Innovative Valorization of Secondary Raw Materials

Petteri Halli
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Petteri Halli

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Abstract
In order to answer the ever-growing demand for more sustainable metal resources, a number of new and distinct approaches for the treatment of different secondary raw materials were investigated in detail. These included recovery of metals from electric arc furnace dust (EAFD), recovery of tellurium from Doré slag, and recovery of noble metals from base metal sulfate solutions. In the first method, the effect of 27 different lixiviants on the dissolution of electric arc furnace dust (about 12 Mt produced globally every year) was explored. From these results, citric acid was selected as the most suitable medium to produce three base metal fractions—Fe-, Pb- and Zn-rich streams—from the EAFD containing 33.2 wt-% Zn, 17.9 wt-% Fe and 1.6 wt-% Pb. The complete process developed consisted of several metallurgical unit processes including an initial alkaline roasting stage with NaOH at 450 °C, followed by selective leaching with 0.8 M citric acid for 120 min. The residue formed after leaching was shown to be a chemically suitable raw material for reuse in the EAF, whereas the related pregnant leach solution (PLS) could be further purified to produce a Pb-rich residue, and a Zn-rich electrolyte appropriate for use in state-of-the-art metallurgical plants. A new, innovative process flowchart for industrial application was proposed as a result of these findings.

The recovery of tellurium from Doré slag produced in a TROF (Tilting, Rotating Oxy Fuel) furnace was also demonstrated via a combined conventional hydrometallurgical and innovative electrochemical route. The Doré slag was first leached (30% aqua regia) to produce a multimetal solution that contained 421 ppm of Te. From the experiments undertaken it was determined that electrowinning (EW) is the preferable Te recovery method at concentrations above 300 ppm, whereas below this threshold value, an innovative method based on electrodeposition redox replacement (EDRR) was demonstrated to be more effective.

EDRR was also investigated for Ag recovery from synthetic zinc sulfate solutions (Zn 60 g/L) where the content of Ag varied between 1 ppb to 250 ppm. The investigations show that an exceptionally high enrichment ratio of Ag (9.80) from solution to the electrode could be achieved. Furthermore, although H2 evolution was also shown to affect overall energy efficiency, EDRR was shown to outperform conventional EW. In addition, Pt—present as a trace amount (~1 ppb) in complex multimetal Ni-rich (>140 g/L) industrial process solution—was also successfully recovered by the EDRR method on a novel electrode comprised of pyrolysed carbon, PyC. In this case, the results indicated that high purity (90 wt-% Pt) and extraordinary enrichment ratio (1011) were detected on the electrode surface compared to the industrial process solution. Moreover, it was also found that other precious metals like Pd and Ag could be simultaneously enriched on the PyC electrode surface.

Keywords Industrial waste/process streams; Hydrometallurgical processing; Precious metals; Circular economy of metals; Sustainability
Tekijä
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Innovatiivinen sekundaaristen raakaaineiden hyödyntäminen

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Tiivistelmä
Tässä väittökirjassa tutkittiin valokaariuunipölyn, Doré kuonon ja sulfaattiophajaisten prosessiliuosten sisältämien metallien hyödyntämistä ja kierrättämistä. Ensimmäisessä työn osassa perehdyttiin valokaariuunin pölyn hyödyntämiseen liuottamalla siinä esiintyviä tyyppillisä metalluja (Fe, Pd ja Zn) 27 eri liuottimeen. Tutkitaista liuottomista prosessikehitykseen valittiin sitruunahappo. Testeissä käytetty pasutetut valokaariuunipölyn sisäisit 33,2 p-% sinkkiä, 17,9 p-% rautaa ja 1,6 p-% liyjiä. Selektiivisen liuotuksen (0,8 M ja 2h) jälkeen saatiin kiinteä liuosjäännös, joka olisi kemiallisesti sopiva syöte valokaariuuniprosessiin, mutta jopa fysiikalaisia ominaisuuksia pitäisi kuitenkin muokata esimerkiksi pelletoinnilla. Liuospuhdistuksen jälkeen tutkittaessa prosessissa tuotettiin kiinteä liyjyptootinen raaka-aine ja sinkkipitoinen liuos, jotka ovat yhdistettävissä raaka-aineeksi nykyisiiin primärimetalliprosesseihin. Lisäksi työssä esitettiin uudenhainen valokaariuunipölyn käsittelevän juoksukaavio.


Työn kolmannessa osassa todettiin, että EDRR:n soveltuvoitus hopean (1 ppb – 250 ppm) talteenottoon sulfaattiophajaista sinkkiliuoksista (60 g/L Zn) on erinomainen, ja menetelmää käytämällä päästii korkeisiin hopean rikastumiskertoimiin (9,8%, määrä liuosessa vs. elektroon pinnalla). Tämän lisäksi EDRR:n todettiin olevan huomattavasti perinteistä hopeantalteenottoelektrolyysiä tehokkaampi. Myös platinan talteenottoa tutkittiin EDRR:n avulla teollisesta nikkelsulfaattiiliuoskesta (> 140 g/L Ni), jossa platinan konsentraatio oli ~1 ppb. Alhaisesta pitoisuudesta huolimatta platinan rikastumiskerron oli korkea (10¹³) samoin kuin puhtauskin (n. 90 p-%). Platinan lisäksi onnistuttiin rikastamaan muita liuoksissa olevia arvometalleja (Pd ja Ag). Työssä käytettiin uuden EDRR-menetelmän lisäksi myös aivan uudenhaista elektrodimateriaalia, pyrolysoituna 3D-hiililtä.

Avainsanat
Teolliset jätte-/prosessiliuokset; Hydrometallurgi; Arvometalli; Kierotalous; Kestävä kehitys

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Acknowledgements

"Jotakin ehkä tietään, olisihan siellä minäkin"

My journey in academia started more than a decade ago at the TKK and continued to Aalto University in the School of Chemical Engineering. Ever since I’ve been learning something new every day. I’m learning something new, where I want to believe, and my trust is built on. However, sometimes I struggle to even understand or explain to myself how I got into this. After many years of iterations, I’d say the best way to describe this journey would be to compare it to an old, Soviet-style locomotive; the speed ain’t the key factor but the strength. It’s a slow-moving item, but once it is started there’s no way to stop it and in the end the destination is reached. On this railroad to success, there have been many interesting stops and layovers, but before the locomotive could even get started, a driver was needed. At this point, Pekka Taskinen comes into the picture, trusting me and providing me with my own locomotive to drive. It was a small one, but it grew larger and larger over the years spent in academia. Many co-pilots were jumping on the cars towed behind and eventually some crashes were expected, since we all shared the same rails but had different engines. The trip from 'no-idea-what-I-am-doing' village to great Pyro city was started and there was no turning back anymore.

On the way there were rather lot of pit-stops, where I and my co-drivers could do some maintenance not only to our own engines but for the others too. Therefore, such persons as Dmitry Sukhomlinov, Joseph Hamuyuni, Fiseha Tesfaye, Hanna Sahivirta, and Markus Aspiala, without forgetting those who came into the picture later like Katri Avarmaa, Rui Zhang, and Longgong Xia, were more valuable than gold. Those guys surely knew how to maintain their locomotives and how to keep them running; they were willing to share that crucial piece of information with newbies and they even listened to me when I was teaching them. I still remember most of the discussions on the way to glory and how they sooner or later almost always turned to humor. Nevertheless, despite all the odds, the journey was educational too, and many phrases and lessons are still used in our everyday lives.

However, when the outskirts of the famous Pyro city were reached and some distance travelled through the Thermodynamic suburbs, a switch-man on duty was apparently sleeping, allowing my locomotive to divert to different tracks than the persons mentioned above. My destination was no longer in the hot temperatures—although I will never forget what I learned on the way—but more in the moist conditions. Of course, there was an even more drastic detour through the Minerals Processing county, where I got to know such persons as Kari Heiskanen, Jan Drzymala, Ted Nuorivaara, Bence Tóth, Éva Radányi, Michal Lewandowski, Jyry Niskala, and Gábor Mucsi. Great times, great people, great wines, and great beers. EMEC must be one of the greatest places to get lost in!
But as always, life will find a way and it was ultimately going to happen to me too. I just didn’t know when and where. Just like out of the mist, a new supervisor appeared on the scene. A new individual, who was going to guide me away from my alternative voyage and pointed me the destination on the horizon. Of course, at that time, it was just a small dot in the distance, but at least the track there was clear. Hence, my deepest gratitude goes to Mari Lundström for being that lighthouse in the dark, illuminating the path to Safe Haven through many obstacles. Without her everlasting support (don’t get me wrong, the previous mentioned persons supported me a lot, too) I would have finished the journey somehow, but it wouldn’t even be anywhere close to what it has been now. Moreover, with her help, new co-drivers jumped on board to help me to conquer this pretty huge distance, the PhD. And this time although the locomotive had taken a different shape and increased in size, the speed remained more or less constant. Fortunately, Jari Aromaa, Benjamin Wilson, and Kirsi Yliniemi were there to help me to handle such a huge piece of machinery. It was a great pleasure to work with such individuals and masterminds. Correspondingly, the senior locomotive driver, Olof Forsén, was almost always there to share his knowledge about techniques from the old times. Techniques that will never grow old, techniques that never die, techniques that are still valid a long time after we have faded away. Furthermore, the other engine drivers who were on the same rails traveling towards the metropolis known as Hydro, were great company too.

With co-drivers such as Sipi Seisko, Arman Dastpak, Zulin Wang, Taina Kalliomäki, Pyry Hannula, Antti Porvali, Sampsa Helin, and all the French ‘traînées’ have been irreplaceable collaborators, even though the latter sometimes tried to break my locomotive with the rails it was traveling on. However, as I said at the beginning, there was no turning back. The show must go on, as somebody famous and gifted character once said. And what a roller-coaster ride this has been: a lot of ups and downs, a lot of stops and layovers, a lot of breakdowns and fixing, a lot of joys and sorrows, and they all brought me to this very point. On this journey, there’ve been too many memorable moments and more of those, which live on their own. Nonetheless, like in every expedition, in this there have also been people travelling with me from all the way from the beginning. People who have been encouraging me since day one. People like old friends—Ville Virtanen and Markus Sundqvist—people like family—Mutsï & Fatsï & Systerï—and people like soulmates—Inka Mäkinen.

But even now, when the final destination of this particular journey seems to be reached, there is something in the air that tells me this locomotive ain’t stopping. Even when it looks uphill from here, the engine is accelerating. Even now, when the platform of the end stop can be seen clearly and there are many people waiting for the ones carried in the cars towed behind. Even then, there is something that keeps whispering to my ear, that the odyssey is not over, not yet. The rails do not end at the platform. There is still quite a journey ahead. Therefore, Mika Paalanne, let’s conquer the world!

Espoo, 24 May 2020

Petteri Halli
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s$</td>
<td>Surface area [$\text{cm}^2$]</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>L</td>
<td>Liter</td>
</tr>
<tr>
<td>m</td>
<td>Milli</td>
</tr>
<tr>
<td>M</td>
<td>Molarity [mol/L]</td>
</tr>
<tr>
<td>mA</td>
<td>Milliampere</td>
</tr>
<tr>
<td>mV</td>
<td>Millivolt</td>
</tr>
<tr>
<td>pH</td>
<td>Power of hydrogen (acidity / basicity of solution)</td>
</tr>
<tr>
<td>vol-%</td>
<td>Volume percentage</td>
</tr>
<tr>
<td>wt-%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency [%]</td>
</tr>
<tr>
<td>$E$</td>
<td>Potential [mV]</td>
</tr>
<tr>
<td>$E^o$</td>
<td>Standard potential [mV]</td>
</tr>
<tr>
<td>$E_1$</td>
<td>Deposition potential [mV]</td>
</tr>
<tr>
<td>$E_2$</td>
<td>Cut-off potential [mV]</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant [96485 C / mol]</td>
</tr>
<tr>
<td>$I$</td>
<td>Current [A]</td>
</tr>
<tr>
<td>$j$</td>
<td>Current density [mA/cm$^2$]</td>
</tr>
<tr>
<td>$K$</td>
<td>Reaction quotient</td>
</tr>
<tr>
<td>$M$</td>
<td>Metal ion</td>
</tr>
<tr>
<td>$n$</td>
<td>Amount of EDRR cycles</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>$Q$</td>
<td>Electric charge [C]</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant [8.314 J / K · mol]</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature [K]</td>
</tr>
<tr>
<td>$t$</td>
<td>Time [s]</td>
</tr>
<tr>
<td>$t_1$</td>
<td>Deposition time [s]</td>
</tr>
<tr>
<td>$t_2$</td>
<td>Cut-off time [s]</td>
</tr>
<tr>
<td>$x$</td>
<td>Number of EDRR pulses</td>
</tr>
<tr>
<td>$z$</td>
<td>Number of electrons transferred (with negative charge)</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
</tr>
</tbody>
</table>
**Abbreviations**

AAS  Atomic absorption spectroscopy  
BF   Blast furnace  
BSE  Back scattered electron  
CE   Counter electrode  
CV   Cyclic voltammogram  
DOI  Digital object identifier  
e-ALD Electrochemical atomic layer deposition  
EAF  Electric arc furnace  
EAFD Electric arc furnace dust  
ED   Electrodeposition  
EDRR Electrodeposition-redox replacement  
EDS  Energy dispersive X-ray spectroscopy  
EW   Electrowinning  
HER  Hydrogen evolution reaction  
HR   High resolution  
ICP  Inductively coupled plasma  
MS   Mass spectroscopy  
O/A  Organic to aqueous ratio  
OCP  Open circuit potential  
OES  Optical emission spectroscopy  
PGM  Platinum group metals  
PLS  Pregnant leach solution  
ppb  Parts per billion  
ppm  Parts per million  
ppt  Parts per trillion  
PyC  Pyrolyzed carbon  
RE   Reference electrode
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>RR</td>
<td>Redox replacement</td>
</tr>
<tr>
<td>S/L</td>
<td>Solid to liquid ratio</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SLRR</td>
<td>Surface-limited redox replacement</td>
</tr>
<tr>
<td>SX</td>
<td>Solvent extraction</td>
</tr>
<tr>
<td>TBRC</td>
<td>Top blown rotary converter</td>
</tr>
<tr>
<td>TROF</td>
<td>Tilting rotating oxy-fuel</td>
</tr>
<tr>
<td>UPD</td>
<td>Underpotential deposition</td>
</tr>
<tr>
<td>vs.</td>
<td>Versus</td>
</tr>
<tr>
<td>WDS</td>
<td>Wavelength dispersive spectroscopy</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>cf.</td>
<td>Conferatur (compared)</td>
</tr>
<tr>
<td>e.g.</td>
<td>Exempli gratia (for example)</td>
</tr>
<tr>
<td>etc.</td>
<td>Et cetera (and other similar things)</td>
</tr>
<tr>
<td>HR</td>
<td>Organic extractant</td>
</tr>
<tr>
<td>i.e.</td>
<td>Id est (in other words)</td>
</tr>
<tr>
<td>MR₂</td>
<td>Metal extractant complex</td>
</tr>
<tr>
<td>N.B.</td>
<td>Nota bene (please note)</td>
</tr>
</tbody>
</table>
List of Publications

This doctoral dissertation consists of a summary and of the following publications, which are referred to in the text by their Roman numerals.

**Publication I:** Halli, Petteri; Hamuyuni, Joseph; Revitzer, Hannu; Lundström, Mari. *Selection of leaching media for metal dissolution from electric arc furnace dust*, Journal of Cleaner Production, **164**, 2017, 265 – 276. DOI: 10.1016/j.jclepro.2017.06.212.

**Publication II:** Halli, Petteri; Hamuyuni, Joseph; Leikola, Maria; Lundström, Mari. *Developing a sustainable solution for recycling electric arc furnace dust via organic acid leaching*, Minerals Engineering, **124**, 2018, 1 – 9. DOI: 10.1016/j.mineng.2018.05.011.

**Publication III:** Halli, Petteri; Agarwal, Vivek; Partinen, Jere; Lundström, Mari. *Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction*, Separation and Purification Technology, **236**, 2020, 116264. DOI: 10.1016/j.seppur.2019.116264.


**Publication V:** Halli, Petteri; Elomaa, Heini; Wilson, Benjamin, P; Yliniemi, Kirsi; Lundström, Mari. *Improved Metal Circular Economy-Selective Recovery of Minor Ag Concentrations from Zn Process Solutions*. ACS Sustainable Chemistry & Engineering, **5** (11), 2017, 10996 – 11004. DOI: 10.1021/acssuschemeng.7b02904.

**Publication VI:** Halli, Petteri; Heikkinen, Joonas, J; Elomaa, Heini; Wilson, Benjamin, P; Jokinen, Ville; Yliniemi, Kirsi; Franssila, Sami; Lundström, Mari. *Platinum recovery from Industrial Process Solutions by Electrodeposition-Redox Replacement*. ACS Sustainable Chemistry & Engineering, **6** (11), 2018, 14631 – 14640. DOI: 10.1021/acssuschemeng.8b03224.
Author’s Contribution

**Publication I:** *Selection of leaching media for metal dissolution from electric arc furnace dust*

The research plan and investigations were mainly conducted by P.H. in collaboration with H.R., who also conducted the elemental analyses. Conceptualization and methodology were formulated by P.H., J.H. and M.L. and P.H. performed the results analysis and validation with J.H.. The original draft was written by P.H. and J.H. and reviewed and edited by P.H., H.R., J.H., and M.L.. Project administration and supervision was by M.L. and funding acquisition and resources by M.L..

**Publication II:** *Developing a sustainable solution for recycling electric arc furnace dust via organic acid leaching*

The research plan and investigations were mainly conducted by P.H. and J.H. whereas conceptualization was by P.H., J.H. and M.Lu., and P.H. and J.H. performed the methodology, validation, and results analysis. M.Le. contributed to the visualization of the results. The original draft was written by P.H. and reviewed and edited by P.H., J.H., M.Le., and M.Lu.. Project administration and supervision was by M.Lu. and funding acquisition and resources by M.Lu..

**Publication III:** *Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction*

P.H. and J.P. conducted the investigations and conceptualization was by P.H. and V.A.. The results were analyzed by P.H. and V.A. and validation and analysis of the results by P.H. and V.A.. The original draft was written by P.H. and reviewed and edited by P.H., V.A., J.P., and M.L.. Project administration and supervision was by M.L. and funding acquisition and resources by M.L..

**Publication IV:** *Electrochemical recovery of tellurium from metallurgical industrial waste*

P.H. and T.H. conducted the investigations. Methodology and conceptualization were formulated by P.H., B.P.W., and K.Y.. The results were analyzed by P.H. and validation and analysis of the results by P.H., B.P.W., and K.Y.. The original draft was written by P.H. and reviewed and edited by P.H., T.H., B.P.W., K.Y., and M.L.. Project administration and supervision was by B.P.W., K.Y., and M.L. and funding acquisition and resources by M.L..
Publication V: Improved Metal Circular Economy-Selective Recovery of
Minor Ag Concentrations from Zn Process Solutions

P.H. and H.E. conducted the investigations. Conceptualization and methodology were formulated by P.H., B.P.W., K.Y., and M.L. and validation and analysis of the results by P.H., B.P.W., K.Y., and M.L. The results were analyzed by P.H., B.P.W., K.Y., and M.L. P.H. wrote the original draft and it was reviewed and edited by P.H., H.E., B.P.W., K.Y., and M.L. Project administration and supervision was by B.P.W., K.Y., and M.L. and funding acquisition and resources by M.L.

Publication VI: Platinum recovery from Industrial Process Solutions by
Electrodeposition-Redox Replacement

Investigations were conducted by P.H. and H.E. and conceptualization and methodology were formulated by P.H., B.P.W., K.Y., and M.L. Validation and analysis of the results were by P.H., B.P.W. and K.Y.. J.H., V.J., and S.F. contributed to the work of creating the special electrodes made in-house. J.H. designed the electrode fabrication procedure in collaboration with V.J. and S.F.. The original draft was written by P.H. and reviewed and edited by all the authors. Project administration and supervision was by B.P.W., K.Y., and M.L. and funding acquisition and resources by S.F. and M.L.
1. Introduction

"Saving the world one atom at a time"

The world needs metals. Global metal resources are becoming ever scarcer and humankind is in danger of exhausting several valuable and critical elements [1] – [5]. At the same time, many valuable minor elements exist in industrial side-streams, process solutions, and the wastewaters of the base and precious metal industries [6]. In several cases the challenge is that there is no feasible, commercially economic, and/or environmentally friendly way to recover the lost elements since their contents are rather low, varying from a few ppm to some ppb, or they may also be present in such a complex form that processing is considered a lost cause. However, with the support of technological innovations, the possibility that some of these secondary raw materials—liquids and/or solids—can be transformed into a more attractive form for metal recovery, is inspiring and consequently fosters the principles of the circular economy and sustainable use of natural resources. Therefore, analyzing a relatively broad range of different metallurgical aspects related to treatment of secondary raw materials is a necessity in order to find the most sustainable and feasible processes for metals recycling. Hence, the aim of this Thesis is to increase the knowledge of secondary raw materials valorization by providing several different approaches for their treatment.

