 2011 (Binnemans et al., 2013).

Secondary sources of neodymium metal such as Nd-Fe-B magnet swarf, rejected magnets and end-of-life products attract research attention since there is no commercial recycling method yet established for magnets (Jha et al., 2017). Binnemans et al., 2018 estimated recycling potential of REEs from magnets between 3,300 tons to 6,600 tons out of 300,000 tons of REEs. This estimation was based on urban mining concept that was developed as a recycling strategy (Binnemans et al., 2013). Material in-use stocks are defined as urban mines (Ciacci et al., 2019). Schulze et al. (2016) estimated that 18-22% of global LRE demand and 20-23% of HRE demand can be supplied by 2030.

There are two major pathways for magnet recycling. Conventional methods are pyrometallurgical methods and hydrometallurgical methods. In pyrometallurgical methods, REE magnet alloys are converted into oxides/ chlorides/ fluorides then reduced to metallic form. (Binnemans et al., 2013). Other method is magnet to magnet recycling where magnets recycle into new magnet without material separation (Jin et al., 2016).

Pyrometallurgical method is commonly used in the processing of high grade ore (Tunsu et al., 2015). High temperature processing separates REEs from non-REE fraction by converting them into another phase (Yang et al., 2019). Separated REEs are more concentrated and can be reduced to metallic form by molten salt electrolysis or metallothermic reduction (Yang et al., 2019).

Hydrometallurgical method is typically leaching out material with acids and separating REEs with methods like precipitation or solvent extraction (Yang et al., 2017). Hydrometallurgical method allows selective leaching-precipitation process which is also capable of total leaching (Binnemans et al., 2013).

Direct alloy recycling method, Magnet to magnet recycling (Resintering scrap magnets), is a novel method with major advantages (Zakotnik et al., 2016). Major advantages of magnet to magnet recycling over other methods are: reusing all magnet materials in new magnet production with minimum waste and depletion, and reduced environmental footprint due to less energy and chemical usage (Jin et al., 2016; Jin et al., 2018; Zakotnik et al., 2016). Jin et al. (2018) showed recycled Nd-Fe-B magnets from electric vehicle motors have similar properties to that of virgin magnets. An overall evaluation of recycling methods are given in Table 6.6.

Table 6.6. Overall evaluation of magnet recycling methods with advantages/ disadvantages, adapted from Binnemans et al. (2013).

Methods	**Advantages**	**Disadvantages**
Direct re-use without altering shape/ form	• Best economically feasible way • No waste generation • Considered best recycling route for HDDs magnets	• Only suitable for large magnets • Not enough magnets in scrap
Hydrometallurgical	• Generally all magnets with different composition is suitable for this method • Can be used for both oxidized and not-oxidized magnet alloys • Extraction processes are same with that of industrial virgin ore production	• Consumption of large amounts of chemicals • Generates large amount of hazardous wastewater • Several processes are required to obtain metal that is suitable to be alloyed for magnet production
Pyrometallurgical	• Magnet composition doesn't affect method, applicable for all compositions • No wastewater generation • Fewer process steps than of hydrometallurgical method • Liquid metal extraction yields metallic REEs • Allows obtaining master alloys from direct melting of magnets	• Consumes highest amounts of energy • Not all extraction methods are suitable for oxidized magnets • Some methods generates large amount of solid waste
Magnet to magnet recycling	• Less energy requirements than conventional methods	• Not suitable for huge magnet waste streams where magnet composition varies • Cannot be used for oxidized magnets

6.6. Neodymium Metal Recycling from Nd-Fe-B Magnets Experiments (IntenC)

IntenC project developed a hydrometallurgical method where neodymium metal is leached by sulfuric acid (Lee et al., 2013) and extracted as neodymium hydroxide. Previous sulfuric acid leaching experiments resulted with a double sulfate salt precipitation (Lyman et al., 1993; Yoon et al., 2003) which were considered expensive and not environmentally friendly to precipitate (IntenC). Experiments for neodymium metal recovery has three major steps; Pretreatment, Chemical leaching and Neodymium metal precipitation (IntenC). Each of these steps are described below.