In the list of EU critical elements [7], many of them can be found around us if one knows where to look. The recovery of these elements is considered to be of such a level of difficulty, not only due to the complex nature of the side and waste streams but also due to the large volumes, and the low concentrations of the valuable elements present. Therefore, a threefold way of recovering lost resources is comprehensively presented in this Thesis; leaching, solvent extraction, and electrochemical recovery are all applied in order to develop advanced procedures for metals recovery from secondary raw materials. The materials investigated in this Thesis include electric arc furnace dust (EAFD), Doré slag, and hydrometallurgical process solutions rich in base metals. All these secondary raw materials are currently under-utilised with respect to their valuable and/or noble element contents. Consequently, the provision of new insights for the better exploitation of these types of resources is the overall driving force of this Thesis.
1.1 Background

1.1.1 Electric Arc Furnace Dust (EAFD) Treatment

The utilization of the metallurgical waste and sidestreams produced in ferrous metal production has been conducted in the past by, e.g. integrating the slag produced in blast furnace (BF) or electric arc furnace (EAF) processes with the cement or concrete industries or utilizing them as asphalt pavements [8] – [11]. However, dusts produced in the ferrous industries are not treated similarly, mainly due to the fact that the smaller particle size requires physical treatment (i.e. pelletizing), due to their more complex mineralogy and chemical structure, and smaller quantity [12]. The dust produced in ferrous smelting can be rich not only in iron but also zinc and therefore the dust produced in the EAF process has been under wide investigation, mainly focusing on the selective leaching of zinc and other elements present in the dust [13] – [15]. Selective leaching has been seen as one of the most lucrative solutions in resolving the challenges related to EAFD (electric arc furnace dust) recycling. Moreover, the fundamental nature of Zn makes it relatively easy to keep it dissolved in most acidic media due to its low standard reduction potential ($E^0 = -760$ mV vs. SHE) [16] – [24]. Therefore, selective leaching of zinc itself has been the most intensely studied field in EAFD leaching, with most studies using either sulfuric acid ($H_2SO_4$) or sodium hydroxide ($NaOH$) as leaching media [13], [16], [18]. However, it must be highlighted that in EAFD zinc does not primarily exist as metallic zinc, but rather as zinc oxides, ferrites, and sulfates, for example [25], [26].

In neutral and alkaline conditions Zn—if dissolved—tends to form hydroxides, Figure 1A. However, there is a narrow potential-acidity area, where iron prevails in non-dissolved form compared to Zn, Figure 1B. Therefore, it can be suggested that by controlling the pH (with additions of acid/base), some selectivity of zinc over iron can be reached when leaching roughly in the pH area between 2 and 6 if the redox potential is kept at approximately 400 mV vs. Ag/AgCl. At lower (or higher) potentials, the pH window narrows to higher pH values due to the increased dominance of dissolved iron species. The other way around would of course be to control the redox potential (e.g. with addition of oxidant or reductant) while maintaining a constant pH. However, the $E$-$pH$ diagram presents the prevailing species and is based on thermodynamics, and the true selectivity must be confirmed in the process conditions in question.
1.1.2 Innovative Electrochemistry

Electrochemistry, a technique widely used for primary base metal production, is utilized in a novel and innovative manner in order to recover even the lowest concentration of valuable elements present in process solutions. A special version of pulsed electrodeposition, namely EDRR (electrodeposition–redox replacement) has been investigated by employing different types of electrode materials for many various types of pure synthetic and real industrial solutions [28] – [38]. The basic principle in EDRR is that during the ED phase, a short current or potential pulse is introduced to the system and during the RR phase, a spontaneous replacement occurs on the electrode surface between less noble and more noble elements. In addition to a pure redox replacement reaction, recovery can take place in the vicinity of the electrode surface via an intermediate, soluble species, potentially improving the efficiency [38]. By repeating the EDRR cycles, eventually a pure layer of the targeted metal is produced on the electrode. Other known techniques related to EDRR are surface-limited redox replacement (SLRR) [39] – [42], pulse plating [43], [44], and electrochemical atomic layer deposition (e-ALD) [45] – [48], which have also been under investigation in the past. The fundamental difference between EDRR and SLRR
/ e-ALD is that, during EDRR, a more porous layer of the targeted metal is produced via electrodeposition, whereas during SLRR and e-ALD, defect-free, thin monolayers are formed via underpotential deposition (UPD).

When compared to traditional electrodeposition (such as electroplating lasting only a few seconds [49], [50]) or electrowinning (a constant current applied for several days or weeks for metal recovery [51] – [53]), in the EDRR process the ED pulse is typically short, only a few seconds maximum. However, the principle in this step is the same, i.e., to drive a non-spontaneous deposition reaction of metal on the electrode surface in a controlled manner, utilizing an external current or potential source. During the RR step, all the reactions between less and more noble elements (solid or soluble) are driven spontaneously by the difference in their reduction potentials [39], [40], [54] – [62]. However, there are also reports that galvanic potential difference between entire compounds may be the driving force [63].

Moreover, Ostwald ripening [64] – [66] may also take place during the RR step. This re-nucleation of small, nano-size particles into larger, micro-size particles can enhance electrodeposition into a more uniform layer. In addition, corrosion, i.e., unwanted dissolution, may take place as well. However, dissolution of metals is also an electrochemical phenomenon; for example, in acidic dissolution hydrogen reduction is thermodynamically driven by the spontaneous oxidation of less noble metals. Nonetheless, this spontaneous dissolution of less noble elements is also one of the key behaviors which can further increase the purity—and potentially even recovery—of more noble deposits on the surface of the working electrode. The redox replacement reactions do not necessary occur on the electrode surface only, but also in the solution [38] and not only solid-liquid reactions, but even liquid-liquid or gaseous-liquid reactions, e.g. H₂ formed during metal dissolution may result in metal deposition if not present in excess amounts [67].

During the EDRR process, a short (typically 10 μs to 10 s) pulse of electricity is applied to the system. After this starts the counting of a waiting time—often also called redox replacement time or cut-off time, which can vary between a few microseconds to several hours. As an alternative to redox replacement time, so-called cut-off potential can be used, i.e., the open circuit potential (OCP) is monitored during the RR step and once the cut-off OCP value is reached, the second pulse can start. In some cases, either the cut-off time (t₂) or cut-off potential (E₂) will control the system, and whichever is reached first will launch the next cycle by starting a new pulse. In addition to recovery of valuable metal, by controlling the cut-off time and/or cut-off potential, the spontaneous dissolution, e.g., corrosion of the elements can be controlled, or avoided; shorter RR times or lower cut-off potentials decrease the direct oxidation (corrosion) of the deposited less noble metals, whereas longer RR times and higher cut-off potentials increase the possibility for direct corrosion, and a potentially smaller amount of less noble metal is deposited on the electrode surface. The rate limiting steps during the EDRR process can be mass transfer (diffusion) i.e. the ion movement in the solution towards the electrode surface and at the electrode surface or charge transfer i.e. the movement of electrons from one element to the other via oxidation and reduction. By understanding the limiting factors, the optimal parameters for EDRR process can be determined.
The other electrochemical process parameters are the deposition potential ($E_1$), deposition time ($t_1$), and amount of cycles ($n$), the deposition potential being one of the most critical factors. The $E_1$ determines the potential where a less noble element acting as a sacrificial metal is deposited on the surface of the working electrode. This potential can also be more cathodic compared to the actual deposition potential, having an impact on the amount, size, and shape of the deposited particles [68]. The cut-off potential ($E_2$) determines the potential where approximately all the deposited sacrificial metals are replaced with the more noble metal (and/or corroded away), if so desired. This also has an impact on the overall recovery as well as the purity and morphology of the deposited surface. In addition, there can also be a sixth parameter ($x$) controlling the system, which is to apply a pulsed ED step between the redox replacement stages. The primary advantage of employing short (few $\mu$s) anodic and cathodic pulses before the longer redox replacement time is that it could lead to more uniform nanoparticle formation [36]. On the other hand, when the repetition ($x$) is not applied, a thicker metal deposition is achieved, resulting in a situation where the recovery of a certain element can be performed.

Figure 2 presents a typical EDRR process where a deposition potential ($E_1$) is applied for a certain amount of time, $t_1$. After that the system is left in an OCP where no external potential or current is applied. After a specific amount of time ($t_2$) or when the pre-determined potential ($E_2$) is reached, one full EDRR cycle ($n$) is completed and the next one can be started. The EDRR process has an advantage over static ED thanks to its more flexible and controllable nature, as there are more electrochemical process parameters to tailor and adjust, depending on the desired end result.

The methodology in its various potential applications is not yet completely understood and parameter selection is subject to discussion, influencing the actual phenomena that can occur in the process. The overarching research aim affects hugely the parameter selection, whether the target is optimal recovery, high purity, or the most even distribution of nanoparticles possible for catalysis purposes, for example. Nonetheless, the employment of innovative and tailored electrochemical deposition followed by a phase of no external energy (including
both RR and corrosion) can form noble metal surfaces of high purity and low base metal content(s).

1.2 Objectives & Scope

The primary aim of the current Thesis is to investigate and develop novel unit processes and process routes to improve metals recovery and valorization from the process and waste streams of metallurgical industries. Therefore, the Thesis is based on the following approaches:

1. Development of a novel processing route for improved metal (Fe residue, Pb precipitate, Zn electrolyte) recovery from steel production EAFD. This is done by the application of conventional pyro- and hydrometallurgical unit operations such as roasting, leaching, precipitation, and solvent extraction (SX). (Publications I – III).

2. Improve Te recovery from Doré slag by the application of a conventional hydrometallurgical unit operation (leaching) combined with both conventional (EW) and innovative (EDRR) electrochemical recovery. (Publication IV).

3. Develop a novel unit process for the recovery of trace concentrations of precious metals (specifically Pt and Ag) from base metal process solutions, via an innovative electrochemical method (EDRR). (Publications V – VI).

To achieve comprehensive solutions for the presented objectives, the scopes had to be rather limited and not too broad. Therefore, for each objective the scopes can also be presented as follows:

1. The treatment of steel mill wastes is usually conducted at the plant or somewhere nearby since the logistics of transferring waste can be rather expensive due to the hazardous nature of certain elements (Pb and Cr$^{6+}$) within the material. As such, the presence of Zn prevents direct recycling of the EAFD back to the steel plant; therefore, the first part of the Thesis (Publications I - III) focuses on Zn recovery, and the consequent production of a Fe-rich secondary raw material to be fed to the EAF furnace. Moreover, the remaining Zn-rich pregnant leach solution (PLS) and Pb-rich precipitate need to be integratable, preferably with existing metallurgical processes.

2. Natural ore as a raw material carries with it a wide number of minor elements into the base and precious metal industries. If possible, the sidestreams and waste generated are treated at the site, and metals are recovered, when feasible. Nevertheless, some of the fractions are currently underutilized, and include rather valuable and/or critical elements. The scope of the current Thesis is Doré slag, and specifically Te recovery and as such Doré slag valorization. However, the development
of a holistic hydrometallurgical process for this waste fraction is beyond the scope of the current Thesis. (Publication IV).

3. The process solutions utilized in the base metal industry—as well as future hydrometallurgical recycling processes—contain a huge amount of the base metals that the process is designed for, but always a small amount of precious (Ag, Publication V) and critical (Pt, Publication VI) elements are present in the solutions. Many of the valuable elements are in trace/minute amounts, typically on the ppb/ppm scale, and currently not considered feasible for recovery. The scope of the work addresses this issue by investigation of EDRR as a method for direct recovery of precious metals from base metal-rich process solutions, potentially providing in future a novel unit process as an additional process step for improved direct recovery of precious metals.

1.3 Structure of the Thesis

As stated earlier, the Thesis is constructed in a threefold manner aiming at a single goal: recovery of currently lost elements back to circulation. Therefore, six scientific publications have been outlined and summarized in this compendium covering several areas of hydrometallurgy: leaching, solvent extraction, and electrochemical recovery. The knowledge provided in this Thesis covers a wide range of hydrometallurgical treatments—some of them can be considered as conventional (leaching, solvent extraction, electrowinning) and the others as innovative (electrodeposition – redox replacement)—but the common theme is the development of unit processes required for the valorization of metallurgical process and waste streams, which aim at improving the circular economy of metals. Moreover, the investigations are not only performed with synthetic experimental solutions, but real industrial materials are also studied in order to draw more comprehensive conclusions of the selected methods.

The structure of the Thesis is shown in Figure 3, illustrating whether the research is based on known conventional unit processes (EAFD recycling) or novel electrochemical recovery (Te recovery from Doré slag, precious metals recovery from base metal solution). The figure also roughly categorizes the process development stage approached in each study—whether the research presented in each publication is in the early stage, or already further along the route of process development. However, it needs to be emphasized that none of the processes presented in Publications I – VI have undergone a full process simulation with mass and energy balances, nor environmental analysis (LCA), and therefore all of this research is still in the early stage when compared to industrial process upscaling and commercialization. However, the secondary raw materials field can be rather scattered, different approaches are required for their treatment by combining conventional unit processes with innovative processes. Furthermore, as the processes from where the secondary raw materials originate are distinct from each other, also their treatment needs to be tailored in order to ensure comprehensive valorization.

Publications I – III describe a new, novel process to treat EAFD, which is currently mainly considered as waste. The first publication discusses suitable
leaching media for EAFD in terms of feasibility and selectivity, specifically between Zn and Fe, which are the two main elements present in the dust. In Publications II and III, a process concept based on citric acid is further investigated and developed to maximize the selectivity between zinc and iron, and to convert the products/side-products into a form that could be readily utilized as a secondary raw material in conventional metal production (Fe-, Pb-, and Zn-rich streams).

Publication IV acts as a bridge and shows how conventional leaching can be combined with innovative and tailored electrochemical treatment. Slag originating from copper anode slime refining is leached in aqua regia [69] and the pregnant leach solution formed is treated using a two-step electrochemical method to maximize tellurium recovery. The electrochemical techniques utilized are traditional EW (electrowinning) and a novel application of EDRR (electrodeposition – redox replacement). With such combined hydrometallurgical processes, tellurium could be recovered from TROF (tilting rotating oxy-fuel) Doré slag. The study focuses on developing Te recovery, rather than on holistic process development. Publications V – VI focus on the EDRR process in more detail: In Publication V, EDRR is utilized for the investigation of the phenomena occurring in silver recovery from synthetic zinc-rich sulfate solution, with Ag content as low as 1 ppb. The approach is investigated further in Publication VI where platinum (Pt content ~1 ppb) was recovered from nickel-rich sulfate solution. This publication demonstrates the direct recovery of precious metals, specifically platinum, directly from an industrial process solution, providing horizons for additional unit process integration into the existing plant set-up.

There are numerous connections between the different publications (Figure 3) including several hidden inner connections between the methods and phenomena studied. For example, old vitreous enamel paint, that is common in households scrap metal is one source of feed material for EAF. This material is rich in a variety of different metals, some of which are precious and valuable like silver and/or palladium [70]. Therefore, the study of upstream processes (in this case leaching) is beneficial when the most suitable recovery method needs to be determined; furthermore, if a low concentration of noble metals is present, an electrochemical method like EDRR would become quite an attempting option. On the other hand, as most of the hydrometallurgical base metal process solutions are primarily sulfate based, the recovery of precious elements from such solutions via EDRR is a highly relevant—and important—opening in the field. In order to further demonstrate the versatility of this new method, EDRR was also studied in chloride-nitride based solutions for Te recovery. Such a connection is also relevant in the other direction; in the case of tellurium recovery, the previously conducted leaching process determined the recovery method, i.e. use of EW and EDRR. Therefore, in the field of valorization of secondary raw materials, it is critically important to study a variety of raw materials and solutions in order to increase general understanding.
1.4 New Scientific Contribution

This Thesis consists of a wide range of different valorization methods including selective leaching, solvent extraction, and electrochemical recovery. The hydrometallurgical unit operations outlined in this Thesis are used to treat raw materials for which they were not originally designed. The following findings are believed to be original:

Publication I – The mapping of the dissolution of Zn, Fe, Mn, Pb, and Cr from EAFD was performed in detail for the first time. The usage of 27 different lixiviants can provide new perspectives not only for the extraction of different metals, but also for the selectivity over certain elements.

Publication II – The combined pyro- and hydrometallurgical route including alkaline roasting and citric acid leaching provided not only high Zn extraction (100%) but also high selectivity between Zn and Fe, resulting in a chemically fully recyclable Fe-rich residue to be fed back to the EAF process.

Publication III – Two secondary raw material streams (Pb and Zn) were extracted from the Zn-rich PLS (pregnant leach solution) by sulfate precipitation (PbSO₄), followed by an SX (solvent extraction) stage where a state-of-the-art Zn EW (electrowinning) electrolyte was produced.
Publication IV – A twofold treatment including conventional EW and novel electrochemistry, EDRR, was developed for tellurium recovery from Doré slag in order to produce either pure tellurium or e.g., silver telluride (Ag₂Te).

Publication V – Utilization of a novel electrochemistry method called EDRR for the first time for the recovery of minute amounts of a valuable metal (Ag) from a zinc-rich sulfate solution (synthetic). The method was proven to support the effective recovery of silver from solutions where its content varied between 250 ppm to 1 ppb. H₂ evolution was found to challenge the energy efficiency of the process.

Publication VI – A novel electrode material (PyC, pyrolyzed carbon) was utilized in the EDRR experiments for the first time for noble metal (Pt) recovery not only from synthetic base metal solutions, but also from real industrial hydrometallurgical process solutions. The method was proven to be capable of recovering predominantly platinum (content of Pt ~1 ppb), but also some of Pd and Ag from complex industrial solutions with high purity. Furthermore, secondary redox replacement between Ag and Pt was suggested for the first time.
2. Secondary Raw Materials

“One man’s trash is another man’s treasure”

What has been considered a waste in the past can nowadays be a valuable resource as a secondary raw material. Moreover, as Nature’s primary resources are being depleted at an accelerating rate, the usage of secondary raw material is not only recommended but mandatory in terms of sustainability. Secondary raw materials are also usually richer in certain elements than primary resources can ever be, but the problem lies in their complexity, since the liberation of elements can be rather extreme. Furthermore, secondary raw materials typically also contain several elements in trace amounts, challenging their recovery for use. Therefore, the focus on urban mining and related processes to utilize waste has raised its head from a long-lasting sleep [71].

As a term ‘urban mining’ belongs to a wider category [71] relating to extracting valuable elements from waste, consideration can be turned to processing these urban sources. Furthermore, just as mines always need further processing steps and unit operations, so does urban mining. Since the dominating unit operations to process the raw materials originating from primary sources have been developed to almost the peak of their evolution, the whole chain of thinking needs to be turned around. Instead of only developing a totally new recycling process for secondary raw materials, products should also be developed for recycling. Moreover, secondary raw materials should also be integrated into current processes by the development and optimization of complementary (pre-treatment/treatment) unit processes.

2.1 Electric Arc Furnace Dust (EAFD)

Base metal (Fe, Cu, Ni, Zn, Pb, Al, etc.) production is no doubt the largest metal producing industry. Therefore it is not a surprise that the same industry is also the main player in secondary raw material treatment, e.g., feeding scrap metal into the electric arc furnace (EAF) or employing scrap copper or printed circuit boards (PCBs) in the copper converting process [72]. In the steel making business, secondary raw materials have been used industrially for several decades by using electric arc furnaces [73].

EAF is the major process for secondary steel production [13], [74] – [76] and the annual global steel production of currently >600 million tonnes relies on state-of-the-art EAF technology [77]. The largest fraction produced in primary steel production is not necessary the end product, but the slags (490 – 620 kg/t) and sludges (~55 kg/t) generated [8]. Part of these fractions are already utilized as secondary raw materials for the cement industry, for example [8].
However, one critical waste fraction is EAFD (electric arc furnace dust). During the EAF process, a huge amount of dust is produced among other main streams (steel, slag & gas), and in fact the dust is a considerable source of pollution [78], [79]. The estimation of the quantity of electric arc furnace dust (EAFD) produced for every metric ton of steel is approximately 11 – 20 kg [80], [81], resulting in 6.6 – 12 million metric tons annually (globally). The EAFD generated may not be the largest waste or secondary raw material originating from the steel industry in quantity, but it is one of the most complex in terms of mineralogy. Characteristically, the main elements in the dust are zinc (Zn), iron (Fe), lead (Pb), chromium (Cr), and manganese (Mn) along with other minor elements as presented in Table 1, where the variation of main elements in EAFD in the published literature is compared to the raw material utilized in the current Thesis.

### Table 1. Variations in main elements between EAFD compositions.

<table>
<thead>
<tr>
<th>Zn [wt-%]</th>
<th>Fe [wt-%]</th>
<th>Pb [wt-%]</th>
<th>Cr [wt-%]</th>
<th>Mn [wt-%]</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>33.16</td>
<td>17.89</td>
<td>1.64</td>
<td>0.23</td>
<td>2.52</td>
<td>Publications I – III</td>
</tr>
<tr>
<td>29.1</td>
<td>24</td>
<td>3.64</td>
<td>0.14</td>
<td>4.11</td>
<td>[16]</td>
</tr>
<tr>
<td>33</td>
<td>26.5</td>
<td>2.17</td>
<td>0.14</td>
<td>2.3</td>
<td>[17]</td>
</tr>
<tr>
<td>5.51</td>
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<td>0.25</td>
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<td>1.95</td>
<td>[79]</td>
</tr>
<tr>
<td>12.20</td>
<td>37.08</td>
<td>1.72</td>
<td>0.22</td>
<td>-</td>
<td>[81]</td>
</tr>
<tr>
<td>18.60</td>
<td>25.90</td>
<td>3.63</td>
<td>0.31</td>
<td>2.81</td>
<td>[82]</td>
</tr>
<tr>
<td>17.05</td>
<td>27.23</td>
<td>1.28</td>
<td>0.81</td>
<td>1.03</td>
<td>[83]</td>
</tr>
<tr>
<td>26.95</td>
<td>27.39</td>
<td>3.75</td>
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<td>[84]</td>
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<tr>
<td>23.86</td>
<td>22.71</td>
<td>2.15</td>
<td>0.31</td>
<td>2.94</td>
<td>[85]</td>
</tr>
<tr>
<td>4.73</td>
<td>59.77</td>
<td>-</td>
<td>-</td>
<td>2.23</td>
<td>[86]</td>
</tr>
<tr>
<td>9.24</td>
<td>48.96</td>
<td>-</td>
<td>2.90</td>
<td>-</td>
<td>[87]</td>
</tr>
<tr>
<td>15.32</td>
<td>39.45</td>
<td>1.53</td>
<td>-</td>
<td>-</td>
<td>[88]</td>
</tr>
<tr>
<td>12</td>
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<td>2.1</td>
<td>0.23</td>
<td>2.3</td>
<td>[89]</td>
</tr>
<tr>
<td>31.4</td>
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<td>-</td>
<td>0.88</td>
<td>[90]</td>
</tr>
<tr>
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<td>-</td>
<td>2.0</td>
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</tr>
<tr>
<td>34.23</td>
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<td>-</td>
<td>2.75</td>
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</tr>
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<td>10.1</td>
<td>0.12</td>
<td>-</td>
<td>[93]</td>
</tr>
<tr>
<td>8.08</td>
<td>45.24</td>
<td>2.12</td>
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<td>-</td>
<td>[94]</td>
</tr>
<tr>
<td>17.99</td>
<td>45</td>
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<td>0.46</td>
<td>1.94</td>
<td>[95]</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>[96]</td>
</tr>
<tr>
<td>20.12</td>
<td>33.66</td>
<td>2.42</td>
<td>0.48</td>
<td>2.52</td>
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</tr>
<tr>
<td>10.31</td>
<td>11.74</td>
<td>2.11</td>
<td>0.72</td>
<td>1.13</td>
<td>Standard deviation</td>
</tr>
</tbody>
</table>

Typically, the composition of the dust depends on the scrap metals fed into the furnace, which can vary from used cars to scrap construction steel [12], [85]. The complexity of EAFD makes it rather difficult to treat further. The large amount of Zn (~10 - ~35 wt-%) in the EAFD prevents its direct recycling back to the electric arc furnace. Zn has a negative effect on the furnace refractory, the overall operation of the steel plant, and thus the economics of the furnace processes [81]. The Zn—which makes up about one third of the dust—causes scaffold formation, compromises the integrity of furnace refractory, and chokes the gas off-take [81]. A huge amount of generated dust is also classified as hazardous waste by the EU [97], [98] since the dust is classified as a pollutant to the environment if disposed of by landfilling [97]. Classification of EAFD as a pollutant...
is based on the content and toxicity of metals such as hexavalent chromium (Cr\textsuperscript{6+}) and lead (Pb) \cite{78, 99, 102}.

So far, the Waelz process \cite{103}, has been utilized widely in EAFD recycling. Also, at Boliden Rönnskär (Sweden) a similar pyrometallurgical process to Waelz has been constructed where the zinc is oxidized in the slag phase \cite{104}. In addition, the hydrometallurgical-based Skorpion Zinc process \cite{105} has also shown economic potential for treating EAFD \cite{106}. During the Waelz process, Zn–originating from EAFD–and other low boiling point metals are converted into oxide form. However, the Waelz oxides formed need many different further processing methods including alkaline scrubbing \cite{107} and/or leaching \cite{107, 108} before pure Zn is produced, mainly via electrowinning \cite{75}. The Waelz process itself is a rather energy-intensive route to transform EAFD into a suitable secondary raw material; in most cases this is ZnO, which is further transported to a Zn refinery for zinc production. During the Waelz process, the zinc oxide (ZnO) present in the dust is first reduced to metallic zinc vapor according to Equations (1) & (2) \cite{103, 109}. The reducing agent during the Waelz process can be either carbon (C) or carbon monoxide (CO), which is formed according to Equation (3) \cite{103}. Furthermore, the solid carbon can also be oxidized straight to carbon dioxide (CO\textsubscript{2}) according to Equation (4) \cite{103}, although, according to Equation (3), it can be reduced back to carbon monoxide. After the zinc vapor is produced, it is further oxidized back to zinc oxide by controlling the oxygen partial pressure, Equation (5) \cite{103, 109}. In Equations (6) and (7) \cite{110} also present how iron and lead oxides behave during the reduction phase of the Waelz process and Equations (8) – (10) show an example of the decomposition of zinc ferrite \cite{111}.

\begin{align*}
ZnO(s) + C(s) &= Zn(g) + CO(g) & \text{(1)} \\
ZnO(s) + CO(g) &= Zn(g) + CO_2(g) & \text{(2)} \\
C(s) + CO_2(g) &= 2CO(g) & \text{(3)} \\
C(s) + O_2(g) &= CO_2(g) & \text{(4)} \\
Zn(g) + O_2(g) + CO(g) &= ZnO(s) + CO_2(g) & \text{(5)} \\
PbO(s) + CO(g) &= Pb(l) + CO_2(g) & \text{(6)} \\
Fe_2O_3(s) + 3CO(g) &= 2Fe(s) + 3CO_2(g) & \text{(7)} \\
3ZnFe_2O_4(s) + CO(g) &= 3ZnO(s) + 2Fe_3O_4(s) + CO_2(g) & \text{(8)} \\
Fe_3O_4(s) + CO(g) &= 3FeO(s) + CO_2(g) & \text{(9)} \\
FeO(s) + CO(g) &= Fe(s) + CO_2(g) & \text{(10)}
\end{align*}

Table 2 presents the compositions of EAFD utilized in this study. As it can be seen, the Zn content is roughly one third and the Fe content is approximately one fourth of the EAFD, which makes the dust rather difficult to recycle. There are currently no industrial base metal processes that could directly integrate EAFD as such into their processes. Therefore, the EAFD needs to be converted into a more suitable form.
Table 2. Compositions of EAFD material—raw and roasted—and the monthly average composition at the plant. (Extended from Publications I – III).

<table>
<thead>
<tr>
<th>Element</th>
<th>Raw EAFD sample [wt-%]</th>
<th>Roasted EAFD sample [wt-%]</th>
<th>Monthly average at the plant [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.23</td>
<td>0.19</td>
<td>0.38</td>
</tr>
<tr>
<td>Mn</td>
<td>2.52</td>
<td>1.63</td>
<td>2.01</td>
</tr>
<tr>
<td>Fe</td>
<td>17.89</td>
<td>11.40</td>
<td>21.27</td>
</tr>
<tr>
<td>Zn</td>
<td>33.16</td>
<td>20.90</td>
<td>33.43</td>
</tr>
<tr>
<td>Pb</td>
<td>1.64</td>
<td>1.35</td>
<td>1.50</td>
</tr>
<tr>
<td>Al</td>
<td>0.36</td>
<td>0.27</td>
<td>0.40</td>
</tr>
<tr>
<td>Na</td>
<td>1.75</td>
<td>14.6</td>
<td>2.50</td>
</tr>
<tr>
<td>Mg</td>
<td>0.64</td>
<td>0.55</td>
<td>0.73</td>
</tr>
<tr>
<td>Si</td>
<td>0.83</td>
<td>1.22</td>
<td>1.77</td>
</tr>
<tr>
<td>K</td>
<td>2.39</td>
<td>2.15</td>
<td>1.93</td>
</tr>
<tr>
<td>Ca</td>
<td>3.59</td>
<td>3.10</td>
<td>2.78</td>
</tr>
<tr>
<td>V</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Cu</td>
<td>0.20</td>
<td>0.13</td>
<td>0.17</td>
</tr>
<tr>
<td>C</td>
<td>1.17</td>
<td>0.97</td>
<td>1.37</td>
</tr>
<tr>
<td>P</td>
<td>0.02</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>S</td>
<td>1.05</td>
<td>0.86</td>
<td>1.02</td>
</tr>
<tr>
<td>Others*</td>
<td>32.51</td>
<td>40.59</td>
<td>28.63</td>
</tr>
</tbody>
</table>

*Mainly oxygen and halogens

From the elements present in EAFD, iron (Fe) and manganese (Mn) can be freely recycled back to the steel process, without causing any challenges in the operations [74]. Also, the alkali elements (K, Mg, Na, and Ca) present in the dust together with silicon (Si) and aluminum (Al) originate from slag formers and fluxing agents [12] in the EAF process and as such they can be tolerated in the EAF feed [112]. Cr and Pb are not problematic for the steel process itself, and they have been used as additives in the steel industry [113]; however, there are currently limitations in the EU for the Pb amount in the feed (0.1 wt-% [114]), due to its toxicity.

The current Thesis presents an alternative metallurgical treatment route for EAFD, to produce fractions integratable with the existing metallurgical infrastructure, Publications I – III.

2.2 Doré Slag

Since the production of valuable and precious metals is in much lower quantities compared to base metal production, the waste generated—such as slags—is also smaller in quantity. Nevertheless, as slags are typically the highest produced quantity of waste / secondary raw materials, precious metal production is no different when it comes to the utilization of slags. However, the slags are known to vary a lot in composition [115].

Anode slime is a residue of base metal refining, and its treatment can be considered part of precious metals refining. Anode slime treatment typically involves pressure leaching and copper recovery, followed by selenium roasting and recovery [116] – [118] before it is fed into a TBRC (top blown rotary converter [119]) or specifically a TROF (tilting rotating oxy-fuel) furnace [120],
Secondary Raw Materials

[121]—similar to a Kaldo furnace [122], [123]—where the Doré process takes place. The anode slime treatment flowsheet is illustrated in more detail in Figure 4.

![Figure 4. Proposed best available technology (BAT) for the copper anode slime treatment flowsheet [124].](image)

The operating principle of the Doré process is that it is run in batches in order to recover the valuable elements present in the treated anode slime. The Doré process itself was developed to convert almost all precious and valuable elements into Doré metal (to be fed to silver electrowinning, for example), leaving other elements in the slag fraction. The process includes several different slag formers, such as borax and silica-based minerals, but it also contains some of the refractory materials used in the furnace. The Doré process produces slag that carries slag-forming agents. In addition, the Doré slag is a general term for a composite of three different slag phases, namely silica slag, soda slag and niter slag [125] which are accompanied by the other elements present in the anode slime, such as Cu, Bi, Sb, and Te, Table 3. However, as industrial processes are never ideal, some of the precious and valuable metals may also end up in the slag phase, i.e., Doré slag.

There are only a few published applications at the precious metal plants where Doré slag has been treated (mostly by conservative grinding and flotation circuits) and the valuable metals present in the Doré slag fraction are enriched [14], [126], [127]. In this study, a new approach—specifically for Te recovery—is studied, including mineral acid leaching combined with two-stage electrochemical recovery, Publication IV. The Doré slag studied in this Thesis was produced as a sidestream of extractive copper metallurgy [14], [126], [127]. Tellurium is essential, not only due to its rarity (~1 ppb in the Earth’s crust [128] in comparison with a gold content of <5 ppb [129]) but also its superior semiconductor properties [130], [131] and its ability to form alloys with other elements in order to enhance the thermoelectric properties of certain applications, for example [132] – [134].
<table>
<thead>
<tr>
<th>Mineral</th>
<th>wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barite (BaSO₄)</td>
<td>24.5</td>
</tr>
<tr>
<td>Niningerite (MgS)</td>
<td>8.9</td>
</tr>
<tr>
<td>Copper Bismuth Antimony Telluride (CuBiTe₃-CuSbTe₃)</td>
<td>0.7</td>
</tr>
<tr>
<td>Tellurium (Te)</td>
<td>3.6</td>
</tr>
<tr>
<td>Sodium Sulfate (Na₂S)</td>
<td>7.3</td>
</tr>
<tr>
<td>Arsenic Sulfide (As₂S₃)</td>
<td>37.6</td>
</tr>
<tr>
<td>Lead Sulfide (PbS)</td>
<td>0.7</td>
</tr>
<tr>
<td>Silver Antimony Telluride (AgSbTe₂)</td>
<td>1.2</td>
</tr>
<tr>
<td>Diantimony-tellurium (Sb₂Te)</td>
<td>0.8</td>
</tr>
<tr>
<td>Silver Bismuth (AgBi)</td>
<td>14.4</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>0.3</td>
</tr>
</tbody>
</table>

2.3 Process Solutions from Base Metal Industry

One source for critical and precious metals recovery could also be the process solutions of the base metal industry. The content of precious, valuable, and critical metals in these solutions is extremely low (from a few ppt to ppm) and usually these metals end up either in the anode slime [6], [135] or they are depleted in the base metal cathodes that are formed [6], [136], [137]. Nevertheless, as the volumes are huge in such metal refineries, the total amount of minor and trace elements can still be rather high. Therefore, recovering even a trace amount of valuable metals and returning them to circulation is a novel approach, and is demonstrated in the current Thesis.

In the current Thesis (Publication V), the EDRR phenomena in the synthetic Zn-Ag system was investigated. However, in the study of the Ni/(Cu) platinum system, real industrial base metal plant solutions were also investigated. Such solutions are rich in nickel, but can also have PGMs (platinum group metal) present at trace levels [138] – [140], Table 4, Publication VI. Novel electrochemical platinum recovery from real industrial solutions is also demonstrated and optimized in the current Thesis.
Table 4. Composition of the two industrial nickel-rich solutions investigated. Contents of the elements were analyzed either by ICP-OES (ppm) or HR-ICP-MS (ppb). (Publication VI).

<table>
<thead>
<tr>
<th>Element</th>
<th>Solution #1</th>
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<th>ppm</th>
<th>ppm</th>
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<td>767</td>
<td>5850</td>
<td>15900</td>
<td>40</td>
<td>236</td>
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<td>Zn</td>
<td>&lt;LOD</td>
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</tbody>
</table>

LOD = Limit of detection, * value below detection limit
3. EAFD – from Hazardous Waste to Valuable Raw Materials

“Impossible things we do immediately, miracles tend to take some time”

Even though the Waelz process is nowadays the predominant way to process EAFD, other well-documented approaches for EAFD recycling have been developed in the past, primarily based on separate hydrometallurgical processes such as leaching [78] – [83]. After the selective leaching process(es), the material is more favorable for disposal in landfills once valuable and toxic metals have been removed from the residue. Moreover, hydrometallurgical processing methods are generally scalable and can provide novel metal processing routes and selective metal recovery cf. pyrometallurgical treatments. Nevertheless, as pyro and hydro are old friends, they should not be separated but combined more effectively. In this study, a comprehensive pyro-hydro-SX-EW process is presented for treatment of EAFD.

3.1 Experimental

The EAFD investigated in this Thesis was obtained from a typical engineering steel plant (Ovako Imatra Oy Ab) and a detailed composition is presented in Table 2. Chemical analyses of the solid samples were performed by total leaching, AAS (atomic absorption spectroscopy, Varian AA240, USA or Thermo Scientific iCE 3000, USA), and ICP-OES (inductively coupled plasma, optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA). The same devices were also utilized for all the solution analyses throughout the investigations in Publications I – III. The sample carbon content was determined with a carbon/sulfur analyzer (Eltra CS-580, Germany), by heating it up to 1400 °C in O2. The sample was covered with FePO4 to ensure that all the carbon fully combusted to CO2 and the exhaust gases were analyzed with an IR detector. More details about the procedure can be found in Publication I.

In the experiments conducted for Publications I – III, the lixivants (Table 5) used were all of technical grade—with the exception of ethylene glycol, which was in commercial grade—and the solutions were made either with distilled water (Publications I & II) or Milli-Q deionized water (Merck Millipore, USA, Publication III). The leaching time used in the mapping experiments was 168 h utilizing a S/L of 100 g/L (batch of 250 mL in a beaker placed on a magnetic stirrer plate) at ambient pressure and room temperature (varying between 20-22 °C) without any gas purging. Stirring at 400 RPM was applied in order to keep the solids in suspension.
In a further EAFD study (Publication II) with citric acid (VWR Chemicals, Belgium), leaching was performed in a 1000 mL lab scale glass reactor immersed in a water bath (LAUDA Aqualine AL 25, Germany). The temperature range was set to vary from 30 to 50 °C in order to avoid unnecessary citric acid decomposition [19], [141] – [143] and the leaching time was reduced from 168 h to 120 min with a constant sampling interval: 5, 15, 30, 60, and 120 min. The citric acid concentrations were 0.05, 0.1, 0.2, 0.4, and 0.8 M and the agitation was increased from 400 to 500 RPM, while the S/L ratio was kept the same at 100 g/L (batch size of 800 mL). Moreover, compared to the mapping investigations, the leach solution was also purged with oxygen (AGA, Finland, industrial grade) at a flow rate of 2 000 mL/min and the pH (HI 11310, Hanna Instruments, USA or S210 SevenCompact™ pH meter by Mettler Toledo, USA) and redox potential (InLab Ag/AgCl 3 M KCl, Mettler Toledo, USA) were measured at each sampling interval. Roasting of the raw material was conducted in a Scandia furnace (Type K4/PDI 40, Denmark) and the leaching residues and other solids analyses were conducted by XRD (X-Ray diffraction, X’Pert PRO Powder, the Netherlands), employing either Cu Kα (45 kV and 40 mA) or Co Kα (40 kV and 40 mA) as a radiation source. A KS 3000i (IKA, Germany) incubated shaker at 250 RPM was used for the SX experiments (Publication III). The Pb removal was conducted by adding droplets of 18 M H₂SO₄ to the PLS obtained after leaching with an agitation of 200 RPM and solution samples were taken every 0.5 pH intervals after 10 min stabilization (Publication III).

3.2 Finding a Suitable Novel Lixiviant for EAF Leaching

Comprehensive lixiviant mapping (Publication I) was performed in order to clarify the effects of both concentration and solution type on the extraction of certain elements, namely Fe, Zn, Cr, Pb, and Mn—the valuable and toxic metals present in the dust. There has been intense investigation related to inorganic mineral acids such as sulfuric, nitric, and hydrochloric acids for the selective dissolution of elements from EAFD in the past [144] – [148], and the most widely investigated acid of them all, H₂SO₄, showed rather promising results [13], [73], [144] – [146]. In addition, organic acids have also been claimed to show advantageous selectivity towards certain elements or compounds, e.g., oxalic acid in the leaching of Fe [149].

In Publication I, 16 different leaching media with different concentrations were tested, resulting in a total of 27 experiments performed during the mapping experiments, Table 5. The specific goal was to find a suitable lixiviant for the selective leaching of Zn and Pb over Fe, in order to turn the leach residue into a recyclable Fe-rich raw material that could be fed back into the EAF at the plant. The main cause of insufficient Zn extraction is the existence of zinc ferrite (ZnₓFe₃₋ₓO₄). According to the XRD of the raw material, ~23.5 % of total Zn is present in the ferrite form and is thus not fully leachable in organic acids [13].
Table 5. Lixivants used for determining the extraction of certain elements from EAFD. (Extended from Publication I).

<table>
<thead>
<tr>
<th>Acids</th>
<th>Concentration</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ (Nitric acid)</td>
<td>15 M</td>
<td>1.5 M</td>
</tr>
<tr>
<td>H₂SO₄ (Sulfuric acid)</td>
<td>18 M</td>
<td>1.8 M</td>
</tr>
<tr>
<td>HCl (Hydrochloric acid)</td>
<td>12 M</td>
<td>1.2 M</td>
</tr>
<tr>
<td>HNO₃ to HCl ratio 1/3 (Aqua regia)</td>
<td>100%</td>
<td>10%</td>
</tr>
<tr>
<td>C₆H₈O₇ (Citric acid)</td>
<td>0.94 M</td>
<td>0.09 M</td>
</tr>
<tr>
<td>C₂H₄O₂ (Acetic acid)</td>
<td>17.5 M</td>
<td>1.75 M</td>
</tr>
<tr>
<td>H₂CO₂ (Formic acid)</td>
<td>2.7 M</td>
<td>0.27 M</td>
</tr>
<tr>
<td>H₃PO₄ (Phosphoric acid)</td>
<td>19.2 M</td>
<td>1.92 M</td>
</tr>
<tr>
<td>C₂H₂O₄ (Oxalic acid)</td>
<td>1.6 M</td>
<td>0.16 M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkalis</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (Sodium hydroxide)</td>
<td>24 M, 12 M</td>
<td>13.6</td>
</tr>
<tr>
<td>KOH (Potassium hydroxide)</td>
<td>20 M, 10 M</td>
<td>14.7</td>
</tr>
<tr>
<td>NH₃ (Ammonium)</td>
<td>25%</td>
<td>13.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Others</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (Distilled water)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>C₂H₅OH (Ethanol)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>(CH₂OH)₂ (Ethylene glycol)</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>(CH₃)₂CO (Acetone)</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5A & B present the measured yields of zinc and iron dissolution into the different lixiviants. As can be seen, 12 M HCl and 100% aqua regia resulted in total dissolution for both Zn and Fe. Moreover, for zinc (Figure 5A), there were four lixiviants that resulted in >80% dissolution, all of which were inorganic mineral acids, whereas the highest Zn yield achieved with organic acids was observed with 0.94 M citric acid, resulting in just over 75% dissolution. In addition, there were five lixiviants that achieved >80% Fe dissolution, Figure 5B, including one organic acid, 1.6 M oxalic acid, which is a well-known organic acid in terms of iron dissolution [149], [150]. The high dissolution of Fe into oxalic acid suggests that the iron remains in the trivalent form (Fe³⁺) within the solution since divalent (Fe²⁺) is known to precipitate as an iron oxalate, FeC₂O₄·xH₂O [150] – [152]. However, the dissolution of a certain element is not only influenced by the lixiviant used but the pH is also known to have an effect [153], which helps explain the observed variances between different concentrations of the same lixiviants.
Figure 5. Achieved Zn (A) and Fe (B) extraction results in decreasing order for the 27 different lixiviants investigated. Experiments were conducted for 168 h at room temperature (varying from 20-22°C) with an agitation of 400 RPM.