6.6.1. Pretreatment Phase

Pretreatment of WEEE consists of three steps, Manuel dismantling, De-magnetization and size reduction (IntenC). First step is manual dismantling of various end of life HDDs (IntenC). Dismantling a single Nd-Fe-B magnet from a HDD took about a minute. After magnet removal, remaining parts of HDDs is discarded for waste treatment which is cut-off. Subsequently magnets are heated in the furnace up to 350 °C to lose its magnetic properties. Finally Magnets are ground with the hammer mill (Fritsch Cross Beator Mill, Pulverisette 16) and further screened down to a particle size of 0.5 mm (IntenC).

6.6.2. Characterization of Nd-Fe-B Magnets

Nd-Fe-B magnets are were widely used in different applications thus elemental composition varies significantly due to different demands (Binnemans et al., 2013). Several studies characterized elemental composition of Nd-Fe-B magnets of HDDs (Sprecher et al., 2014; Kucuker et al., 2017; Zakotnik et al., 2016). Table 6.3 compares characterization result of selected studies. For this study; elemental composition of Nd-Fe-B magnet is based on Kucuker et al. (2017) results.

There are non-metal ingredients such as bonding agents (Zapotnik et al., 2016) used in industrial magnets. Also magnets contain some elements such as Terbium which can replace dysprosium metal (Binnemans et al., 2018), detected as trace level (personal communication with Mehmet Ali Küçüker). Some magnets use natural mix (4:1 atomic ratio respectively) of neodymium-praseodymium (didymium) alloy instead of pure neodymium metal (Binnemans et al., 2018). In such situations, desired properties are met and separating praseodymium would further increase the cost (Binnemans et al., 2018). However, not knowing full elemental composition of magnets can affect the data quality of study. Iron content of magnet was increased to 71.8% from 67.4, to create a mass balance and compensate.

6.6.3. Chemical Leaching of Neodymium Metal

Magnet dust was added into glass beakers that are filled with of 2M sulfuric acid. 20 g/L solid/liquid ratio was set (IntenC). Leaching experiments were conducted at 27 °C and took about 15 minutes (IntenC). Stirring rate is 170 rpm (IntenC). After leaching process, filtration separated solid and liquid fractions (IntenC).

Leaching reactions are given below for two major metals by content, Neodymium and iron metals (Lee et al., 2013).

$$2Nd\ (s) + 6H^{+}\ (l) \rightarrow 2Nd^{3+}\ (s) + 3H_2\ (g) \tag{6.1}$$

$$Fe\ (s) + 2H^{+}\ (l) \rightarrow Fe2+\ (s) + H_2\ (g) \tag{6.2}$$

Metallic fraction of magnets reacted rapidly with the acid and formed Nd(III), Fe(II) and B(II) ions (Lee et al., 2013). At the same time hydrogen bubbles forms and leave the beaker (Lee et al., 2013).

6.6.4. Neodymium Metal Precipitation

All metal components of Nd-Fe-B magnet were dissolved in the leaching solution after sulfuric acidic leaching (IntenC). Neodymium metal precipitates easily with the adjustment of pH before any other metal (IntenC). Neodymium fully precipitates (100%) at the pH value of 0.8 with the addition of 0.5M sodium hydroxide (IntenC). Settling of neodymium metal occurred after 15 minutes at 170 rpm (IntenC). Precipitation reaction of Neodymium metal is given below (Lee et al., 2013).

$$Nd^{3+}\ (l) + 3NaOH\ (s) \rightarrow\ Nd(OH)_3\ (s) + 3Na^{+} \tag{6.3}$$

6.6.5. Small Scale Model for Neodymium Metal Recovery from Nd-Fe-B Magnets

Following the procedure of Piccinno et al. (2016), a basic flowchart was created for small scale neodymium metal recovery model. A life cycle inventory table was created for the 1000 mL working volume. All chemicals are modelled to be 100% pure in the Ecoinvent database.