Most of the leaching conditions applied in the mapping experiments did not favor the dissolution of zinc ferrite and when the zinc ferrite was leached, large
amounts of unwanted Fe (originating from the ferrite fraction) also dissolved, resulting in poor selectivity between Zn and Fe and iron losses. Although positive results were observed with most of the inorganic mineral acids, their application tends to be expensive due to the requirement for subsequent washing circuits following treatment. Nitric and hydrochloric acids, for example, would require a water-intensive washing circuit for the removal of nitrates or chlorides, to avoid these species ending up in the furnace [127]. Moreover, since lead cannot be leached into sulfuric acid (Publication I), it will end up accumulating in the Fe-rich residue. Conversely, organic acids, like citric and acetic, are highly selective for Zn [127], whilst consisting of elements that are fully compatible with the EAF.

Zinc and iron are the key elements that determine the selectivity—and therefore impact the overall profitability—of the leaching process, even though the leaching of toxic (Pb) and carcinogenic (Cr⁶⁺) metals is also relevant when it comes to the final process selection. In terms of the selectivity between zinc and iron, the highest results were not observed with acids but with alkalis, such as ammonium, NaOH, and KOH, Figure 6. Furthermore, there are many different lixiviants that have a Zn/Fe ratio over 1, meaning more zinc is dissolved cf. iron. Nevertheless, the highest selectivity (>25000) between zinc and iron was observed with 25% ammonium solution, where the dissolution of total zinc was as low as ~16%. In contrast, the lixiviants resulting in the highest dissolution of zinc (100%)—12 M HCl and 100% aqua regia (Figure 5)—displayed no selectivity.
Table 6 displays the five most suitable leaching media for EAFD treatment in terms of desired yield for Zn and Fe dissolution. In order to avoid unnecessary Pb accumulation in the EAF due to feeding back the recycled dust, high Pb selectivity was also considered an advantage. According to Table 6, the two most suitable lixiviants were 1.2 M HCl and 10% aqua regia, however, as stated earlier, the industrial use of chloride-based leaching solutions would also require high-cost washing circuits, which also excludes HNO₃ (due to nitrates) from further consideration. Of the two best organic acids, acetic acid was shown to provide lower Zn extraction. Therefore, citric acid was selected for the next process optimization phases.

Table 6. Top five lixiviants in terms of selectivity between Zn and Fe together with the total leached amount of Zn, Fe, Pb, Mn, and Cr. Experiments were conducted for 168 h at room temperature (varying from 20-22°C) with an agitation of 400 RPM.

<table>
<thead>
<tr>
<th>Leaching Media</th>
<th>Zn [%]</th>
<th>Fe [%]</th>
<th>Pb [%]</th>
<th>Mn [%]</th>
<th>Cr [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 M Hydrochloric acid</td>
<td>79</td>
<td>4</td>
<td>49</td>
<td>33</td>
<td>49</td>
</tr>
<tr>
<td>10 % Aqua regia</td>
<td>75</td>
<td>4</td>
<td>48</td>
<td>33</td>
<td>46</td>
</tr>
<tr>
<td>0.94 M Citric acid</td>
<td>75</td>
<td>17</td>
<td>49</td>
<td>36</td>
<td>53</td>
</tr>
<tr>
<td>1.5 M Nitric acid</td>
<td>78</td>
<td>14</td>
<td>18</td>
<td>30</td>
<td>65</td>
</tr>
<tr>
<td>1.75 M Acetic acid</td>
<td>58</td>
<td>6</td>
<td>60</td>
<td>28</td>
<td>36</td>
</tr>
</tbody>
</table>
3.3 Maximizing the Selectivity between Zn and Fe

The results of Zn and Fe dissolution, obtained after the factorial tests (Publication II), are shown in Figure 7 and, as it can be seen, the concentration of citric acid seems to have a major impact on the dissolution of both elements. Additionally, the leaching kinetics achieved at 30 °C were slower as the endpoint was not reached after 120 min even with the higher (≥ 0.4 M) citric acid concentrations, whereas at 40 °C equilibrium was reached after only one hour. A comparison of the results obtained at the lower citric acid concentration and after a much shorter leaching time—Figure 5 vs. Figure 7—shows the content of dissolved iron is approximately half with 0.8 M and 120 min compared to the result achieved in the mapping leaching tests (0.94 M and 168 h).

![Figure 7](image)

**Figure 7.** Zn and Fe extractions as a function of time for citric acid lixiviant at 30 °C (A & B) and 40 °C (C & D) with an agitation of 500 RPM. (Publication II).

As stated previously, the decomposition of citric acid during leaching was one of the key points to avoid, therefore no leaching tests above 50 °C were conducted. Even at 50 °C, the dissolution of Zn was found to be drastically decreased, Figure 8A. The redox potential, Figure 8B, was almost the same at each investigated temperature at the beginning of the experiments when the highest citric acid concentration (0.8 M) was used, unlike in the case of 0.4 M citric acid. Nevertheless, a notable increase in the redox potential is evident along with the dissolution of various species into the solution in all the experiments. For example, the dissolved $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox pair is known to have a relatively high redox potential ($E^0 = +770$ mV vs. SHE) but in citrate media, the redox potential of $\text{Fe}^{3+}\text{cit}/\text{Fe}^{2+}\text{cit}$ is considerably lower, $+372$ mV vs. SHE [154], [155]. Moreover, during dissolution more redox pairs exist in solution, increasing the oxidation power of the solution even further together with dissolved oxygen. The increase
in redox potentials during the leaching experiment at 0.4 M solution appears to be rather constant regardless of the temperature, and equilibrium was not achieved even after 120 min of leaching. Quite similar behavior was evident at 0.8 M $T = 30 \, ^\circ\text{C}$, with higher acidity providing a greater increase. In 0.8 M solution, equilibrium was reached at 40 and 50 °C. This may reflect either the almost complete dissolution of elements that are thermodynamically alike, or the decomposition of citric acid impacting the solution redox pairs present, or a combined effect.

![Figure 8. Dissolution of Zn and Fe (A) to 0.4 M citric acid as a function of temperature (A, Publication II) and (B) the measured redox potentials for the highest citric acid concentration. The applied agitation was 500 RPM.](image)

Zn extraction was found not to exceed 80%, Figure 7, due to the presence of zinc ferrite. Also, the XRD analysis performed on the leach residue revealed that even though zinc oxide (ZnO) had fully leached from the solids, zinc ferrite ($\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$) remained undissolved, Figure 9. In terms of recycling the residue back to the EAF process, a Zn content of more than 20% in the solids is not acceptable, because Zn can lead to scaffold formation and block the gas off-take of the furnace [81]. Therefore, pyrometallurgical treatment, namely alkaline roasting, was investigated in order to address the challenges related to zinc ferrite dissolution [19], [156], [157].
In order to transform the zinc ferrite present in the EAFD to a form where zinc can be dissolved into citric acid whilst maintaining the high selectivity towards Fe, alkaline roasting at 450 °C for 60 min with an EAFD/NaOH ratio of 2:1 was investigated. This method was selected as it is known that alkaline thermal treatment decomposes insoluble zinc ferrite into the more soluble sodium zincate (Na₂ZnO₂), insoluble sodium ferrate (NaFeO₂), and water vapor according to Equation (11) [19], [156], [157], (Publication II).

$$\text{ZnFe}_2\text{O}_4(s) + 4\text{NaOH}(s) = \text{Na}_2\text{ZnO}_2(s) + 2\text{NaFeO}_2(s) + 2\text{H}_2\text{O} \uparrow$$ (11)

Roasting efficiency was confirmed by XRD measurements and the resulting patterns can be seen in Figure 10A. It is noteworthy that, when the unroasted raw material is compared to the roasted version, ZnO remains in the EAFD but Zn₂Fe₃₋₄O₄ has disappeared, as thermodynamically caustic soda (NaOH) favors the reaction with zinc ferrite rather than zinc oxide. At the given temperature (450 °C), $\Delta G = 99.5 \text{ kJ}$ [27] for zinc oxide decomposition and $\Delta G = 71.4 \text{ kJ}$ [27] for zinc ferrite decomposition. Based on the stoichiometry in Equation (11) and the ratio between EAFD and NaOH of 2:1, one mole of zinc ferrite requires 4 moles of NaOH; therefore, almost all of the caustic soda present is consumed for the zinc ferrite decomposition.

When taking a detailed look at the thermodynamics, the $\Delta G$ values for the proposed leaching reactions presented in Equations (12) – (27), Table 7, suggest which reactions are the most likely to occur. Naturally, the metal extraction during leaching is controlled by the kinetics of all the possible leaching reactions; nevertheless, reactions with highly positive $\Delta G$ values are unlikely to occur under the investigated leaching conditions. Moreover, as the EAFD also included some zinc sulfide (ZnS) and lead sulphide (PbS), the sulfur is expected to oxidize...
to sulfate ion rather than form a gaseous compound with oxygen according to Equations (25) and (27), due to the more negative ΔG value shown in Equations (24) and (26).

Table 7. Possible chemical reactions suggested to occur during the citric acid leaching of EAFD, including their calculated ΔG values [27] at 40 °C under standard conditions. (Extended from Publication II).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>#</th>
<th>ΔG (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{3}{2}ZnO(l) + C_6H_5O_2(aq) = \frac{3}{2}Zn^{2+} + C_6H_5O_2^- + \frac{3}{2}H_2O(l))</td>
<td>(12)</td>
<td>-77</td>
</tr>
<tr>
<td>(Na_2ZnO_2(\text{aq}) + C_6H_5O_2^- + H^+ = Zn^{2+} + C_6H_5O_2^- + 2Na^+ + 2H_2O(l))</td>
<td>(13)</td>
<td>-399</td>
</tr>
<tr>
<td>(\frac{3}{2}MnO(l) + C_6H_5O_2^- = \frac{3}{2}Mn^{2+} + C_6H_5O_2^- + \frac{3}{2}H_2O(l))</td>
<td>(14)</td>
<td>-131</td>
</tr>
<tr>
<td>(3\frac{1}{2}PbO(l) + C_6H_5O_2^- = \frac{3}{2}Pb^{2+} + C_6H_5O_2^- + \frac{3}{2}H_2O(l))</td>
<td>(16)</td>
<td>-89</td>
</tr>
<tr>
<td>(\text{NaFeO}_2(\text{aq}) + C_6H_5O_2^- + H_2O(l) = Fe^{3+} + C_6H_5O_2^- + Na^+ + 2H_2O(l))</td>
<td>(17)</td>
<td>-89</td>
</tr>
<tr>
<td>(Zn^{2+} + 2C_6H_5O_2^- = Zn^{2+} + 2C_6H_5O_2^- + 4OH^{-} + 2H^+)</td>
<td>(18)</td>
<td>326</td>
</tr>
<tr>
<td>(Fe_3O_4(s) + 2C_6H_5O_2^- = 3Fe^{2+} + C_6H_5O_2^- + 3H_2O(l))</td>
<td>(19)</td>
<td>64</td>
</tr>
<tr>
<td>(Fe_3O_4(s) + C_6H_5O_2^- = 3Fe^{2+} + C_6H_5O_2^- + 3H_2O(l))</td>
<td>(20)</td>
<td>46</td>
</tr>
<tr>
<td>(Fe_3O_4(s) + 3C_6H_5O_2^- = 6Fe^{2+} + 3C_6H_5O_2^- + 4H_2O(l))</td>
<td>(21)</td>
<td>15</td>
</tr>
<tr>
<td>(Fe_3O_4(s) + 2C_6H_5O_2^- = 6Fe^{2+} + 2C_6H_5O_2^- + 3H_2O(l))</td>
<td>(22)</td>
<td>45</td>
</tr>
<tr>
<td>(ZnS(s) + C_6H_5O_2^- + O_2(l) = Zn^{2+} + C_6H_5O_2^- + 2e^- + 3H^+)</td>
<td>(24)</td>
<td>-228</td>
</tr>
<tr>
<td>(2ZnS(s) + C_6H_5O_2^- + 6O_2(l) = 2Zn^{2+} + C_6H_5O_2^- + 3H_2O(l) + 3SO_2(g))</td>
<td>(25)</td>
<td>-2032</td>
</tr>
<tr>
<td>(3PbS(s) + C_6H_5O_2^- + O_2 = Pb^{2+} + C_6H_5O_2^- + 2e^- + 3H^+ + 2SO_2(g))</td>
<td>(26)</td>
<td>-206</td>
</tr>
<tr>
<td>(3PbS(s) + C_6H_5O_2^- + 6O_2(g) = 3Pb^{2+} + C_6H_5O_2^- + 3H_2O(l) + 3SO_2(g))</td>
<td>(27)</td>
<td>-1967</td>
</tr>
</tbody>
</table>

As the ΔG for Equation (17) is more negative than that of Equation (12), the dissolved iron from sodium ferrate is most likely to precipitate, since the pH value (~4) of the leaching solution is not sufficiently low for iron dissolution. Moreover, when comparing the leaching conducted with the citric acid concentration of 0.4 M to 0.8 M, a relatively significant amount of zinc remains undisolved in the residue: around 34%. The reason for this phenomenon is that, after alkaline roasting, the EAFD includes a rather significant amount of sodium (Table 2), which gives the dust a highly alkaline character and therefore forms alkalis (i.e., strong bases capable of neutralizing acids) when introduced to aqueous solutions. With a citric acid concentration of 0.4 M, the pH increased up to 8, causing Zn hydrolysis—precipitation as Zn(OH)_2—[141], Figure 10A. In 0.8 M solution the pH remained more or less stable throughout the whole leaching experiment, indicating that the citric acid was not fully consumed during the leaching at 0.8 M. Moreover, as can be seen in Figure 10B, the redox potential shows that the leaching conditions with 0.4 M remained less oxidative.
Table 8 presents the final metal extractions obtained when unroasted and roasted EAFD were leached with 0.4 M and 0.8 M citric acid, respectively. When roasting was not performed for the EAFD, the final extractions of Zn and Fe showed no significant variation regardless of the citric acid concentration utilized, although Pb, Mn, and Cr had a wider variation. It is worth noting that the Zn extraction reached 100% while that of Fe remained below 10% and almost all Pb was also removed from the EAFD when roasted EAFD was leached with 0.8 M citric acid. The reason for such behaviour could be that according to Figure 1 and Figure 10B, the leaching conditions were not the most optimal for iron dissolution. However, as the E-pH diagrams presented in Figure 1 are representing a metal-H2O systems (constructed according to the data obtained from XRD analysis and Rietveld refinement [158], [159]), they can be considered only indicative towards the leaching behaviour of EAFD in citric acid medium. The Zn-citrate speciation diagrams predicts that Zn could be in forms of Zn^{2+} [160], [161], Zn(cit)⁻ [160], [162], Zn(cit)^{2+} [160] or ZnH(cit) [160], [162] at pH 4. Moreover, redox potentiometric titration (with K₂Cr₂O₇) [164] confirmed that the total Fe^{2+} content was only ~14 mg/L and therefore, only ferric (Fe³⁺) citrate species are taken into account on the Fe-citrate speciation. Therefore, Fe is present mostly in FeH(cit) [163], FeOH(cit)⁻ [165], FeH(cit)^{2+} [166] or Fe₂(OH)₂(cit)^{2-} [162]. Furthermore, with higher Zn concentrations in the solution, at pH 4 (according to Figure 10B), Zn is more likely present in form of Zn(cit)₂⁺, Zn(cit)⁻ and/or ZnH(cit) than in simple ion, Zn^{2+}, whereas Fe is believed to be present as FeH(cit). In addition, according to reactions presented in Table 7, the reaction between zinc and citric acid is thermodynamically more likely (more negative ΔG) to occur, resulting in more dissolved zinc than iron and when the results presented in Figure 7 are compared, this appears to be the case regardless of the citric acid concentration. The reactions presented in Table 7 do not include the formed metal-citrate complexes (due to lack of citrate complexes information in HSC9 database), and therefore they can also be considered as indicative, however, providing still enough information of the leaching reactions.

Furthermore, the remaining leach residue was found to be chemically suitable for the EAF process, although it needs to meet the physical requirements prior to being fed back into the process. Consequently, a conventional pelletizing process—not conducted experimentally within the current Thesis—needs to
be performed for the leaching residue before feeding it back to the EAF process [19].

Table 8. Extraction results for the elements of interest achieved with 0.4 and 0.8 M citric acid leaching for unroasted and roasted EAFD performed at 40 °C with an agitation of 500 RPM. (Publication II).

<table>
<thead>
<tr>
<th>Roasting</th>
<th>Leaching parameters</th>
<th>Metal extractions [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4 M, 40 °C</td>
<td>Zn  Fe  Pb  Cr  Mn</td>
</tr>
<tr>
<td>No</td>
<td>0.4 M, 40 °C</td>
<td>78  9  70  40  20</td>
</tr>
<tr>
<td>No</td>
<td>0.8 M, 40 °C</td>
<td>71  12  89  50  29</td>
</tr>
<tr>
<td>Yes</td>
<td>0.4 M, 40 °C</td>
<td>66  3  17  3  20</td>
</tr>
<tr>
<td>Yes</td>
<td>0.8 M, 40 °C</td>
<td>100 8  88  6  43</td>
</tr>
</tbody>
</table>

3.4 Recovering Pb and Zn from the Citrate PLS

The PLS composition after the 0.8 M citric acid leaching is shown in Table 9 and as can be seen, the Zn content is relatively high (~20 g/L) compared to the other elements present. The impurities in Zn EW (electrowinning) are often categorized into three different subgroups: Group 1 being the worst impurities (Ge, Sb, Te, and Se), Group 2 worse impurities (As, Ni, Sn, Co, Ag, and Fe), and Group 3 bad impurities (Ga, Bi, Hg, Cd, In, and Pb) [167]. As can be seen in Table 9, no elements with a high content from Groups 1 and 2 were present. Only a minor amount of Fe remains in the PLS after citric acid leaching; however, Fe is known to be rather difficult to strip away from loaded organics, due for instance to the stability of the complex between iron and D2EHPA [168], leading to a situation where it accumulates within the organic phase. Therefore, the greatest attention prior to SX was paid to the removal of the Group 3 elements, namely Pb, which has an adverse effect on zinc EW [169]. In addition, halogen species (Cl-, F-, etc.) are known to occur in significant amounts in metallurgical residue [170] – [174] and thus potentially end up in the PLS after EAFD citric acid leaching. Their analyses from the solution were not performed, however, it is thermodynamically likely that the majority ends up in the gaseous phase during NaOH roasting, due to the high vapor pressure at low temperatures (<300 °C) [171], [175]. Moreover, the XRD analysis showed no halogens in the roasted EAFD, Figure 10A.
The removal of Pb was conducted in such a way that the formed precipitate could possibly be used in either state-of-the-art Pb processing [176] or in lead batteries after further purification steps [177]. Figure 11 shows the precipitation efficiency of Pb and the co-precipitation of Mn—together with sulfate ion consumption—as a function of pH. Lead was fully precipitated at pH = 2 and simultaneously around 30% of the manganese was also removed, while the sulfate ion content was around 0.012 M. After precipitation, XRD analysis of the formed precipitate showed a PbSO$_4$ content of ~34% and at the same time, sodium was also precipitated, mainly as sodium thiosulfate, Na$_2$S$_2$O$_3$. In addition to the additional cleaning processes, the solubility of sodium thiosulfate in water is much higher (209 g/L [178]) cf. lead sulfate (PbSO$_4$), which is practically insoluble [179]. Consequently, a simple washing circuit would be required prior to secondary lead smelting. In addition, sodium carbonate (NaCO$_3$) is known as a desulfurization chemical in the lead smelting process [180], [181] and therefore, the relatively high Na content in the Pb feed material can be tolerated.
After lead removal, the PLS was subjected to a Zn separation and enrichment stage. In Zn SX, the most common reagents used are organophosphorus extractants including the most generally used, di(2-ethylhexyl)phosphoric acid (D2EHPA) [18], [182] – [192], as well as 2-ethylhexyl phosphonic acid mono-2-ethyl hexyl ester (PC88A) [184], [188], [193], and bis(2,4,4-trimethylpentyl)phosphonic acid (Cyanex 272) [18], [186], [188], [194]. As D2EHPA is an acidic organophosphorus reagent, the extraction reaction of divalent metal ions is suggested to be cation exchange, as presented in Equation (28).

\[
M^{2+}_{(aq)} + 2HR_{org(l)} \leftrightarrow MR_2^{org(l)} + 2H^+_{(aq)}
\]  

(28)

where \( M \) is the metal ion, \( HR \) the organic extractant, and \( MR_2 \) the metal extractant complex [195] – [197]. As Equation (26) predicts, the extraction of Zn is favored by increasing the pH during the extraction stage, which is demonstrated in Figure 12A. Similar behavior for Zn [182], [183], [185], [186], [198] – [200] and Mn [184], [201], [202] have also been observed earlier, primarily for inorganic mineral acids. In contrast, when the extraction of Zn and Mn increased as a function of pH, that of Fe decreased. One possible explanation for such a phenomenon could be that the bond formed between iron and citrate ion is relatively strong compared to that of zinc and citrate ion. As the reported stability constants for different Fe-citrate and Zn-citrate complexes are in the range of 2 – 9 for Fe\(^{2+}\) [161], [203] and 11 – 15 for Fe\(^{3+}\) [161], [203], [204] and 3.0 – 4.9 for Zn\(^{2+}\) [203], [204], respectively, the Fe-citrate complex is harder to break, i.e., to perform cation exchange. Furthermore, as it was confirmed by redox potentiometric titration (with K\(_2\)Cr\(_2\)O\(_7\)) [164] that most of the iron was in the form of Fe\(^{3+}\) and according to the Fe-citric acid speciation diagrams, the most dominant Fe\(^{3+}\)-citrate complex at pH 4 is FeH(cit) [163], which stability constant have been reported to be in the range of 11.7 – 12.5 [203] and for example Zn(cit\(^{-}\)) has reported stability constant of 3.0 – 5.2 [203], [205]. The stability of e.g. Zn(cit\(^{-}\)) has shown to be temperature depended, where higher temperature results in higher stability [205]. However, the stability increase from 5.0 to 5.2 is rather marginal but so was the decrease in zinc extraction at higher temperatures (89.7% at 25 °C vs. 87.9% at 55 °C, Figure 12C, as well. In addition, the stability constant for Mn-citrate complex has been reported to be in the range of 2.1 – 4.2 [203], [206], which means that Mn extraction should follow Zn extraction by some margin. In terms of speciation diagrams for Fe-citrate species in aqueous solution, it has been demonstrated that iron can form either a rather stable neutral [161] or anionic [162] complex within the investigated pH range of 1 – 6 and that free iron species do not predominate at pH levels > 1.5 [162]. This indicates that the Fe-citrate complex could be stable enough not to react with the acidic extractant and therefore the extraction of iron into D2EHPA decreases with increasing pH.

According to Figure 12B, the contact time did not have a major impact on Zn and Mn extraction, whereas Fe extraction increased when the contact time was prolonged, possibly supporting the earlier claim of Fe-citrate resistivity towards acidic extractant. However, as the experimental setup was rather small in terms of volume (20 mL), it was assumed that a longer contact time would be beneficial with upscaled solution volumes, therefore \( t = 15 \) min was selected to be used as contact time. Moreover, Figure 12C suggests that the extraction of
zinc and iron into D2EHPA were exothermally driven, whilst that of manganese was endothermic in nature. Figure 12D shows the effect of D2EHPA concentration on the extraction of the targeted elements. With the lowest D2EHPA concentration (10 vol-%), the extractions of Mn and Fe were rather marginal, and at the same time, the extraction of Zn was below 50%. Similarly to this study, comparable extraction behavior of Fe from chloride and sulfuric media has been reported earlier [190], [192]. According to the extraction results achieved, the following parameters for SX operation in the current process development could be defined as $T = 25\, ^\circ\text{C}$, $[\text{D2EHPA}] = 20\, \text{vol-\%}$, $t = 15\, \text{min}$, and pH = 5.

![Figure 12. Extraction of Zn, Fe and Mn into 20 vol-% D2EHPA as a function of (A) pH, (B) time, (C) temperature, and (D) as a function of D2EHPA concentration. The constant parameters were 250 RPM, $t = 15\, \text{min}$, $T = 25\, ^\circ\text{C}$, O/A = 1/1 and $[\text{D2EHPA}] = 20\, \text{vol-\%}$.

In addition to Figure 12, a McCabe-Thiele diagram [207], [208] for zinc extraction was drawn in order to initially determine the number of counter-current stages required, Figure 13A. With the operating line of 1:1, only two theoretical countercurrent stages would be required to load almost all the zinc ($\sim99\%$) from citric acid PLS into D2EHPA. Furthermore, the zinc stripping from the loaded organic was performed with sulfuric acid in a range of 0.005 – 2 M, Table 10. The stripping time and temperature were selected to be the same as those used for the extraction process—15 min and 25 °C, respectively—and the results showed that a 1 M sulfuric acid concentration provided the highest level of Zn recovery. It is noteworthy that with such stripping conditions (low acid concentration and short time), iron remained in the organic phase and was not stripped into sulfuric acid. Similar slow stripping kinetics phenomena for iron have also been observed earlier [192]. As the total content of iron in the organic phase is rather marginal ($\sim100\, \text{mg/L}$), circulation of the extractant used,
D2EHPA, could be performed several times before the cumulative iron content becomes too high and the organic phase requires purification with stronger sulfuric acid [191], [209], [210] or even with strong HCl acids. Figure 13B shows the McCabe-Thiele analysis for stripping. All the O/A experiments were undertaken with 1 M H₂SO₄. The results suggest that with an operating line of 3:1, three theoretical counter-current stages would be required and the Zn content could be increased up to ~55 g/L, which is a similar concentration to that used in state-of-the-art Zn EW processes [211].

<table>
<thead>
<tr>
<th>H₂SO₄ [M]</th>
<th>Zn recovery [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.3</td>
</tr>
<tr>
<td>0.1</td>
<td>27.0</td>
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<tr>
<td>1</td>
<td>93.9</td>
</tr>
<tr>
<td>2</td>
<td>79.8</td>
</tr>
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</table>

Table 10. Effect of sulfuric acid concentration on the stripping efficiency of Zn (O/A of 1/1 at 25 °C for 15 min with 250 RPM).

Figure 13. McCabe-Thiele diagrams for (A) the extraction of Zn with 20 vol-% D2EHPA at 25 °C for 15 min at pH = 5 and (B) stripping of Zn using 1 M H₂SO₄ solution at 25 °C for 15 min. Agitation of 250 RPM was applied in every experiment.

To simulate citric acid PLS SX stripping, a single-stage SX-stripping experiment was performed on a larger scale (200 mL vs. 20 mL) under optimal conditions. As can be observed, the zinc enrichment ratio was over 2.5 (~20 g/L, Table 9, vs. ~52 g/L, Table 11). Mn, which showed a minor increase, is not considered problematic in Zn EW [167], [169], [212] – [217]. Sb, on the other hand, is known to have a negative effect by increasing the overpotential leading to possible H₂ evolution [218], i.e., increasing the energy consumption in zinc electrowinning. Nevertheless, its content in the purified PLS is relatively low and if the electrolyte produced undergoes conventional Zn electrolyte purification with several cementation stages, the zinc content could be further increased with an associated reduction in the content of the other metals [219].
Table 11. Composition of the purified EAFD citrate PLS. (Publication III).

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Fe</th>
<th>Ca</th>
<th>Mg</th>
<th>Al</th>
<th>Cr</th>
<th>Mn</th>
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</thead>
<tbody>
<tr>
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<td>&lt; LOD</td>
<td>580</td>
<td>36</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>585</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>30700</td>
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<tr>
<td>Ga</td>
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<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
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<td>Ge</td>
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</tr>
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<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td></td>
</tr>
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<td>Sb</td>
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<td></td>
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<tr>
<td>Ag</td>
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<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
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<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>20</td>
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<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

LOD = limit of detection

3.5 Innovative EAFD Processing Flowchart

An alkaline roasting process for the recycling of EAFD has been proposed previously [157]; however, only relatively low zinc extraction levels (~30 – 60%) were achieved. Moreover, the economical aspects of roasting were not investigated in the current thesis, and it can be speculated that the roasting could challenge the economics. On the other hand, also increased amount of washing steps for the leach residue after e.g. the mineral acid leaching could challenge the economics or water footprint as well. These aspects needs to be investigated in detail in future. However, the route for EAFD treatment proposed here is of significant interest and is displayed as a flowchart in Figure 14. The first part (outlined with the gray dotted line) can be readily integrated into the current EAF process. The second part (dotted orange line) consists of straightforward unit operations, where the zinc- and lead-rich PLS solution is first treated by the addition of sulfate ions. The sulfate ions in the current study originated from sulfuric acid; however, in the process design the continuous adjustment of pH back and forth (~4 → 2 → 5) is unlikely to be economically attractive. Therefore, lead could also be precipitated as PbSO₄ by addition of alkali sulfate solutions [220], although the use of Na₂SO₄, for example, as an anion donor would further increase the Na loading of the PLS (Table 9). Moreover, addition of sulfuric acid was demonstrated to decrease the sodium content in the solution through the formation of sodium thiosulfate, Na₂S₂O₃. Nevertheless, if the EAF steel mill already has pickling and rolling lines, handling of the PLS obtained after citric acid leaching for lead precipitation at the EAF plant could also be performed.

The third stage of the proposed flowchart (lime color dotted line) could potentially be integrated into state-of-the-art Zn EW processes. The proposed flowchart is uncomplicated, although in reality, no current metallurgical operations exist that produce all the main metals (Fe, Pb, and Zn) at the same plant, therefore some logistics not only between a plant’s unit operations, but also between different metallurgical facilities would be required. Nevertheless, the proposed innovative flowchart for EAFD treatment has been investigated on laboratory scale (in non-continuous mode) with EAFD provided by an EAF steel plant and the results are promising. One alternative approach is, rather than utilizing
the Zn-rich electrolyte for EW, potentially to precipitate the Zn directly as oxides, which can be used, for example, in the rubber, pharmaceutical, cosmetics, or photocatalysis industries [221]. Overall, these findings demonstrate that the development and optimization of selective EAFD leaching followed by solution purification provides fractions suitable for integration into existing metallurgical plant processes.
Figure 14. Proposed flowchart for EAFD processing divided into three stages (dotted lines) according to the metal stream produced.
4. TROF Doré Slag – Source of Valuable Metals

"Inexperience causes young ones to do what the older ones claim to be impossible"

The composition of Doré slag is rather complex, Table 3, and includes not only elements that are classified as toxic (As [222], [223] and Ba [223]) but also valuable and critical elements (Ag, Sb, Bi, and Te). Consequently, the further processing of such a raw material is not only recommended in terms of the circular economy but is also essential in terms of sustainability. Therefore, tellurium recovery from leached Doré slag is discussed here. The current study employed EW and EDRR (electrodeposition-redox replacement) processes to support Te recovery from Doré slag.

4.1 Experimental

Conventional mineral acid leaching was performed for Doré slag with 10 – 30% aqua regia (HCl to HNO₃ ratio of 3:1) for 120 min over a temperature range of 30 – 50 °C. The solution was also purged with O₂ (AGA, Finland, industrial grade) at a rate of 2000 mL/min and agitation of 500 RPM was applied with and without H₂O₂ addition. All the solutions utilized were of technical grade purity and were diluted with distilled water. The S/L ratio was 100 g/L with a batch size of 800 mL, and experiments were performed in a 1000 mL lab scale glass reactor immersed in a thermostatically controlled water bath (LAUDA Aqualine AL 25, Germany). The dissolution kinetics and the possible mechanisms of Cu, Bi, and Sb were determined—and have been previously discussed by the author [69]—after which the remaining PLS batches were combined, and comprehensive solution analyses were performed by ICP-OES (inductively couple plasma – optical emission spectroscopy, Thermo Fisher Scientific iCAP 6500 Duo, USA) and ICP-MS (inductively couple plasma – mass spectroscopy, Thermo Fisher Scientific iCAP Qc, USA). Table 12 presents the PLS composition from the Doré slag leached in 30% aqua regia [69]. This PLS was subsequently used as the raw material for the EW as well as EDRR investigations for Te recovery, Publication IV.

AAS standards (Te, As, Ag, Bi, Cu, Pb, and Fe, all of 1000 mg/L concentration, Sigma-Aldrich, USA) were selected as the basis for the synthetic solutions. A standard three-electrode cell was used that included a saturated calomel electrode (SCE, B521, SI Analytics, Germany) as a reference electrode (RE), a 0.1
mm thick \( (A_s = 24 \, \text{cm}^2) \) Pt plate as a counter electrode (CE), and a 0.1 mm thick \( (A_s = 0.24 - 0.4 \, \text{cm}^2) \) Pt plate as a working electrode (WE, both Kultakeskus, Finland). A potentiostat (IviumStat 24-bit CompactStat, Ivium Technologies, Netherlands) was used to carry out the electrochemical experiments and SEM-EDS (scanning electron microscope, Mira^3 Tescan GM, Czech Republic, energy dispersion spectroscopy, Thermo Scientific 50 mm^2 UltraDry, USA) with an acceleration voltage of 15 keV was used for the chemical analyses of the metal deposits on the surface of the working electrode. A total of 6 to 8 point and 2 to 4 area \( (25 \, \mu\text{m} \times 25 \, \mu\text{m}) \) spectra were measured and characterised against appropriate standard reference material. The variance in spot analysis was in order of magnitude higher than that of area analysis, however, both were still rather marginal (±2 wt-% vs. ±0.2 wt-%) and therefore the average wt-% are reported.

<table>
<thead>
<tr>
<th>Table 12. Composition of the Doré slag PLS obtained after leaching conducted with 30% aqua regia. (Publication IV).</th>
</tr>
</thead>
<tbody>
<tr>
<td>As ( \text{[g/L]} )</td>
</tr>
<tr>
<td>3.7</td>
</tr>
<tr>
<td>Al ( \text{[ppm]} )</td>
</tr>
<tr>
<td>508</td>
</tr>
<tr>
<td>Ag ( \text{[ppm]} )</td>
</tr>
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<td>54</td>
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<tr>
<td>Cd ( \text{[ppb]} )</td>
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<tr>
<td>390</td>
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</tbody>
</table>

### 4.2 Determination of the Electrochemical Parameters

Conventionally, tellurium is recovered by the treatment of copper anode slime with numerous different pyro- (roasting) and hydrometallurgical (leaching) unit operations [224] – [228]. Tellurium is a metalloid element [229] that is used in semiconductors [130], [131], solar panels [132], [230], [231], and in thermoelectric materials [132] – [134] as well as an alloying element in steel [132], [232]. Due to the increasing demand for electrical devices and renewable energy applications—particularly solar panels—demand for tellurium has been increasing [233], [234]. Consequently, the ability to recover even a minor amount of Te is crucial not only for technological innovation, but also potentially to provide sustainable growth.

The slag produced in the Doré process typically includes elements that are characteristic of precious metal smelting: B, Fe, Ba, Pb, Na, and Si [235], [236], Table 12. However, there are also relatively large amounts of elements that originate from anode slime (Cu and Bi), as well as other valuable elements, like Te.

Cyclic voltammetry (CV) was performed for synthetic solutions with single metals and for the PLS produced (Table 12) in order to determine the potentials for \( \text{H}_2 \) and \( \text{O}_2 \) evolution, also known as the electrochemical window. Additionally, the deposition and stripping peaks, *i.e.*, cathodic and anodic peaks, of the
elements of interest were also investigated. CV for the separate elements was carried out in 30% aqua regia at a concentration of 100 ppm, Figure 15.

Figure 15. CVs of synthetic solutions containing 100 ppm of (A) Te, (B) Ag, (C) As, (D) Fe, (E) Cu, (F) Pb, and (G) Bi in 30% aqua regia at room temperature (varying from 20 to 22 °C). The 10th cycle is presented with a scan rate of 20 mV/s. (Publication IV).
According to Figure 15A, the reduction peak of tellurium is around +150 mV and the oxidation peak at +320 mV vs. SCE. At +300 and +500 mV vs. SCE another reduction/oxidation pair is visible and at +750 mV vs. SCE, the third oxidation peak is evident; however, no clear corresponding reduction peak was observed. It is likely that the third oxidation peak relates to the change in the oxidation state of Te in the solution, as tellurium is known to have several different oxidation states (Te2-, Te-, Te+, Te2+, Te4+, Te5+, and Te6+ [237], where the most dominant ones are Te2-, Te4+ and Te6+ [238]) depending on the pH, which allow tellurium to form numerous complexes and/or compounds with other metals like Bi, Ag, and/or Cu [133], [134], [239] – [246]. Moreover, during the reverse scan direction (+1000 mV \(\rightarrow\) -200 mV vs. SCE), the reduction of Te could take place over such a wide potential range that it is not visible in Figure 15A. It is also worth noting that the standard reduction potentials for tellurium species can vary in a wide potential range: e.g. for reaction Te + 2e\(^-\) \(\rightarrow\) Te\(^2-\) it is \(E^0 = -1387\) mV vs. SCE, for 2Te + 2e\(^-\) \(\rightarrow\) Te\(^2-\) it is \(E^0 = -1084\) mV vs. SCE and for Te\(^{4+}\) + 4e\(^-\) \(\rightarrow\) Te + 6Cl\(^-\) the standard potential is \(E^0 = +306\) mV vs. SCE and for Te\(^{4+}\) + 4e\(^-\) \(\rightarrow\) Te + 4Cl\(^-\) it is \(E^0 = +501\) mV vs. SCE [247]. Based on the observations in Figure 15A and when comparing them to the standard potentials presented in the literature, the possible Te species in solution are Te\(^{4+}\) or TeCl\(^6-\).

The reduction and oxidation peaks obtained for Ag (Figure 15B) are present at -110 mV and -25 mV vs. SCE, respectively and the results are in agreement with literature on experiments conducted in chloride media [248]. Like tellurium, arsenic also has several different oxidation states (As\(^{3-}\), As\(^{5-}\), As\(^{-}\), As\(^{3+}\), As\(^{5+}\), As\(^{7+}\), As\(^{6+}\), and As\(^{8+}\) [249]) but in the measured CV, Figure 15C, a single reduction peak was observed at around -50 mV vs. SCE, whereas the oxidation peak was observed to occur at approximately +250 mV vs. SCE.

Since iron is known to have two oxidation states (Fe\(^{2+}\) and Fe\(^{3+}\)), as expected, the measured CV (Figure 15D) features two clear reduction peaks. The reduction peak at -100 mV vs. SCE represents the reaction between Fe\(^0\)/Fe\(^{2+}\) and the other reduction peak at +400 mV vs. SCE relates to Fe\(^{2+}\)/Fe\(^{3+}\), although in concentrated chloride media Fe\(^{3+}\) can be complexed as FeCl\(^{3+}\) resulting in a slightly lower reduction potential cf. the standard electrode potential [250], [251]. Cu also has two oxidation stages–mono- and divalent–and the corresponding reduction peaks for Cu\(^0\)/Cu\(^-\) and Cu\(^+\)/Cu\(^2+\) can be seen at -150 mV and +200 mV vs. SCE, respectively, Figure 15E. However, in chloride media, copper is known to form chloride complexes such as CuCl\(^+\) and CuCl\(^2-\) [252] and therefore the observed peaks most likely represent the chloride complexes rather than ions. The measured CVs for Pb and Bi (Figure 15F and G) look almost similar as both elements have a reduction peak at around -150 mV vs. SCE, although the oxidation peaks have some differences: Pb at +60 mV and Bi at +75 mV vs. SCE.

According to Figure 16, the Doré slag PLS has a multimetal composition, and several reduction and oxidation peaks are evident. Based on previous electrochemical investigations [253] – [257] and measured CVs, the parameters utilized in the subsequent electrochemical experiments with the Doré slag PLS for
Te recovery are presented in Table 13 and in Figure 16. During the electrochemical measurements (EW and EDRR), only one parameter at a time was changed, while the others were kept constant. More details about the potentials selected can be found in Publication IV.

Table 13. EDRR and EW parameters investigated for tellurium recovery from Doré slag PLS.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$ [mV vs. SCE]</td>
<td>-500, -300, -100</td>
<td>$E_1$ [mV vs. SCE]</td>
<td>-600, -500, -360, -245, +75, +150, +250</td>
</tr>
<tr>
<td>$E_2$ [mV vs. SCE]</td>
<td>-50, +50, +150</td>
<td>$t_1$ [s]</td>
<td>2, 4, 6, 8, 10</td>
</tr>
<tr>
<td>$t_2$ [s]</td>
<td>1000</td>
<td>$n$</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 16. CV of the Doré slag PLS with a scan rate of 20 mV/s; 10th cycle presented with the illustrated $E_1$, $E_2$, and EW potentials applied. The experiment was performed at room temperature (20-22 °C).