For the 50 mL working volume, 5.44 mL 2M sulfuric acid (H_2SO_4) is required. It is scaled up to 108.8 mL for 1 L working volume. 106.609 mL of pure (100%) sulfuric acid and 893.39 mL deionized water are required for 2M, 1000 mL sulfuric acid solution. Stock solution is at 95% concentration and density is 1.84 g/mL. Sulfuric acid solution (100%) volume is adjusted to 112.2 mL and it weighs 196.16 g.

For 20 mL 0.5M sodium hydroxide solution, 0.4 g sodium hydroxide salt was used (98%). Thus when total volume is scaled-up to 1000 mL, 20 g sodium hydroxide is required. Database sodium hydroxide is modelled as 100% in solution state without water so further conversion is neglected.

6.6.5.1. Proxy process; Neodymium hydroxide reduction to neodymium metal. In industrial applications, Rare earth hydroxides are washed with hot water and separated from leachate (Qi, D., 2018). Then neodymium hydroxides dissolve by hydrochloric acid to produce neodymium chloride (Qi, D., 2018). Finally with solvent extraction separation, neodymium oxide is directly separated from leachate (Qi, D., 2018). In theory, Neodymium hydroxide decomposes to neodymium oxide around 400-600 °C (Phuruangrat et al., 2012; Bian et al., 2016). A proxy reduction process was created with single input, energy. 2 MJ heating energy value of cobalt oxide reduction is adjusted by a 0.302 factor and adapted (see section 5.5.4). Process output neodymium oxide would reduce to neodymium metal following virgin production procedure (Sprecher et al., 2014)

6.6.6. Scaled-up Model for Metal Recovery System

It has been pointed out that 7% of shredded WEEE was lost during size reduction process (Classen et al., 2009) thus output was set to 93% of input material. There has been reports of machine specialized at dismantling HDDs (Hitachi HDD dismantling machine) since sorting and dismantling are bottlenecks for commercial operations, (Zakotnik et al., 2016).

Nd-Fe-B magnets are quite brittle. An industrial application data about energy consumption for demagnetization is 0.075 kWh for 1 kg magnet (Zakotnik et al., 2015).

Batch operations were considered for the leaching and precipitation operations. It has been assumed that tanks with 1000 L volume were selected for this operation. 20 kg of magnet dust would require 1000 to 2000 HDD magnet thus selected tank volume is sufficiently large. Stirring energy was found to be 0.1725 kWh (both steps) and pumping energy was found to be 60.5 KJ.

Since experimental data was not available for treating solution after removing neodymium, wastewater treatment of iron-rich solution is cut-off from study. Metal rich industrial wastewaters use neutralization as a pretreatment system (Wang et al., 2005). At high pH, most metals come out as hydroxides (Wang et al., 2005).

Life cycle inventory for recycling 1 kg of Neodymium metal recycling is given in Table 6.7 below. Out of 20 kg magnet dust, 4.86 kg is neodymium metal (Küçüker et al., 2017) and weighs 6.58 kg as neodymium hydroxide.

Table 6.7. Life cycle inventory for 1 kg of Neodymium metal recycling.

Input	**Amount**	**Unit**
Magnet dust	4.11	kg
Electricity, medium voltage, TR mix	0.071	kWh
Electricity, medium voltage, TR mix	25.12	KJ
Chemical factory, organics	8.23E-11	unit(s)
Sulfuric acid, market GLO	40.15	kg
Water, deionized, from tap water, at user	183,80	kg
Sodium hydroxide, market GLO	4.11	kg
Output		
Neodymium metal (neodymium hydroxide)	4.86 (6.58)	kg

6.7. Life Cycle Assessment of Neodymium Metal Recovery's Effect on Neodymium Iron Boron Magnets

Rare earth elements have been targeted as critical materials and each element has been evaluated by its supply risk and economic importance in various reports (European Commission 2014, European Commission 2017). Recently, neodymium element replaced dysprosium element as the highest critical element (European Commission, 2017). Thus recovery of Neodymium metal from magnet scraps, end-of-life appliances or industrial applications gained even more strategic importance. LCA analysis was conducted to evaluate recovery of rare earth element neodymium from used HDDs magnets. Neodymium magnet production has two pathways for neodymium metal production. First pathway is the virgin metal production from mineral ores and the latter is scaled-up metal recycling pathway based on laboratory scale.