4.3 Tellurium Recovery via EW

Table 14 shows the content of electrode surface metal deposits after electrowinning (EW) was performed for 1200 s. At the optimal deposition potential (+75 mV vs. SCE), the average Te content was found to be relatively high at 55.1 wt-%, but it remained almost constant and low (at approx. 3 - 3.5 wt-%) when the deposition potentials used were below -360 mV vs. SCE, where Cu and Bi can also be deposited, Figure 16. Moreover, over the potential range from -245 mV to +75 mV vs. SCE, the level of deposited Te increased significantly, whilst the Bi and Cu contents decreased. At potentials above +75 mV vs. SCE, the content of Te was also found to decrease since the potentials above are not thermodynamically suitable for tellurium deposition. Therefore +75 mV vs. SCE was
defined as the optimal potential for EW, regardless of minor co-deposition by other elements. Similar co-deposition behaviour with other metals has also been reported previously for other EW processes [258] – [261].

Table 14. Quantitative SEM-EDS analysis of the metal deposits on the surface of the working electrode after EW experiments performed at various potentials at room temperature (20-22 °C). (Publication IV).

<table>
<thead>
<tr>
<th>$E$ [mV vs. SCE]</th>
<th>Te [wt-%]</th>
<th>Bi [wt-%]</th>
<th>Cu [wt-%]</th>
<th>Ag [wt-%]</th>
<th>As [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-600</td>
<td>3.5</td>
<td>44.0</td>
<td>34.3</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>-500</td>
<td>3.3</td>
<td>35.8</td>
<td>39.1</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>-360</td>
<td>2.6</td>
<td>32.8</td>
<td>48.7</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>-245</td>
<td>12.8</td>
<td>59.3</td>
<td>14.5</td>
<td>1.9</td>
<td>0.5</td>
</tr>
<tr>
<td>+75</td>
<td>55.1</td>
<td>17.4</td>
<td>1.6</td>
<td>1.9</td>
<td>2.9</td>
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<tr>
<td>+150</td>
<td>4.3</td>
<td>18.1</td>
<td>0.0</td>
<td>32.2</td>
<td>0.5</td>
</tr>
<tr>
<td>+250</td>
<td>0.4</td>
<td>42.2</td>
<td>0.0</td>
<td>10.4</td>
<td>3.7</td>
</tr>
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</table>

The morphology of the deposits on the electrode was also investigated by SEM and the micrographs obtained are shown in Figure 17. The electrode surfaces shown in Figure 17A and B are from the same electrode area and the only difference is that A is a SEM-BSE (backscattered electron) micrograph, whereas B is a SEM-SE (secondary electron) micrograph. However, the applied EW time was only 200 s, therefore the detected tellurium content of the deposits was only 8 wt-%. Te could be easily detected with the BSE set-up; however, the SE detector revealed that deposit thicknesses varied between a few hundreds of nm to slightly less than μm. In addition, SE also revealed the presence of Ag/AgCl crystals (determined by SEM-EDS), which can potentially act as nucleation points for tellurium deposition since electrochemical deposition can initiate on the surface inhomogeneities of a working electrode [31], [32], [262]. Figure 17C shows the morphology of the surface after a longer deposition time, 72 h at +75 mV vs. SCE, during which a dendritic type deposit was formed. Similar dendritic growth for tellurium has been observed previously, especially at high overpotentials [263] – [265]. As can be seen, the deposit on the electrode was rather thick—ranging from several μm to tens of μm—after 72h of EW and the SEM-EDS revealed that the tellurium content of the deposit was ~57 wt-%. Nevertheless, with such a long EW, Ag (29 wt-%) and Cu (6 wt-%) were also enriched within the deposit, whereas the content of Bi was fairly low, at only ~1.3 wt-%.

Figure 17. (A) BSE micrograph and (B) SE micrograph of the surface metal deposits of the working electrode from the same area, after EW experiments. (C) SE micrograph showing the surface morphology after prolonged (72 h) EW. (Publication IV).
4.4 Tellurium Recovery via EDRR

Figure 18A presents the metal contents measured on the electrode surface by SEM-EDS following EDRR experimentation. As can be observed, the shortest deposition time of $t_1 = 2$ s provided the highest concentration tellurium deposit, whilst a doubling of the deposition time up to $4$ s resulted in the lowest level of Te. Moreover, according to the SEM-EDS, with the shortest deposition time, tellurium was also distributed more evenly across the working electrode surface.

Figure 18B-D presents the measured metal content of the deposits on the surface of the electrode used. As can be seen in Figure 18B, for the highest anodic potential applied ($E_1 = -100$ mV vs. SCE), the Te content on the electrode is rather modest, with a maximum value equal to approximately 40 wt-%. The reason for this observation could be that at $E_1 = -100$ mV vs. SCE the amount of sacrificial elements (most likely Cu and Bi, Table 14) deposited is rather limited and therefore, the replacement between Te and the sacrificial element(s) is not as efficient as it could be. When more cathodic deposition potentials were applied (Figure 18C and D) the tellurium content increased, which further suggests that the deposition potential required to achieve a suitable amount of sacrificial elements and thus, reducing elements, is more negative than that of tellurium reduction, i.e., $+150$ mV vs. SCE, Figure 15A. Moreover, whereas $+75$ mV vs. SCE was found to be the optimal tellurium deposition potential when applying constant potential to the system, i.e., electrowinning, this was not the case with EDRR. As shown in Figure 18B to D, the highest tellurium recovery was achieved with $E_2 = +150$ mV vs. SCE, whereas $E_2 = +75$ mV vs. SCE provided only a relatively low efficiency for Te recovery, Table 15.

<table>
<thead>
<tr>
<th>$E_2$ [mV vs. SCE]</th>
<th>Te [wt-%]</th>
<th>Bi [wt-%]</th>
<th>Cu [wt-%]</th>
<th>Ag [wt-%]</th>
<th>As [wt-%]</th>
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</thead>
<tbody>
<tr>
<td>+75</td>
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<td>5.92</td>
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<tr>
<td>+150</td>
<td>63.77</td>
<td>20.62</td>
<td>1.89</td>
<td>8.67</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 15. Quantitative SEM-EDS results from the metal deposits on the electrode surface after EDRR experiments conducted with deposition potential $E_1 = -500$ mV vs. SCE, $t_1 = 2$ s, and $n = 100$ at room temperature (20-22 °C). The base material (Pt electrode) is excluded from the results. (Publication IV).

It is suggested that the cut-off potential of $E_2 = +75$ mV vs. SCE was not sufficient to allow the tellurium to replace the sacrificial elements on the surface of the electrode. At the too anodic cut-off potential of $E_2 = +350$ mV vs. SCE, the lowest purity of any metal on the deposits was detected due to corrosion of the deposited elements. Quantitative SEM-EDS analysis showed that the tellurium purity of the deposits on the electrode surface was only ~42 wt-% with a cut-off potential $+75$ mV vs. SCE, whereas with the same parameters and an $E_2 = +150$ mV vs. SCE, the purity of Te achieved was ~64 wt-%. According to Figure 18, the optimum deposition time in EDRR was $2$ s and the deposition potential - $500$ mV vs. SCE, even if $H_2$ evolution cannot be avoided at this potential, Figure 16. However, with such a short deposition time ($t_1 = 2$ s), $H_2$ evolution was not observed to be dominant or result in high energy losses when compared to the level of tellurium recovery.
Figure 18. Quantitative SEM-EDS results of the electrode surface metal deposits as a function of (A) deposition time and as a function of cut-off potentials when varying the deposition potential (B) \( E_1 = -100 \text{ mV} \) vs. SCE, (C) \( E_1 = -300 \text{ mV} \), and (D) \( E_1 = -500 \text{ mV} \) vs. SCE. All experiments were conducted at room temperature (20-22 °C).

From Figure 18 it can also be determined that both bismuth and silver display a similar behavior to that of tellurium. Based on the literature, tellurium has the capability to form several different, stable complexes and compounds with many of the elements present in the Doré slag PLS [239] – [246]. This may partly explain why the content of other elements within the deposits increases when the Te content increases. Furthermore, this alloying ability of tellurium could enhance its recovery since the alloying element could potentially be replaced by another tellurium atom due to the order of nobility for the elements present in the PLS [266]. The tellurium detected by SEM-EDS in the deposits is most likely a combination between pure tellurium and the telluride complexes formed, e.g., between silver [267] and bismuth [268]. The ratio between Ag and Te within the electrode deposits follows the same pattern as in the PLS; however, it is also clear that Bi exhibits different behavior. This difference is potentially explained by the lower nobility of Bi, as bismuth is probably replaced by both metallic Te and Ag together to form a combined deposit of both, such as \( \text{Ag}_2\text{Te} \), for example.

Deposits obtained after EDRR were shown to be porous, Figure 19. In EW, the elements were distributed across the whole electrode area, whereas in EDRR silver and copper were enriched in separate areas from tellurium. The elevated and bright, dendritic structures are composed mostly of Te (~64 wt-%), whereas the flat surface underneath is the Pt electrode. Figure 19A shows an SEM-SE micrograph with a magnification of 1k, whereas Figure 19B is the same area at higher magnification, 7k. Especially at the higher magnification (Figure 19B),
the formed porous dendritic structure of the deposits can be seen. This finding is similar to those observed in previous studies where sulfuric [269] and hydrochloric [270] acids have been utilized. In addition, as during the ED step, high overpotential is applied. This is known to create such dendritic structures, particularly with Cu in chloride solutions [271] – [275], which is considered to be one of main sacrificial elements together with Bi.

The differences between the deposition behaviors when applying a constant potential to the system (EW) or cycling between applied potential and open circuit conditions (EDRR) could be explained that during EW, much higher anodic deposition potential (+75 mV vs. SCE) was applied than that of EDRR (-500 mV vs. SCE) and by applying different potentials, different elements are deposited, the deposition rate is altered and also different competing (unwanted) reactions like H₂ evolution can take place. In addition, in EDRR the deposition takes place in cycles while EW has a constant potential throughout the whole experiment. All these factors influence the deposition behaviour. With lower cathodic potential (-500 mV vs. SCE), the local current density is higher in areas of local inhomogeneity, leading to situation where the different metals are enriched on different areas of the surface. During EW, the more anodic potential (+75 mV vs. SCE) will result in relatively lower local current density in similar inhomogeneous areas, consequently the elements are more evenly distributed around the immersed electrode surface. Moreover, there is a possibility for selective dissolution also during the RR step, which can change the surface composition even further.

![Figure 19](image.png)

Figure 19. Morphology of the tellurium deposits at (A) magnification of 1 kx and (B) 7 kx on the electrode surface after the EDRR experiments. EDRR parameters applied were \( E_1 = -500 \text{ mV} \) and \( E_2 = +150 \text{ mV} \) vs. SCE, \( t_1 = 2 \text{ s} \), \( t_2 = 1000 \text{ s} \) and \( n = 100 \). (Publication IV).

### 4.5 Tellurium Recovery via Combined EW-EDRR Route

Since both EW and EDRR are capable of recovering tellurium from Doré slag PLS and EW is fundamentally operated at higher concentrations (20-350 g/L [255], [266], [277]) than EDRR, the threshold value for combined EW-EDRR operation was studied. A comprehensive investigation was performed with a Te concentration range from 400 to 1 ppm in 30% aqua regia. Figure 20 shows the Te content detected within surface deposits as a logarithmic function
of the Te content in the solution. Although the potential applied during EW was +75 mV vs. SCE and the duration only 200 s, nevertheless, a remarkable amount of Te was deposited with a 400 ppm Te solution. When the content was decreased to 300 ppm or less, the decrease in tellurium recovery was found to be an order of magnitude lower. At the point where Te ≤300 ppm, the energy efficiency vs. recovered amount of tellurium was found to be too high, and therefore 300 ppm was determined as the optimal threshold level where EW needs to be substituted with EDRR.

![Figure 20. Tellurium content of the metal deposits obtained on the electrode surface after EW experiments conducted at room temperature (20-22 °C) as a function of tellurium solution concentration. (Publication IV).](image)

After optimization of both electrochemical techniques separately, a combined electrochemical recovery route was demonstrated. The total processing time was increased up to 192 h to guarantee that almost all of the tellurium was recovered from the Doré slag PLS. The 192 h duration was divided into two equal parts: during the initial 96 h, Te was recovered by EW at the optimal potential (+75 mV vs. SCE) and, after that, EDRR with the optimized parameters ($E_1 = -500$ mV, $E_2 = +150$ mV vs. SCE and $t = 2$ s) was used. The results are shown in Table 16 and a suggested process flowsheet for tellurium recovery is outlined in Figure 21. Three different samples were produced, all in the same solution. One sample (called EW in Table 16) experienced only 96 h EW treatment from a fresh solution after which it was removed from the solution. A clean Pt sample was inserted to the cell but the solution was kept the same, i.e. some Te was already recovered from the solution by the EW step; in this stage 96 h EDRR treatment was performed resulting in the second sample in Table 16, namely EDRR. The third sample was removed (called EW+EDRR in Table 16) only after the whole 192 h measurement was finished, i.e. it experienced first 96 h EW treatment followed by 96 h EDRR treatment in the same solution.

As can be seen, the tellurium content of the surface deposits on the working electrode is relatively high (>60 wt-%) after conducting EW at +75 mV vs. SCE for 96 h. However, similar studies of long duration EW for tellurium recovery have achieved significantly higher levels of Te [254], [278]. In contrast, the tellurium content of the metal deposits after the EDRR segment is somewhat lower than previously presented for EDRR alone in Figure 18. Nevertheless, it needs
to be kept in mind that the starting solution for EDRR optimization was the original Doré slag PLS, whereas in this combined EW-EDRR investigation, the PLS content of tellurium was much lower due to the previous 96h of EW treatment.

Figure 21. Suggested procedure for tellurium recovery from Doré slag via mineral acid leaching with combined electrochemical recovery.

Table 16. Quantitative SEM-EDS results from the electrode surface metal deposits for three different experiments performed at room temperature (20-22 °C): Stage 1: EW, Stage 2: EDRR, and combined EW-EDRR. (Publication IV).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Te [wt-%]</th>
<th>Bi [wt-%]</th>
<th>Cu [wt-%]</th>
<th>Ag [wt-%]</th>
<th>As [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1: EW</td>
<td>61.51</td>
<td>0.79</td>
<td>10.37</td>
<td>26.98</td>
<td>0.34</td>
</tr>
<tr>
<td>Stage 2: EDRR</td>
<td>17.23</td>
<td>2.58</td>
<td>7.33</td>
<td>24.42</td>
<td>48.43</td>
</tr>
<tr>
<td>Combined: EW + EDRR</td>
<td>37.60</td>
<td>3.77</td>
<td>15.96</td>
<td>20.06</td>
<td>22.61</td>
</tr>
</tbody>
</table>

This study suggests that EDRR is a rather powerful technique for the recovery of elements from low concentration solutions, but that it also has its own drawbacks. The advantage is that the ED phase can be performed in a controlled manner and the subsequent RR phase does not require any externally applied current or voltage as the driving force for the reactions comes from the spontaneous oxidation/reduction that occurs between more and less noble elements. The results demonstrate that EDRR is more effective at lower concentrations than conventional EW; however, the overall energy efficiency of EDRR is reduced by capacitive double layer charging. This phenomenon occurs at the beginning of each ED cycle and therefore—depending on the number of EDRR cycles performed—is repeated hundreds or even thousands of times [279], [280], whereas during EW the capacitive double layer is charged only once.

In addition, the low concentrations of metals applied for EDRR recovery may hinder the mass transfer, requiring more time and/or solution flow to come into contact with the reductive surface, a fact that is further augmented by the porous nature of the deposits. On the other hand, the sacrificial elements are most likely not controlled by the mass transfer (due to much higher concentration) but more with the charge transfer. Therefore, in a non-stirred system, the suitable ions close to the electrode surface are consumed faster than the ones, which are further away. This leads to a situation where the local concentration
of suitable metal ions decreases such that the process is no longer effective, and more time is required to obtain full redox replacement cycle before the next one could be started. However, an increase in the electrolyte flow rate, via stirring for example, could lead to the removal of the porous deposits formed, as the level of adhesion of the deposited tellurium to the electrode surface material (Pt) is also relatively low. Consequently, the optimization of solution movement will require further detailed investigations. Another potential challenge is corrosion, which increases energy consumption as the sacrificial metal is dissolved back into the solution without recovery. On the other hand, corrosion can also be beneficial to the system if controlled (by controlling the RR time) as it simultaneously improves the product quality by selectively dissolving the sacrificial element(s). Also, the lixiviant used for Doré slag leaching as such was highly aggressive (30% aqua regia) and this can pose challenges in solution and waste stream management. To obtain improved understanding of the suggested Te recovery, further development of the recovery of other metals and solution purification is a necessity, as well as process-based simulation, revealing the holistic mass- and energy balance, and the consequent environmental impacts [281].

"Boundaries of wisdom - that is what we call madness"

In hydrometallurgical industries, there is a significant amount of valuable and critical elements that pass through different plants via the main process streams [123]. Currently, there are no feasible methods for recovery of all minor metals, and consequently part of these metals that are present in trace concentrations are either lost as waste or end up as impurities in the end products. Therefore, EDRR was investigated as a method for the recovery of platinum and other noble metals from hydrometallurgical type process solutions.

5.1 Experimental

Valuable metals recovery from two sulfate-based systems were investigated electrochemically, based on the EDRR method: the zinc sulfate system with Ag and the nickel sulfate system with Pt, Pd, and Ag. As stated earlier, the next EDRR cycle commenced when either one of the cut-off potential ($E_2$) or cut-off time ($t_2$) was reached.

5.1.1 Zinc Sulfate System with Ag

A typical electrochemical cell comprised of a three-electrode cell, with platinum (Kultakeskus, Finland) as both working electrode (WE, $A_w = 0.4 \text{ cm}^2$) and counter electrode (CE, $A_c = 24 \text{ cm}^2$) and a saturated calomel electrode (SCE, B512, SI Analytics, Germany), was used as the reference electrode (RE). The silver recovery (Publication V) was conducted from synthetic zinc solutions where a Zn content of 60 g/L (from ZnSO$_4$·7H$_2$O, Sigma-Aldrich, USA) was dissolved in 10 g/L of H$_2$SO$_4$ (VWR Chemicals, Belgium) solution. The Ag (from AgNO$_3$, Sigma-Aldrich, USA) content was varied between 1 ppb and 250 ppm. All the chemicals utilized were of technical grade and the solutions were made with distilled water. A potentiostat (24-bit IviumStat CompactStat, Ivium, the Netherlands) was used to carry out the electrochemical measurements and a SEM-EDS (scanning electron microscope, LEO 1450 VP, Carl Zeiss, Germany – energy dispersion spectroscopy, 50 mm$^2$ Thermo Scientific detector, USA, combined with INCA-software, Oxford Instruments, UK) was used to analyze the metal deposits formed.
Prior to the EDRR Ag recovery experiments, a CV with a scan rate of 30 mV/s (10 sweeps starting from 0 mV → +1000 mV → -1000 mV → 0 mV) was carried out in a solution containing 60 g/L Zn, 10 g/L H₂SO₄, and 100 ppm Ag, Figure 22.

![Figure 22. CV (10th cycle presented) of a 60 g/L Zn, 10 g/L H₂SO₄ and 100 ppm Ag solution, measured with a scan rate of 20 mV/s at room temperature (20-22 °C). (Modified from Publication V).](image)

The cathodic Ag deposition peak occurred at +300 mV vs. SCE and the corresponding anodic stripping peak around +450 mV vs. SCE. The following peak was evident around -750 mV vs. SCE when going in the cathodic direction during the CV. According to Nernst Equation (29), the reduction potential of Zn (with 60 g/L) is around -1005 mV vs. SCE and its deposition should be thermodynamically favored only at that and more cathodic potentials. However, zinc is known to undergo UPD (underpotential deposition) on platinum [282] (the electrode material) in chloride [283], [284], phosphate [285], [286], and sulfate [282], [287] media and even on silver in a sulfate medium [288]. Moreover, even the EW performed at -700 mV vs. SCE for 1 h in zinc sulfate media resulted in remarkably high zinc enrichment, ~90 wt-% (the rest was O and S), shown in the dark areas in Figure 23. Also, H₂ evolution is thermodynamically favored in this potential region. Therefore, it is suggested that the cathodic peak around -750 mV vs. SCE overlaps with Zn UPD and H₂ evolution.

\[
E = E^0 - \frac{RT}{zF} \ln K
\]  

(29),

where \(E^0\) is the standard electrode potential (mV), \(R\) is the universal gas constant (8.314 J / K · mol), \(T\) is the absolute temperature (K), \(z\) is the number of electrons (with a negative charge) transferred in the half reaction, \(F\) is the Faraday constant (96485 C / mol), and \(K\) is the reaction quotient (simplified calculation with concentrations, not taking activities into account).
Consequently, in the subsequent EDRR investigations the deposition potentials ($E_1$) studied were from -650 mV to -750 mV vs. SCE. Table 17 summarizes all the parameters studied for silver recovery from zinc sulfate solutions.