6.7.1. Goal and Scope

Goal of study is to evaluate the impact of hydrometallurgical neodymium metal recycling on Nd-Fe-B magnet production. Comparisons were made to evaluate both environmental effects and production cost. Reference flow of system is 1 kg Nd-Fe-B magnet production. Neodymium metal used in Nd-Fe-B magnet production was reference flow. Geographical reference is Istanbul, Türkiye. Technological scope of the study is experiments conducted at laboratory scale.

6.7.1.1. System boundaries and small scale model. Production, use, collection, sorting or any other phases concerning end of life HDDs are not part of metal recovery system. Also treatment of other parts of HDDs or process synergy such as material recovery reuse or heat recovery techniques were not included in the system. System boundaries of production system were given in Figure 6.1. Collection, sorting and any previous step involving end of life HDDs, were not modelled in this study.

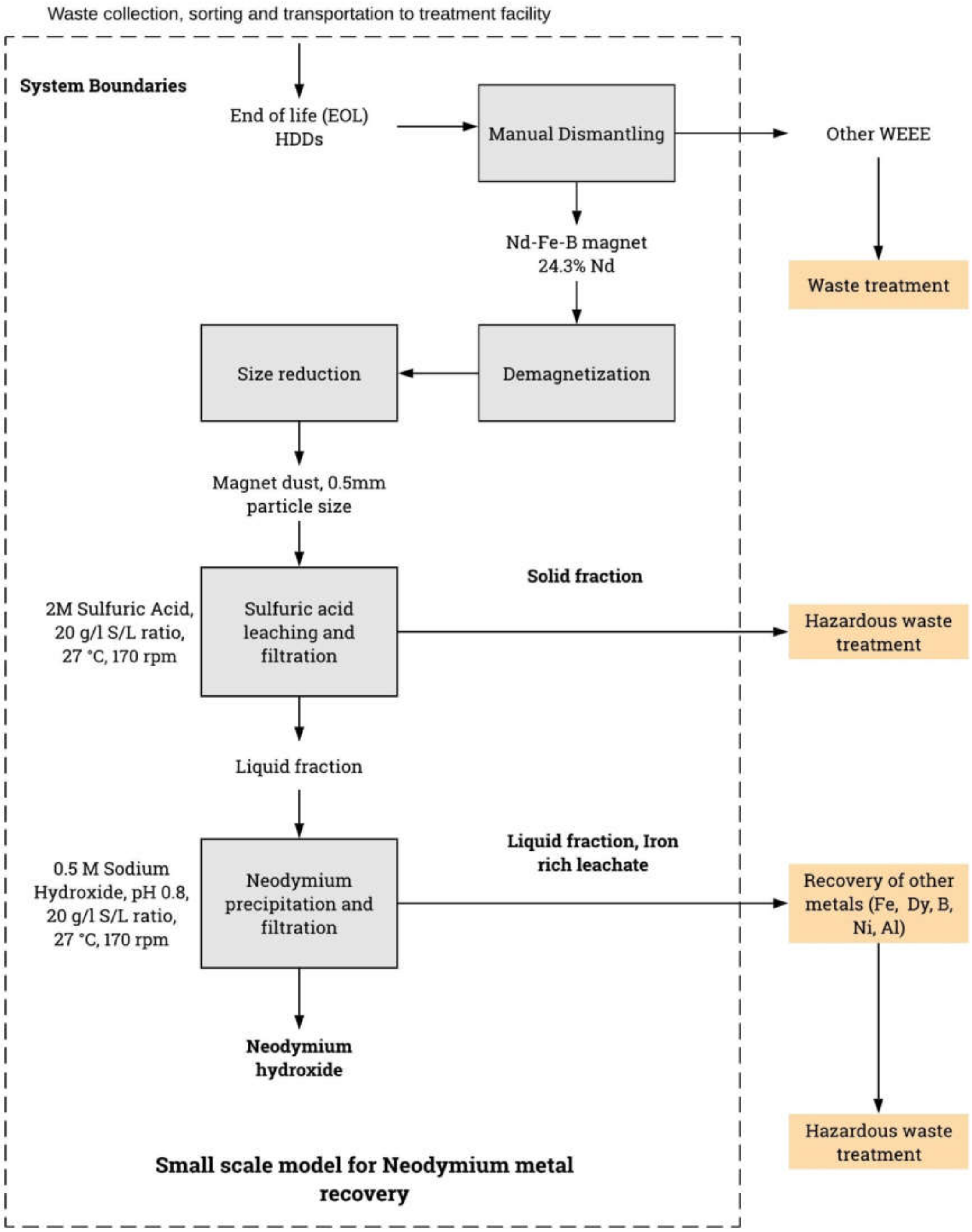

Figure 6.1. System boundaries and small scale model for neodymium metal recovery system (IntenC).

6.7.2. Life Cycle Inventory of Neodymium Iron Boron Magnets Production

LCA database Ecoinvent has neodymium oxide production from Bastnäsite/ monazite production dataset. A virgin magnet production model was created with available data from Sprecher et al. (2014). There are three magnet production scenarios, based on different technology levels, were given in the study. Baseline scenario is selected for the LCA study. Process flowchart of an industrial scale magnet production is given in Figure 6.2.

Neodymium oxide production from bastnäsite/ monazite ores is modelled in Ecoinvent database (Classen et al., 2009). According to de Castro J.A. et al. (2014), there are three main methods for reducing neodymium oxide to metallic neodymium; electrolysis using fluoride salts, electrolysis using chloride salts and calciothermic reduction. Reduction of neodymium oxide to metallic form by metal electrolysis modelled with available data (Sprecher et al., 2014). Since the study used Ecoinvent v2.2 database, adaptations were made for v3.3. A two-step metal oxide reduction process (Hall-Héroult process for aluminium metal reduction) was adapted for neodymium metal reduction process.

Dysprosium metal concentration is not found significantly high in bastnäsite/ monazite ores (see to Table 6.3) thus an alternative production route was modelled (Zapp et al., 2018). It has been assumed that rare earth elements are mined, separated and processed to metal form in China then transported to Turkey. Generic transportation methods and distances are given in Ecoinvent database. Market of rare earth oxides datasets are used for the study. Dysprosium metal production model is given in section 6.7.2.1. Life cycle inventory of 1 kg Nd-Fe-B magnet production is given in Table 6.8.

Table 6.8. Life cycle inventory for production of 1 kg Nd-Fe-B magnet (Sprecher et al., 2014; Kucuker et al., 2017; IntenC).

Input	**Amount**	**Unit**
Aluminum, virgin production, ingot	11.33	g
Boron carbide	2.17	g
Cobalt	12.74	g
Dysprosium metal	1.557	g
Electricity, medium voltage, TR	8.169	kWh
Iron pellets	954.18	g
Neodymium metal	386.49	g
Liquid hydrogen	0.0061	kg
Electricity, medium voltage, TR	4.056	kJ
Water, unknown source	0.0024	m^3
Chemicals, organics	0.17	g
Nickel	9.55	g
Sodium hydroxide	3.4E-5	kg
Sodium phosphate	0.136	g
Sulfuric acid	0.125	g