Table 17. Parameters investigated for silver recovery from zinc sulfate solutions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$ [mV vs. SCE]</td>
<td>-650, -700, -750</td>
</tr>
<tr>
<td>$E_2$ [mV vs. SCE]</td>
<td>+250, +300, +350</td>
</tr>
<tr>
<td>$n$</td>
<td>10, 25, 50, 100, 160</td>
</tr>
<tr>
<td>$t_1$ [s]</td>
<td>2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60</td>
</tr>
<tr>
<td>$t_2$ [s]</td>
<td>1000</td>
</tr>
<tr>
<td>Ag content in the solution [ppm]</td>
<td>0.001, 0.05, 0.5, 1, 2, 5, 10, 100, 250</td>
</tr>
</tbody>
</table>

The first evaluation of Ag recovery was conducted based on the analysis of the silver stripping curve, i.e., the size of the anodic stripping peak when starting the CV (3 sweeps) just after Ag deposition but before its stripping, i.e., from +300 mV vs. SCE with a scan rate of 20 mV/s, up to potential of +1000 mV and back to -1000 mV vs. SCE, although only the area of interest, e.g., silver stripping is presented. Moreover, by applying Faraday’s law of electrolysis—Equation (30)—the mass of stripped Ag was determined.

$$m = \frac{QM}{zF} = \frac{IM}{zF} \cdot \frac{\int I(t)dt \cdot M}{zF}$$  \hspace{1cm} (30),

where $m$ is the mass of the deposited metal (g), $Q$ is the electric charge (C), $M$ is the molar mass of the certain element (g/mol), $F$ is the Faraday constant (96,485 C/mol), $z$ is the number of electrons (with a negative charge) transferred in the half reaction, $I$ is the current applied (A), and $t$ is the total time that current is applied (s). The peak area (between 350 mV – 600 mV vs. SCE) was integrated and multiplied by the time spent during the peak by taking into account the scan rate applied, 20 mV/s. The electric charge during the ED phase was calculated similarly by integrating the current applied during the ED steps.
separately. Moreover, for simplified calculation, it was assumed that only silver was stripped off of the electrode and all deposited zinc was either subjected to redox replacement with silver or dissolved (corroded) back to solution during the RR step.

5.1.2 Nickel Sulfate System with Pt

The electrochemical setup used for platinum recovery (Publication VI) was similar to that described above for silver recovery, with the exception that the counter electrode (CE) was comprised of a 25 mm x 25 mm x 3 mm type 1 glassy carbon plate (Alfa Aesar, Germany) and the working electrode (WE) was PyC (pyrolyzed carbon) prepared on top of a 100 mm <100> silicon wafer (Siegert Wafer, Germany) [289]. The cleaned wafers were spin coated with SU-8 50 (negative photoresist, MicroChem) using a BLE spinner (Georgia Tech, USA for 45 s at 9000 RPM) before being pyrolyzed in a furnace at 900 °C for 60 min in a nitrogen atmosphere (Nabertherm RS 170/1000/13, Germany). The advantage of pyrolyzed electrodes is that, as a result of the pyrolysis process, a 3D structure is obtained, which provides a specific surface area of an order of magnitude higher cf. to, for example, a glassy carbon with similar outer dimensions.

All the chemicals used (Pt in 20% HCl and Ag in 5% HNO₃ AAS standards, Alfa Aesar, Germany and sulfuric acid, VWR Chemicals, Belgium) in the investigations of Pt recovery from Ni sulfate solutions were of high purity grade with the exception of nickel sulfate (Alfa Aesar, Germany), which was of technical grade. All the solutions were prepared using distilled water. Prior to Pt recovery from industrial Ni EW solutions (Table 4), a synthetic and more simplified version of these real process solutions was made with a nickel content of 60 g/L and with ~1 ppm Cu (due to NiSO₄·6H₂O technical grade impurities), 10 ppm Ag, 20 ppm Pt, and 10 g/L H₂SO₄. In addition to the SEM-EDS analysis (performed with LEO), a Mira³ Tescan GM (Czech Republic) was also used for higher magnification imaging. ICP-OES (Iris intrepid, Thermo Fisher Scientific, USA) and ICP-HR-MS (high resolution mass spectroscopy, Nu AttoM, Nu Instruments™ Ltd, UK) were utilized for the solution analysis. The difference between solutions #1 and #2—presented in Table 4—is that solution #2 is a purified version of solution #1 via an industrial precipitation process [290].

Prior to the EDRR platinum recovery experiments, a cyclic voltammetry in a synthetic solution of 60 g/L Ni, 10 ppm Ag, 20 ppm Pt and 10 g/L H₂SO₄ was conducted, Figure 24 (10 sweeps starting from 0 mV → 1100 mV → -250 mV → 0 mV). Due to the slightly lower purity of the nickel sulfate used, a minor amount of Cu (~1 ppm) was also present as an impurity within the solution. Nevertheless, as shown in Table 4 (Chapter 2), copper is present in relatively high concentration in solution #1 and therefore, its presence in the synthetic solution is also justified. Although the concentration of nickel in synthetic solution was slightly less than half that of a real process solution and the levels of Ag and Pt were of an order of magnitude higher, the composition of nickel process solutions is known to vary drastically [139], [291] – [293]. Moreover, from the parameter optimization point of view, smaller concentration differences between the sacrificial and recovered elements are essential in order to be able to detect the relevant reduction/oxidation peaks in the CV, which allows the correct potential ranges for E₁ and E₂ to be more easily determined.
The oxidation and reduction peaks of Cu, Ag, and Pt are shown in Figure 24, along with the areas of O₂ and H₂ evolution. The observed increase in current density as the number of cycles was increased can be explained by the PyC electrode geometry. PyC electrodes are porous in nature, and as a result, contain small pores in which gas (mainly air) can be trapped inside, thus it takes time before it is released. Consequently, when the gas is released from these pores, the surface area exposed to the solution increases, resulting in a change to the overall surface area with time. Furthermore, during the CV experiment, Pt and Ag are deposited on the surface and may have a catalyzing effect on H₂ evolution and metal deposition that increases the current density obtained.

The characteristic peaks related to Ni ($E^o = -494$ mV vs. SCE) are obscured by the H₂ evolution in Figure 24 and therefore, Figure 25 presents the cathodic (Figure 25A) and anodic (Figure 25B) peaks separately, i.e., the reduction and oxidation peaks of Ni, with the competing H₂ evolution reaction. The CV curves presented in Figure 25 were obtained after a separate CV experiment conducted on the same solution at a potential range of 0 mV → -1000 mV → 0 mV (scan rate of 20 mV/s) in order to avoid any precious metal deposition from disturbing the Ni anodic and cathodic peak formation.

![Figure 24. Cyclic voltammograms obtained when employing a PyC electrode with a scan rate of 20 mV/s of a solution with 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm Cu, and 10 g/L H₂SO₄ at room temperature (20-22 °C). (Publication VI).](image)
Figure 25. (A) Ni reduction and (B) oxidation peaks obtained by employing a PyC electrode in the competing H₂ evolution area in a solution containing 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm Cu, and 10 g/L H₂SO₄ at room temperature (20-22 °C). (Publication VI).

The EDRR parameters selected based on Figure 24 and Figure 25 are presented in Table 18. Moreover, as the measured OCP of the system under study was approximately +370 mV vs. SCE, a cut-off potential of \( E_2 = +350 \) mV vs. SCE was chosen. This is also lower than the Ag oxidation peak, Figure 24.

Table 18. Parameters investigated for platinum recovery from nickel sulfate solutions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_1 ) [mV vs. SCE]</td>
<td>-175, -500, -750</td>
</tr>
<tr>
<td>( E_2 ) [mV vs. SCE]</td>
<td>+350</td>
</tr>
<tr>
<td>( n )</td>
<td>10, 100, 200, 400</td>
</tr>
<tr>
<td>( t_1 ) [s]</td>
<td>2, 5, 10</td>
</tr>
<tr>
<td>( t_2 ) [s]</td>
<td>1000</td>
</tr>
<tr>
<td>Pt content in the solution [ppm]</td>
<td>20</td>
</tr>
<tr>
<td>Ag content in the solution [ppm]</td>
<td>10</td>
</tr>
<tr>
<td>Ni content in the solution [g/L]</td>
<td>60</td>
</tr>
</tbody>
</table>

5.2 Silver Recovery from Zinc-containing Solutions

Although silver is not typically found in Zn electrowinning solutions, as it is typically recovered by other process routes [294] – [296], minute amounts may end up in the electrolyte. Furthermore, in future the hydrometallurgical solutions resulting from recycled raw materials such as silver button batteries [297] – [299] or jarosite treatment [300], [301] could increase the silver content in aqueous zinc sulfate solutions. Moreover, the sulfuric acid content employed in the Thesis (10 g/L) was smaller than the industrial Zn EW contents [302], and consequently the solution composition was representing more of the zinc sulfate solutions, where the required acid concentration is not necessarily high, rather than Zn EW solutions. Furthermore, none of the current methods are known to be able to recover silver in very low concentrations (<1 ppm, or even <1 ppb) from concentrated base metal solutions, and therefore the current Thesis investigated the possibility for electrochemical Ag recovery.

It is evident that the EDRR method used could enrich Ag on the electrode surface (Publication V). However, the redox replacement mechanism in zinc sulfate solution for silver is not completely understood and it may be that the
interpretation in Publication V of the redox replacement mechanism between Zn and Ag is oversimplified. Therefore, this chapter attempts to discuss the possible reaction routes in more detail cf. Publication V.

During the ED phase ($E_i = -650$, -700 or -750 mV vs. SCE), Zn deposition is suggested to overlap with H$_2$ evolution. Furthermore, it should be noted that during every ED step silver can also deposit directly at potentials below +350 mV vs. SCE. The deposition potential of -650 mV vs. SCE was shown to result in the lowest Ag stripping peak compared to the other two potentials ($E_i = -750$ mV or -700 mV vs. SCE), Figure 26A. SEM-EDS analysis (Table 19) of the metal deposits showed the highest Ag/Zn ratio at -700 mV vs. SCE. Table 19 also presents the calculated electrical charge efficiency ($\eta$) where the electrical charge consumed during the ED phase is compared to that obtained during silver stripping. This analysis suggests that most of the current applied in the ED phase is not consumed on depositing zinc (the sacrificial element) and co-depositing silver, but predominantly on non-effective phenomena such as excess H$_2$ evolution. This also suggests that the large cathodic peak shown in Figure 22 is largely due to H$_2$ evolution, starting already at around -200 mV vs. SCE (Figure 22). Also, charging of the double capacitive layer at the beginning of each ED cycle consumes energy, which is also considered to be lost, hence decreasing the efficiency. However, the amount of stripped silver was similar to $E_i = -700$ and -750 mV vs. SCE, and the electrical charge efficiency ($\eta$) was the lowest at -750 mV vs. SCE, due to the higher proportion of energy lost to excess H$_2$ evolution.

The ED phase is followed by the RR phase, where any zinc reduced on the electrode surface is subject to redox replacement by silver but may also undergo acidic dissolution (corrosion) via H$_2$ formation [303]. Any H$_2$ formation on the surface (either during the electrodeposition step or formed via Zn dissolution) may also potentially provide reductive power for further silver deposition, increasing the silver concentration on the surface. However, with excess formation, the majority of the reductive power of H$_2$ is lost. It can be suggested that an increase in the RR potential and therefore also the RR time (+250 $\rightarrow$ 300 mV) provides more time for Ag reduction, and therefore a larger stripping peak (Figure 26A). However, a further increase (+300 mV $\rightarrow$ +350 mV) approaches the Ag stripping region, already dissolving some of the silver that was deposited spontaneously. Moreover, assuming that the cathodic peak at -750 mV vs. SCE in Figure 22 is in the H$_2$ evolution area, it is still a species known to provide strong reductive power in a hydrometallurgical solution [67] and as such the reductive power is not necessarily lost if no excess H$_2$ is reduced.
Figure 26. Current densities measured at a sweep rate of 20 mV/s when (A) the deposition potential $E_1$ was varied ($E_2 = +300$ mV vs. SCE) and (B) the cut-off potential $E_2$ was varied ($E_1 = -700$ mV vs. SCE). N.B. The added base line (black dotted line) shows a reference at the silver stripping potential when no EDRR was performed. All experiments were conducted at room temperature (20-22 °C).

Table 19. Quantitative SEM-EDS analysis of the surface metal deposits on the Pt working electrode after EDRR experiments conducted in a solution containing 60 g/L Zn, 10 g/L H$_2$SO$_4$ and 100 ppm Ag (Publication V) with the calculated amount of deposited silver and the calculated efficiency. The constant EDRR parameters were $t_1 = 10$ s, $t_2 = 1000$ s and $n = 10$.

<table>
<thead>
<tr>
<th>Potentials (vs. SCE)</th>
<th>Zn [wt-%]</th>
<th>Ag [wt-%]</th>
<th>Ag/Zn</th>
<th>Ag [mg]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_1 ) optimization</td>
<td>$E_1 \rightarrow E_2$</td>
<td>0.17</td>
<td>16.34</td>
<td>97.7</td>
<td>0.012</td>
</tr>
<tr>
<td>-0.65 V $\rightarrow$ +0.30 V</td>
<td></td>
<td>0.08</td>
<td>14.30</td>
<td>191</td>
<td>0.019</td>
</tr>
<tr>
<td>-0.70 V $\rightarrow$ +0.30 V</td>
<td>3.97</td>
<td>26</td>
<td>6.6</td>
<td>0.019</td>
<td>1.71</td>
</tr>
<tr>
<td>( E_2 ) optimization</td>
<td>$E_1 \rightarrow E_2$</td>
<td>0.19</td>
<td>10.27</td>
<td>53.8</td>
<td>0</td>
</tr>
<tr>
<td>-0.70 V $\rightarrow$ +0.25 V</td>
<td></td>
<td>0.08</td>
<td>14.30</td>
<td>191</td>
<td>0.019</td>
</tr>
<tr>
<td>-0.70 V $\rightarrow$ +0.30 V</td>
<td>44.2</td>
<td>5.5</td>
<td>0.1</td>
<td>0.008</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Optimization of the deposition time was conducted over a range of 2-60 s, Figure 27 ($E_1 = -700$ mV and $E_2 = +300$ mV vs. SCE). The highest current density for silver stripping was obtained with a deposition time of $t_1 = 45$ s. Subsequently, measurements with SEM-EDS confirmed that the same deposition time gave the highest Ag content, 26 wt-%, on the electrode surface, and the level of the remaining zinc was 0.26 wt-%. This resulted in an Ag/Zn ratio of 100, which is almost half of that obtained with $t_1 = 10$ s, Table 19. Nevertheless, although longer deposition times provided higher Ag content metal deposits, in terms of selectivity, a deposition time of 10 s was chosen as the optimal value for further investigation. In addition, H$_2$ evolution was also found to increase due to prolonged ED times.
Figure 27. Measured current densities with a sweep rate of 20 mV/s at silver stripping potential where the deposition time $t_1$ was varied. The constant EDRR parameters were $E_1 = -700$ mV and $E_2 = +300$ mV vs. SCE, $t_2 = 1000$ s and $n = 10$ at room temperature (20-22 °C). (Modified from Publication V).

Table 20 presents the calculated amounts of silver with the corresponding electric charge efficiency, and as it can be seen, the amount of deposited silver increased when the deposition time ($t_1$) was increased. However, the electric charge efficiency was highest with $t_1 = 10$ s. With longer deposition times, more silver is co-deposited on the electrode but at the same time, more energy is consumed for $H_2$ evolution. This also leads to the situation, where the local concentration of silver is decreased, resulting to longer RR times. In addition, with shorter deposition times, the efficiency was not equally high, potentially because charging the capacitive double layer consumed part of the electricity feed at shorter deposition times. However, with a longer time it seems that the efficiency also decreases since silver nanoparticles are known to promote the HER (hydrogen evolution reaction) [304], [305] similarly to Pt [306]. Moreover, the charging of the double capacitive layer is shown in Figure 28, where a significantly higher current density is observed at the beginning of each ED step than that observed during the rest of the ED step. Even though the energy lost in double layer charging is negligible in EW, it must be taken into account in EDRR as it takes place in the beginning of each ED step. This is true especially in shorter ED times as the number of cycles increases. Furthermore, also during the RR step, no external current is applied to the system.

<table>
<thead>
<tr>
<th>$t_1$ [s]</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag [\mu g]}$</td>
<td>1.9</td>
<td>1.8</td>
<td>1.0</td>
<td>8.5</td>
<td>22.3</td>
<td>15.8</td>
<td>18.9</td>
<td>23.5</td>
</tr>
<tr>
<td>$\eta [%]$</td>
<td>2.05</td>
<td>1.18</td>
<td>0.44</td>
<td>2.66</td>
<td>6.75</td>
<td>2.61</td>
<td>2.36</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Table 20. Calculated amounts of deposited silver and efficiency.
Figure 28. Absolute value of the current density during EDRR procedure. The EDRR parameters applied at room temperature (20-22 °C) were $E_1 = -700 \text{ mV}$ and $E_2 = +300 \text{ mV}$ vs. SCE, $t_1 = 35 \text{ s}$ and $t_2 = 1000 \text{ s}$, and $n = 10$. The next EDRR cycle was started whenever the $E_2$ or $t_2$ was reached.

The range of cycles ($n$) investigated was varied between 10 and 160, as shown in Table 17 and Figure 29. A threshold value of $n = 160$ was selected, Figure 29, as after 160 cycles, the local concentration of Ag ions proximal to the Pt electrode was so low that it was insufficient for continued experimentation. This finding indicated that without stirring and constant solution refreshment, the Ag ions were consumed. It can be concluded that, when increasing the amount of cycles the content of silver increased, whereas the related content of zinc was reduced, Table 21.

Figure 29. Demonstration of the threshold value for EDRR cycles ($n$). The experiment was conducted at room temperature (20-22 °C). (Modified from Publication V).
Table 21. Quantitative SEM-EDS results of the electrode surface metal deposits after varying the amount of EDRR cycles at room temperature (20-22 °C). (Publication V).

<table>
<thead>
<tr>
<th>Amount of cycles [n]</th>
<th>Zn [wt-%]</th>
<th>Ag [wt-%]</th>
<th>Ag/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.08</td>
<td>14.30</td>
<td>190</td>
</tr>
<tr>
<td>25</td>
<td>2.69</td>
<td>21.43</td>
<td>8.0</td>
</tr>
<tr>
<td>50</td>
<td>1.72</td>
<td>21.36</td>
<td>12</td>
</tr>
<tr>
<td>100</td>
<td>0.25</td>
<td>21.79</td>
<td>86</td>
</tr>
<tr>
<td>160</td>
<td>0.05</td>
<td>69.13</td>
<td>1500</td>
</tr>
</tbody>
</table>

In order to test the capability of EDRR more completely in terms of silver recovery, the Ag content was investigated over a concentration range from 1 ppb to 250 ppm in a solution containing 60 g/L Zn and 10 g/L H₂SO₄, Table 22. The findings showed that the Ag/Zn ratio in the deposit obtained remained relatively high even with the lowest investigated Ag content (1 ppb). Moreover, the level of Ag found on the electrode surface increased in parallel with the increased Ag concentration in the solution; in contrast, the content of Zn remained rather moderate in the metal deposits for all concentrations investigated. The results presented in Table 22 clearly indicate the power of the EDRR type of tailored electrochemical method in terms of silver recovery from synthetic Zn sulfate solutions, even with extremely low Ag contents (<1 ppm). However, the time needed to complete the required 10 cycles was found to be an order of magnitude longer for the lowest concentration (11 500 s for 1 ppb) compared to that of 10 cycles when the Ag content was higher (1000 s for 100 ppm). This phenomenon can be explained by one of the limiting factors of electrochemical recovery: mass transfer. When there are fewer suitable ions in the solution, it takes more time to reduce a detectable amount on the surface of the electrode, Figure 29. Moreover, when there are no more silver ions available to replace the zinc, the spontaneous dissolution of zinc back into the solution, i.e., corrosion due to the acidic environment, still occurs. In addition, the change in the optimized conditions when decreasing the silver content to very minor levels (in ppb scale) could be expected. However, the selection of deposition potential (E₁) is mostly dominated by the sacrificial element (Zn), which concentration remains much higher in all solutions and therefore the same value is relevant also for lower silver concentrations. The cut-off potential (E₂), on other hand, is based on the OCP of the system and is not affected by the Ag content that dominantly (due to its low concentration) than sacrificial elements (high concentrations). Therefore, when long enough cut-off time (t₂) is allowed, cut-off potential can also be kept the same. The deposition time (t₁) naturally controls the amount of sacrificial element(s) deposited on the electrode surface and shorter deposition times applied could be beneficial with lower Ag content in order to produce higher purity product; however, purity can be guided also with cut-off potential (or cut-off time) too.
Table 22. Ag and Zn contents of the electrode surface metal deposits and their ratio as a function of Ag content in the solution. Constant EDRR parameters applied at room temperature (20-22 °C) were $E_1 = -700$ mV and $E_2 = +300$ mV vs. SCE, $t_1 = 10$ s, $t_2 = 1000$ s, and $n = 10$.