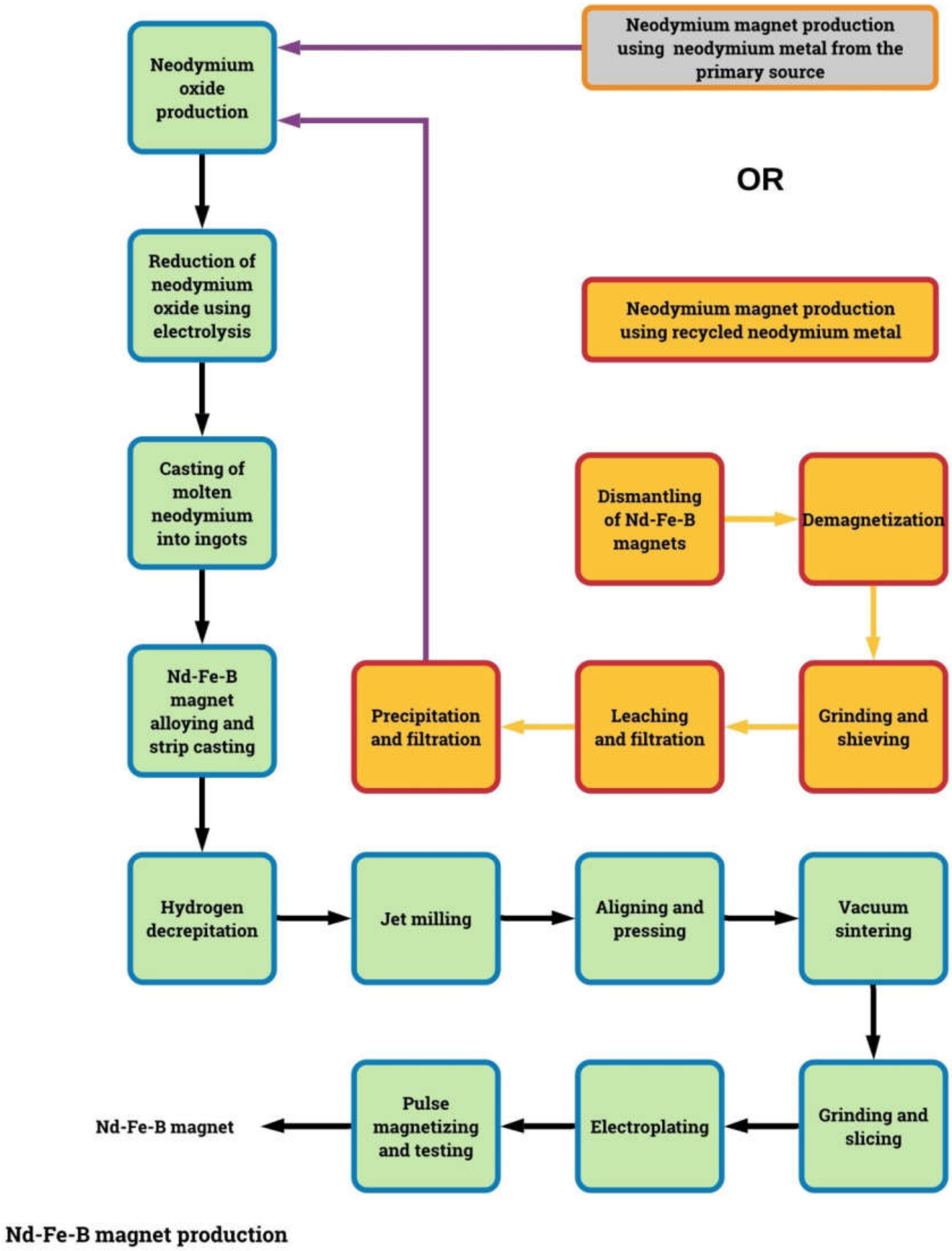

Figure 6.2. Production routes for neodymium iron boron magnet production (Sprecher et al., 2014, IntenC).

6.7.2.1. Dysprosium metal production. Dysprosium metal content (%) increases maximum operating temperature of magnets as well as the Curie temperature but decreases its magnetic properties (Binnemans et al., 2018). Magnets lose their magnetic properties at Curie temperature

(Lucas, J., 2015) which is about 300 °C for most magnets. However in some appliances such as high performance magnets that are used in engines (Binnemans et al., 2018), it can be higher.

In the Ecoinvent database, only five light rare earth oxides (La, Ce, Nd, Pr, Sm-Gd-Eu mix) production from bastnäsite / monazite ores are modelled. However, no dataset for heavy REE oxides production exists (v3.3). Heavy REEs concentrations are significantly lower in bastnäsite / monazite ores. Therefore a new production path was created for dysprosium metal from Chinese ion adsorption clays. Composition of rare earth oxides in rare earth minerals varies by ore types. Ion Adsorption Clays are also known as weathered clays are formed with process unique to certain parts of world (Vahidi et al., 2016). Examples of REE oxides composition in different minerals and Ion Adsorption Clays (IOCs) were given in Table 6.3. It has been stated that collected IOCs data likely provides similar results with mining sites.

Dysprosium metal production is adapted from Zapp et al. (2018). Three dysprosium metal production pathways were given in the study (Zapp et al., 2018). Chinese IACs source and high estimates pathway was chosen for this study. It's the most common method for production of heavy REEs in China due to its high concentration of heavy REE oxides. Instead of custom "natural gas mix" dataset described in the original study (Zapp et al., 2018), generic natural gas mix for China is used in LCA due to complications. Transport distances were adapted from light REEs.

6.8. Life Cycle Impact Assessment of Neodymium Metal Recovery from Neodymium Iron Boron Magnets

LCIA results were obtained for both virgin neodymium metal and recycled Neodymium metal in Nd-Fe-B magnet production. A comparison of LCIA is given in Table 6.9 to see the effect of recycling neodymium metal on neodymium iron boron magnet production. Production cost comparison for Nd-Fe-B magnets production is given in Table 6.10.

Table 6.9. Effect of Neodymium metal recycling on 1 kg of Nd-Fe-B magnet production.

Environmental Impact Categories	**Virgin neodymium metal**	**100% recycled neodymium metal**	**Change (%)**
Acidification potential - average Europe	0.26	0.30	13.81
Climate change - GWP100	30.49	22.82	-25.15
Terrestrial ecotoxicity - TETP inf	0.47	0.16	-65.21
Photochemical oxidation - high Nox	0.013	1.31E-02	1.31
Eutrophication - generic	0.67	0.67	-1.15
Freshwater aquatic ecotoxicity - FAETP inf	16.04	13.78	-14.09
Marine aquatic ecotoxicity - MAETP inf	6.74E+05	4.74E+05	-29.65
Ozone layer depletion - ODP steady state	3.96E-06	2.70E-06	-31.71
Human toxicity - HTP inf	72.83	52.540	-27.85
Depletion of abiotic resources - elements, ultimate reserves	0.00022	0.00043	95.45
Depletion of abiotic resources - fossil fuels	440.87	297.04	-32.62

Table 6.10. Cost effect of neodymium metal recycling on Nd-Fe-B magnet production.

Neodymium metal source	**Virgin neodymium metal**	**Recycled neodymium metal**	**Change (%)**
Cost (USD/kg magnet)	8.54	3.98	-53.34

6.8.1. Interpretation of LCA

LCA was conducted for Nd-Fe-B magnets, using only one source of neodymium metal each time. Based on results, recycling neodymium metal reduced environmental effects of Nd-Fe-B magnet production for some environmental impact categories. Neodymium metal recycling had major negative impact on depletion of abiotic resources-elements ultimate reserves environmental impact category while it's less on environmental impact categories: acidification potential and photochemical oxidation. Environmental benefits are most significant for respective LCIA categories: terrestrial ecotoxicity, depletion of abiotic resources-fossil fuels, ozone layer depletion, marine aquatic ecotoxicity, climate change, freshwater aquatic ecotoxicity and eutrophication. Economically recycling decreased the production cost of Nd-Fe-B magnets by 53.34%. Primary neodymium production has the highest contribution to the environmental effects of magnet production while dysprosium metal production has the second biggest contribution despite the low mass content.

This work is an ex ante LCA study. LCIA results highlight environmental profile of new technologies at early stage and contribute to prevent unintended environmental consequences in future. There were several limitations for scaling-up since similar technologies operate at pilot plant at best (Zakotnik et al., 2016). Certain data gaps exist such as reusing chemicals (especially acids), recovery of other acid leached metals, hazardous wastewater treatment and scaling-up issues which could affect the contribution of streams.

Sensitivity analyses were conducted for Nd-Fe-B magnet production using recycled neodymium metal route. Electricity consumption and sulfuric acid were selected as parameters. Selected impact categories were: acidification, Climate change and Depletion of abiotic sources, fossil fuels. Sensitivity analysis results for electricity production and sulfuric acid production are given in Tables 6.11 and 6.12 respectively. Based on results, sulfuric acid production has more significant effect on for environmental impact categories acidification than electricity production. On the other hand, electricity played more significant role on cost, environmental impact categories climate change and ultimate reserves, fossil fuels.