<table>
<thead>
<tr>
<th>Ag content in the solution [ppm]</th>
<th>Zn [wt-%]</th>
<th>Ag [wt-%]</th>
<th>Ag/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.03</td>
<td>0.18</td>
<td>6.0</td>
</tr>
<tr>
<td>0.05</td>
<td>0.04</td>
<td>1.10</td>
<td>27.5</td>
</tr>
<tr>
<td>0.5</td>
<td>0.03</td>
<td>0.33</td>
<td>11.0</td>
</tr>
<tr>
<td>1</td>
<td>0.13</td>
<td>0.33</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>0.15</td>
<td>0.53</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.84</td>
<td>4.2</td>
</tr>
<tr>
<td>10</td>
<td>0.07</td>
<td>4.94</td>
<td>70.6</td>
</tr>
<tr>
<td>100</td>
<td>0.08</td>
<td>14.30</td>
<td>178.8</td>
</tr>
<tr>
<td>250</td>
<td>0.06</td>
<td>38.67</td>
<td>644.5</td>
</tr>
</tbody>
</table>

The EDRR method for Ag recovery from Zn sulfate solutions was also tested against conventional EW in a solution containing 60 g/L Zn, 10 g/L H$_2$SO$_4$, and 100 ppm Ag. The EDRR parameters applied were $E_1 = -700$ mV and $E_2 = +300$ mV vs. SCE, $t_1 = 10$ s, $t_2 = 1000$ s, and $n = 10$, whereas the EW was performed at $E = +300$ mV for 200 s, i.e., with a deposition time that was twice as long. The quantitative SEM-EDS data (Table 23) clearly demonstrates the power of the EDRR method over conventional EW process when the content of transferred elements is quite low (~100 ppm). However, not all the phenomena that occur during EDRR are yet fully understood; therefore, the results presented in the Zn-Ag system are currently only indicative of the possibilities offered by such a pulsed electrochemical procedure.

Table 23. Quantitative SEM-EDS results of the metal deposits on the electrode surface after EDRR and EW procedures conducted at room temperature (20-22 °C). (Publication V).

<table>
<thead>
<tr>
<th>Method</th>
<th>Zn [wt-%]</th>
<th>Ag [wt-%]</th>
<th>Ag/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDRR</td>
<td>0.10</td>
<td>23.35</td>
<td>230</td>
</tr>
<tr>
<td>EW</td>
<td>0.08</td>
<td>0.87</td>
<td>11</td>
</tr>
</tbody>
</table>

5.3 Nickel Plant as a Source of Platinum

In the investigated nickel (60 g/L) sulfate system, with platinum (20 ppm) and silver (10 ppm) present (as well as ~1 ppm Cu), platinum was generally found to enrich on deposits compared to the other elements present in the metal deposits, Table 24. Moreover, the most anodic deposition potential ($E_1 = -175$ mV vs. SCE) resulted in the highest platinum content. As this potential was not sufficient to directly deposit nickel (Figure 25), it could be surmised that during the first EDRR cycle, copper and silver were deposited and acted as the sacrificial element. After the redox replacement with platinum, the UPD of nickel [307], [308] could potentially then occur, resulting in an enhancement of platinum recovery, nickel also acting as a sacrificial element in preference to copper and silver, due to the significantly (60 g/L vs. ~1 ppm / 10 ppm) higher concentration. At $E_1 = -175$ mV vs. SCE the H$_2$ evolution is assumed not to interfere
with the ED phase, whereas at -500 and -750 mV vs. SCE, its formation starts to dominate, similar to the Zn-Ag system presented in Section 5.2.

Since each experiment was given the same amount of total time (16h), the completed EDRR cycles (n) varied from 723 (at -175 mV vs. SCE) to 79 full cycles (at -750 mV). This is a result of the amount of time needed to reach the cut-off potential (E₂ = +350 mV vs. SCE), which was longer at more cathodic deposition potentials: on average ~80 s for -175 mV vs. SCE and ~730 s for -750 mV. The difference in time required to reach the cut-off potential can be explained by the fact that the platinum content in the solution was originally so low that there was an insufficient amount to fully replace the sacrificial elements deposited with more cathodic potentials. Consequently, for further parameter optimization the deposition potential of E₁ = -175 mV vs. SCE was selected.

Table 24. Averaged quantitative SEM-EDS results of the metal surface deposits on the working electrode. The constant EDRR parameters at room temperature (20-22 °C) were E₂ = +350 mV vs. SCE, t₁ = 10 s, and t₂ = 1000 s. (Publication VI).

<table>
<thead>
<tr>
<th>E₁ vs. SCE</th>
<th>-175 mV</th>
<th>-500 mV</th>
<th>-750 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt [wt-%]</td>
<td>97.68</td>
<td>95.95</td>
<td>94.95</td>
</tr>
<tr>
<td>Ag [wt-%]</td>
<td>1.52</td>
<td>2.00</td>
<td>1.49</td>
</tr>
<tr>
<td>Cu [wt-%]</td>
<td>0.67</td>
<td>0.63</td>
<td>0.99</td>
</tr>
<tr>
<td>Ni [wt-%]</td>
<td>0.12</td>
<td>1.42</td>
<td>2.56</td>
</tr>
</tbody>
</table>

The concentrations of all of the sacrificial elements (Ni, Cu, Ag) under consideration displayed the same behavior: at low n values, their share of the deposit was higher whereas an increase in the number of EDRR cycles leads to a reduction in their content, Figure 30A-C. However, the behavior of the most noble metal—platinum—was the opposite. At shorter n values (10), the platinum content varied between 40 and 75 wt-%, whereas with n = 200-400, platinum was clearly dominant (> 90 wt-%), Figure 30D. Additionally, it was determined that the applied deposition time of t₁ = 2 s resulted in the lowest Pt content in the metal deposits on the electrode surface overall. It is suggested that with longer deposition times, more sacrificial elements (in this case Ni, Cu, and even Ag) are deposited, and consequently more sacrificial elements provided for re-do-x replacement. In the investigated case with the optimized parameters, the ratio of Pt / (Ni + Cu + Ag) in the solution (3·10⁻⁴) increased to ~10⁵ times higher in the electrode surface metal deposits (33.6).

It has been shown earlier that Ag can replace Cu on the deposit [28]. In Publication VI, it was evident that the most noble metal, Pt, could replace both Ag and Cu, in addition to Ni. This emphasizes the versatility of the EDRR method and the potential enrichment routes as direct replacement between Ni-Pt, Cu-Pt and Ag-Pt is possible; however, step-wise reduction in the nobility order of the elements present, i.e., Ni-Cu-Ag-Pt (or some parts of the route) is also possible.
Figure 30. Content of (A) Ni, (B) Cu, (C) Ag, and (D) Pt in the electrode surface metal deposits as a function of EDRR cycles \((n)\) with three different deposition times, \(t_1 = 2\) s, 5 s, or 10 s. The solution contained 60 g/L Ni, 20 ppm Pt, 10 ppm Ag, \(-1\) ppm Cu, and 10 g/L H\(_2\)SO\(_4\) and the constant EDRR parameters applied were \(E_1 = -175\) mV, \(E_2 = +350\) mV vs. SCE, and \(t_2 = 1000\) s. All experiments were performed at room temperature (20-22 °C).

The average size of the metal deposits ranged from a few tens of nanometers to several hundreds, Figure 31, and the metal deposits were found to consist of smaller particles that tended to form larger clusters. Nucleation of the metal deposition on the PyC surface most likely initiates preferentially on areas of inhomogeneity [31], [32], [262]. Furthermore, the formation of the Pt clusters followed the same pattern regardless of the EDRR parameters applied and these results are consistent with previous findings detailed in the literature [309] – [313].

Figure 31. Secondary electron micrograph of the PyC electrode with a magnification of 20,000x. EDRR parameters were \(E_1 = -175\) mV and \(E_2 = +350\) mV vs. SCE, \(t_1 = 10\) s and \(t_2 = 1000\) s and \(n = 400\). (Publication VI).
Optimized EDRR parameters were compared to EW performed for the same amount of time. The metal clusters deposited after the EDRR experiments were found to be ubiquitous across the whole electrode surface. In contrast, after the EW, the deposits were so small that SEM-EDS point analysis could not be performed and therefore an area analysis (30 ± 10 x 15 ± 5 \( \mu m \)) was implemented for all electrodes. The platinum contents obtained with EDRR were found to be an order of a magnitude higher than with EW, Table 25. As the solution composition was the same in every experiment (60 g/L Ni, 20 ppm Pt, 10 ppm Ag, ~1 ppm Cu and 10 g/L H\(_2\)SO\(_4\)), these results clearly demonstrate how crucial the redox replacement step is in terms of platinum recovery from such low concentration solutions.

Table 25. Effect of EW and EDRR parameters applied at room temperature (20-22 °C) on the purity of Pt in the electrode surface metal deposits. Base material (PyC electrode) is excluded from the results.

<table>
<thead>
<tr>
<th></th>
<th>EDRR -175 mV → +350 mV</th>
<th>EW -175 mV</th>
<th>EW +350 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 s x 100 cls</td>
<td>5 s x 100 cls</td>
<td>10 s x 100 cls</td>
</tr>
<tr>
<td>Pt content [wt-%]</td>
<td>4.96</td>
<td>10.47</td>
<td>24.35</td>
</tr>
<tr>
<td></td>
<td>200 s</td>
<td>500 s</td>
<td>1000 s</td>
</tr>
<tr>
<td></td>
<td>1.47</td>
<td>4.31</td>
<td>9.71</td>
</tr>
<tr>
<td></td>
<td>200 s</td>
<td>500 s</td>
<td>1000 s</td>
</tr>
<tr>
<td></td>
<td>1.23</td>
<td>1.21</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Although the EDRR method was proven to be successful at recovering Pt from synthetic low concentration Pt solutions, the true test of the methodology comes from a real hydrometallurgical nickel-rich process solution. Figure 32 displays the SEM-EDS results as a function of deposition time for Solution #1; the applied EDRR parameters were \( E_1 = -175 \) mV and \( E_2 = +350 \) mV vs. SCE, \( n = 10 \), and \( t_2 = 1000 \) s. When taking into account the fact that Solution #1 had a very minor amount of Pt (~1.3 ppb)—when compared to the synthetic solution (20 ppm)—the results are truly outstanding, as the Pt content varied from 40 wt-% to over 80 wt-%. It is also noteworthy that Ag and some Pd could also be recovered from the solution whilst the Ni content was minimized, even though its concentration was 140 g/L (Table 4).
Figure 32. Quantitative SED-EDS results (an average of 6-10 spectra consisting of
~25 μm x ~25 μm areas) of the elements present in the electrode surface metal
deposits recovered from Solution #1. EDRR parameters applied were $E_1 = -175$ mV
and $E_2 = +350$ mV vs. SCE, $t_2 = 1000$ s, and $n = 10$ at room temperature (20-22 °C).
Standard deviation for Pt was ~30 regardless of the applied EDRR parameters.

Whereas the SEM-EDS results shown in Figure 32 represent only $n = 10$,
Table 26 presents the SEM-EDS results for metal deposits after $n = 100, 200,$
and 400 obtained with two deposition times, $t_1 = 8$ s or 10 s. As can be seen, the
nickel content remained <1 wt-% regardless of the deposition time or amount of
EDRR cycles performed. Moreover, the level of copper also stayed approximately constant throughout the experiments, with the exception of $t_1 = 10$ s and
$n = 200$, where its content was remarkably higher. The reason for this observation
is not fully understood and could be merely a consequence of the analytical
procedure. Nevertheless, the content of platinum was still substantially high
compared to that in solution (~1.3 ppb, Table 4); furthermore, silver and palladium also demonstrated signs of enrichment.

Table 26. Quantitative SEM-EDS results of the electrode surface metal deposits re-
covered from Solution #1. EDRR parameters were $E_1 = -175$ mV and $E_2 = +350$ mV
vs. SCE and $t_2 = 1000$ s at room temperature (20-22 °C). Base material (PyC ele-
ctrode) is excluded from the results. The standard deviation for Pt varied from ~20 to ~30.

<table>
<thead>
<tr>
<th>Element</th>
<th>Metal content [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_1 = 8$ s</td>
</tr>
<tr>
<td></td>
<td>$n = 100$</td>
</tr>
<tr>
<td>Ni</td>
<td>0.7</td>
</tr>
<tr>
<td>Cu</td>
<td>2.1</td>
</tr>
<tr>
<td>Ag</td>
<td>1.3</td>
</tr>
<tr>
<td>Pd</td>
<td>0.2</td>
</tr>
<tr>
<td>Pt</td>
<td>66.5</td>
</tr>
</tbody>
</table>

Since Solution #2 contained significantly fewer other elements (apart from
Ni) than Solution #1, Table 4, the cut-off time was reached much more quickly
than the pre-determined cut-off potential. Therefore, the maximum cut-off time
investigated was increased 10-fold up to $t_2 = 10000$ s, although $t_2 = 1000$ s was
also tested. With \( t_2 = 10\,000\, \text{s} \), 15 EDRR cycles were conducted, resulting in a total RR time of >40 h (150,000 s), whereas with \( t_2 = 1000\, \text{s} \), 300 EDRR cycles were completed, giving a total RR time of >80 h (300,000 s). Table 27 shows that the platinum content measured was high, irrespective of the EDRR parameters used.

**Table 27. Quantitative SEM-EDS results of the surface metal deposits recovered from Solution #2.** EDRR parameters were \( E_1 = -175 \, \text{mV} \) and \( E_2 = +350 \, \text{mV} \) vs. SCE and \( t_1 = 10\, \text{s} \). With \( n = 15 \), \( t_2 \) was \( 10\,000 \, \text{s} \) and with \( n = 300 \), \( t_2 \) was \( 1000 \, \text{s} \) at room temperature (20-22 °C). The standard deviation for Pt was approximately 1.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Metal content [wt-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n = 15 )</td>
</tr>
<tr>
<td>Ni</td>
<td>0.6</td>
</tr>
<tr>
<td>Cu</td>
<td>2.4</td>
</tr>
<tr>
<td>Ag</td>
<td>1.9</td>
</tr>
<tr>
<td>Pd</td>
<td>0.2</td>
</tr>
<tr>
<td>Pt</td>
<td>89.6</td>
</tr>
</tbody>
</table>

Figure 33 presents the enrichment ratios of Pt, Pd, and Ag, which were calculated taking into account the specific elemental content in solution when compared to the metal deposit SEM-EDS analyses. As can be seen, the enrichment ratio for platinum is remarkably high, when taking into account the fact that the content of the original process solutions was below the detection limit of HR-ICP-MS (~1.3 ppb). Furthermore, although the enrichment ratio of platinum displays a slight reduction with Solution #2, palladium and silver showed a higher enrichment ratio when compared to Solution #1. In addition, possible contamination with e.g. Pd could be expected due to the relatively low standard electrode potential difference between Pt and Pd, \( (E^0_0 = +1188 \, \text{mV} \) vs. SHE | Pt vs. \( E^0_0 = +915 \, \text{mV} \) vs. SHE | Pd). Furthermore, when the results for Ag and Pd recovery obtained are compared (Figure 32 and Ag results from Figure 30C) Ag was enriched with the shortest deposition times (\( t_1 = 2 \, \text{s} \) ) and lower amount of EDRR cycles (\( n = 10 \) ). For Pd the longer deposition times (\( t_1 = 6-8 \, \text{s} \) ) could possible be better than relatively short ones. Moreover, as with silver, also palladium was enriched with a lower amount of EDRR cycles than was needed for platinum enrichment, Table 26. Therefore, the future research could possible be based on those two EDRR parameters as well as to apply the different potentials \( (E_1 \) and/or \( E_2 \) ) or e.g. by studying the bimetallic particle formation [28].
5.4 Integration of EDRR into State-of-the-Art EW Processes

In the current Thesis, it has been demonstrated on laboratory scale that the EDRR method can be tailored for the recovery of valuable, precious, and critical elements not only from synthetic solutions, but also from real multimetal industrial waste or process solutions. Moreover, the targeted metal concentrations within these solutions was extremely low (on ppm / ppb scale) and the process solutions of hydrometallurgical processes may include almost the whole periodic table, with elements in very different concentrations. Nevertheless, the results detailed in this Thesis show that the EDRR method can recover the targeted metals with high purities and therefore outlines the fact that EDRR is one more possible method for utilizing solutions previously considered to be uneconomic. However, with such a low concentration of valuable elements in the system, the diffusion of the ions to the surface starts to control the replacement rate. Therefore, the ability to constantly provide fresh solution to the system (e.g. via constant solution flow) is essential on the industrial scale.

Figure 34 illustrates one possible route for EDRR integration into a current state-of-the-art base metal electrowinning plant. Alternatively—or additionally—EDRR could be utilized in an advanced purification stage prior to the EW process, allowing the electrolyte to be further purified without any addition of chemicals. Furthermore, EDRR could also be utilized after the conventional EW process to recover the valuable elements still present in the solution in such extremely low concentrations that the traditional EW process could not operate feasibly. In addition, the recovery of the deposited metals from the surface of the electrode could be conducted via either traditional mechanical stripping of the electrodes [314] – [316] or via (electro) chemical stripping as well to a different solution, where the targeted metals could be recover e.g. by precipitation/cementation.

Furthermore, the optimal conditions determined in the laboratory scale would not necessarily apply on the industrial scale. The main challenge in the
scaling up process would perhaps be providing constantly new and fresh solution to the system, in such a manner that the already deposited metals would not be unintentionally stripped away.

Figure 34. Schematic of possible EDRR integration into a state-of-the-art electrowinning process.
6. Conclusions

“Do we have to find a solution? Can’t we just enjoy the problem for a while?”

This Thesis consists of several different valorization and proof-of-concept methodologies aimed at the treatment of materials that are currently considered to be wastes or, at least, not secondary raw materials. Moreover, many metallurgical streams are treated solely as process solutions, which means that sustainability or secondary raw material characteristics are not taken into account, especially with regard to the low levels of some lost (critical/precious) elements. In terms of the circular economy and sustainable development, the recovery of even a small amount of these lost resources can have a major impact on the metal circulation required for the ever-growing global demand for materials. In addition, the study of electrochemical phenomena in minor metals recovery—not addressed earlier—may provide routes for the development of future recovery methodologies.

The recovery of valuable, precious, and critical metals from very different sources including EAFD, Doré slag, and base metal rich process solutions has been the subject of this Thesis research. The target in the EAFD studies was to convert hazardous waste into a recyclable secondary raw material, whereas the focus in the Doré slag and EW electrolyte investigations was to show the capabilities of a novel electrochemical method (EDRR) to recover minor amounts of valuable metals from complex hydrometallurgical solutions. Based on the findings, the following conclusions can be drawn:

1. This Thesis demonstrates an alternative route for EAFD processing, where the dust is transformed into three different raw material streams, thus reducing the amount of waste. In that context, the following conclusions can be made:

   a. Several lixiviants may result in good extraction for zinc leaching from EAFD. The selectivity toward the target elements depends not only on the lixiviant but also on the concentration used. Therefore, the aim and process approach, as well as potential feasibility of the lixiviant need to be estimated prior to the selection of leaching media.

   b. In terms of maximizing the Zn removal and minimizing Fe losses, direct citric acid leaching for roasted EAFD resulted in approximately 100% Zn extraction into solution, while Fe remained primarily in the leach residue, resulting in a chemically suitable iron-rich residue to be recycled back to the EAF process.
Conclusions

c. The remaining Zn-rich PLS can be treated with conventional hydrometallurgical methods in order to produce a suitable solid raw material feed for Pb production and an electrolyte that could be integrated in a state-of-the-art Zn EW process. Furthermore, a novel hydrometallurgical process flowsheet for Fe, Zn, and Pb recovery from EAFD was proposed.

2. Since tellurium is mainly produced as a side product of copper anode slime treatment, the combination of Doré slag leaching followed by direct EW and EDRR was demonstrated. The innovative combination of EW and EDRR was confirmed to be relatively selective (EW resulted in ~55 wt-% and EDRR in ~64 wt-%) toward tellurium, even though the Doré slag consisted of significant amounts of other elements with much higher concentrations. It was also shown that, in the case of a tellurium content of 300 ppm or above, EW is preferred, whilst below this threshold value, EDRR should be used.

3. EDRR was demonstrated to be capable of recovering elements present on the ppm and ppb scale not only in synthetic process solutions, but also in complex, multi-metal hydrometallurgical industrial process solutions. The Thesis also provides insights into the phenomena occurring in the process and suggests that, in addition to direct noble metal redox replacement driven deposition, the corrosion of less noble metals and increased time for mass transfer during the RR phase play a significant role in the recovery of valuable, precious, and critical metals with high purity. However, mass transfer could be improved by either pumping/circulating the solution through the system or by having a stirring system inside the reactor. Therefore, the following conclusions can be drawn:

a. With the EDRR technique, silver was successfully recovered from zinc sulfate solution with an Ag content of 250 ppm to 1 ppb. Hydrogen evolution was shown to interfere with the process, decreasing its efficiency. Moreover, it was also found that, when the silver content in solution was increased, the required process time could be decreased, resulting in faster silver recovery.

b. When a high surface area pyrolyzed 3D carbon (PyC) electrode material was used, platinum could be recovered with high purity from nickel-rich sulfate media. All the less noble elements investigated (Ni, Cu, Ag) could act as sacrificial elements for platinum. From the actual industrial hydrometallurgical process solutions not only platinum but also Pd and Ag could be enriched.

c. Furthermore, EDRR provides a high degree of versatility for metal recovery. It is highly tailorable (variables such as: \( E_1, E_2, t_1, t_2, n, \) and \( x \)) and therefore, the process can be driven via alternative routes including direct replacement, step-wise replacement, or replacement via \( H_2 \) formation. Also, the solution composition i.e., the process from where it originates, determines
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the matrix of the potential electrochemical reactions. When operated skilfully, it can also provide an energy efficient route for valuable metals recovery.

d. EDRR is a novel and exceptional method for metal recovery from side- and waste streams and hydrometallurgical process solutions and thus, it can have a significant impact in the circular economy in future.
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Innovative Valorization of Secondary Raw Materials

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