Table 6.11. Sensitivity analysis results for electricity production parameter.

	Percentage change				
Category	-20	-10	0	10	20
Acidification	-3.2	-1.6	0	1.6	3.2
Climate change	-10.8	-5.4	0	5.4	10.8
Ultimate reserves, fossil fuels	-7.5	-3.7	0	3.7	7.5
Cost	-8.5	-4.2	0	4.2	8.5

Table 6.12. Sensitivity analysis results for sulfuric acid production parameter.

	Percentage change				
Category	-20	-10	0	10	20
Acidification	-12.9	-6.4	0	6.4	12.9
Climate change	-4.0	-2.0	0	2.0	4.0
Ultimate reserves, fossil fuels	-9.4	-4.7	0	4.7	9.4
Cost	-3.5	-1.7	0	1.7	3.5

7. CONCLUSION AND RECOMMENDATIONS

Demand for clean technologies, high-end technological applications for industrial, commercial and military products pressure REE production towards an unsustainable future. Although virgin production supplies demand for now, politic risks put REE supply at strategic risk. Thus secondary REE sources like end-of-life products and material recycling has gained increased attention in recent years.

Life cycle assessment was conducted to evaluate biohydrometallurgical and hydrometallurgical metals recycling from WEEE for economical and environmental aspects. The goal of LCA was investigating possible environmental effects and cost of metal recycling system by making comparisons. Functional unit for metal recovery from WEEE is 1 kg copper metal and functional unit for neodymium magnet production system is the 1 kg Nd-Fe-B magnet. System models were scaled-up from laboratory experiments level to pilot scale following the methodology. Several assumptions were made to fill data gaps where certain data is not available from experiments or literature.

The search for a commercial scale, environmentally friendly and low cost recycling methods for REEs has been ongoing. Two recycling methods proposed by IntenC research project and LCA models were created based on experiments and several assumptions were made. Recycling facilities that operate with similar technologies are on pilot or demonstration scale at best. Thus LCA models scaled-up accordingly to reach pilot plant level. Certain data gaps forced to adapt data from similar technologies at same level. As an ex-ante LCA study, the best this study can do is highlighting potential hot spots of experimental procedure and make a brief evaluation of experiments conducted at laboratory scale to help avoiding future commercial level, environmentally hostile technological applications.

LCA study was conducted for recovering only copper metal using IntenC experiment data, a framework developed for multi-metal recovery system. Based on this LCIA comparison, recycling only copper metal through bioleaching and copper precipitation is not environmentally friendly and does not provide economic advantage. Main contributors to the environmental impacts are high electricity consumption, hydrogen peroxide consumption and air supplying for bioleaching process beyond current global production scenario. However real life applications bioleaches and extracts more metals step by step including precious metal gold. Such recycling methods would have performed better than single metal recovery and virgin metal production after system expansion and economic allocation. Hot spots of experiment were compressed air demand, hydrogen peroxide consumption and sodium hydroxide consumption.

Neodymium metal recovery experimental procedure performed better than virgin metal production according to LCA results. Metal recovery method reduced both production cost of neodymium iron boron magnet and most of environmental impact categories. Hotspots were high acid consumption and hazardous wastewater treatment which was cut-off due to lack of data. Results of this LCA study revealed that recycling of neodymium metal has clear economic and environmental advantage over virgin metal production. Scaled-up experimental neodymium metal recycling system reduced environmental impacts of Nd-Fe-B magnet production system from 1.15% to 65% for eight of eleven environmental impact categories. Acidification potential and depletion of abiotic resources - elements, ultimate reserves categories pointed out that recycling have increased environmental emissions for respective impact categories. Recycling also reduced production cost from 8.55 USD to 3.98 USD.

Gold recycling was not part of study and cut-off. However, adding a recycling system for gold and other precious metals could yield an economical and environmental advantage over virgin production. This must be considered for future studies. Biohydrometallurgical processes are novel processes thus requiring further research to design and optimize processes to recover base metals, precious metals and rare earth elements.

Overall more research is required to find more environmentally and cost friendly processes to recycle metals from complex WEEE.

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