

Sami Virolainen

## **HYDROMETALLURGICAL RECOVERY OF VALUABLE METALS FROM SECONDARY RAW MATERIALS**

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## **ABSTRACT**

Sami Virolainen

### **Hydrometallurgical recovery of valuable metals from secondary raw materials**

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Wastes and side streams in the mining industry and different anthropogenic wastes often contain valuable metals in such concentrations their recovery may be economically viable. These raw materials are collectively called secondary raw materials. The recovery of metals from these materials is also environmentally favorable, since many of the metals, for example heavy metals, are hazardous to the environment. This has been noticed in legislative bodies, and strict regulations for handling both mining and anthropogenic wastes have been developed, mainly in the last decade.

In the mining and metallurgy industry, important secondary raw materials include, for example, steelmaking dusts (recoverable metals e.g. Zn and Mo), zinc plant residues (Ag, Au, Ga, Ge, In) and waste slurry from Bayer process alumina production (Ga, REE, Ti, V). From anthropogenic wastes, waste electrical and electronic equipment (WEEE), among them LCD screens and fluorescent lamps, are clearly the most important from a metals recovery point of view. Metals that are commonly recovered from WEEE include, for example, Ag, Au, Cu, Pd and Pt. In LCD screens indium, and in fluorescent lamps, REEs, are possible target metals.

Hydrometallurgical processing routes are highly suitable for the treatment of complex and/or low grade raw materials, as secondary raw materials often are. These solid or liquid raw materials often contain large amounts of base metals, for example. Thus, in order to recover valuable metals, with small concentrations, highly selective separation methods, such as hydrometallurgical routes, are needed. In addition, hydrometallurgical processes are also seen as more environmental friendly, and they have lower energy consumption, when compared to pyrometallurgical processes.

In this thesis, solvent extraction and ion exchange are the most important hydrometallurgical separation methods studied. Solvent extraction is a mainstream unit operation in the metallurgical industry for all kinds of metals, but for ion exchange, practical applications are not as widespread. However, ion exchange is known to be particularly suitable for dilute feed solutions and complex separation tasks, which makes it a viable option, especially for processing secondary raw materials.

Recovering valuable metals was studied with five different raw materials, which included liquid and solid side streams from metallurgical industries and WEEE. Recovery of high

purity (99.7%) In, from LCD screens, was achieved by leaching with H<sub>2</sub>SO<sub>4</sub>, extracting In and Sn to D2EHPA, and selectively stripping In to HCl. In was also concentrated in the solvent extraction stage from 44 mg/L to 6.5 g/L.

Ge was recovered as a side product from two different base metal process liquors with N-methylglucamine functional chelating ion exchange resin (IRA-743). Based on equilibrium and dynamic modeling, a mechanism for this moderately complex adsorption process was suggested.

Eu and Y were leached with high yields (91 and 83%) by 2 M H<sub>2</sub>SO<sub>4</sub> from a fluorescent lamp precipitate of waste treatment plant. The waste also contained significant amounts of other REEs such as Gd and Tb, but these were not leached with common mineral acids in ambient conditions.

Zn was selectively leached over Fe from steelmaking dusts with a controlled acidic leaching method, in which the pH did not go below, but was held close as possible to, 3. Mo was also present in the other studied dust, and was leached with pure water more effectively than with the acidic methods. Good yield and selectivity in the solvent extraction of Zn was achieved by D2EHPA. However, Fe needs to be eliminated in advance, either by the controlled leaching method or, for example, by precipitation. 100% Pure Mo/Cr product was achieved with quaternary ammonium salt (Aliquat 336) directly from the water leachate, without pH adjustment (pH 13.7). A Mo/Cr mixture was also obtained from H<sub>2</sub>SO<sub>4</sub> leachates with hydroxyoxime LIX 84-I and trioctylamine (TOA), but the purities were 70% at most. However with Aliquat 336, again an over 99% pure mixture was obtained. High selectivity for Mo over Cr was not achieved with any of the studied reagents.

Ag-NaCl solution was purified from divalent impurity metals by aminomethylphosphonium functional Lewatit TP-260 ion exchange resin. A novel preconditioning method, named controlled partial neutralization, with conjugate bases of weak organic acids, was used to control the pH in the column to avoid capacity losses or precipitations. Counter-current SMB was shown to be a better process configuration than either batch column operation or the cross-current operation conventionally used in the metallurgical industry.

The raw materials used in this thesis were also evaluated from an economic point of view, and the precipitate from a waste fluorescent lamp treatment process was clearly shown to be the most promising.

**Keywords:** Secondary raw material, Urban mining, Waste electrical and electronic equipment (WEEE), Hydrometallurgy, Solvent extraction, Ion exchange

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## TIIVISTELMÄ

Sami Virolainen

### **Arvokkaiden metallien hydrometallurginen talteenotto sekundäärisistä raaka-aineista**

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Kaivosteollisuuden jätteet ja sivuvirrat, sekä erilaiset ihmisperäiset jätteet sisältävät usein sellaisia määriä arvokkaita metalleja, että niiden talteenotto voi olla taloudellisesti kannattavaa. Tällaisia raaka-aineita kutsutaan yhteisellä nimityksellä sekundääriset raaka-aineet. Metallien talteenotto niistä on lisäksi myös ympäristön kannalta järkevää, koska niiden sisältämät metallit, esimerkiksi raskasmetallit, ovat usein ympäristölle haitallisia. Tämän ovat havainneet maailmanlaajuisesti myös erilaiset lainsäädäntöelimet, ja etenkin viimeisen vuosikymmenen aikana on säädetty useita lakeja metalleja sisältävien, sekä kaivosteollisuuden että ihmisperäisten, jätteiden käsittelystä.

Kaivosteollisuuden tärkeimpiä sekundaarisia raaka-aineita ovat mm. terästeollisuuden pölyt (talteen otettavia metalleja esim. Zn ja Mo), sinkkitehtaiden jätteet (Ag, Au, Ga, Ge, In) ja alumiinin valmistuksen Bayer prosessin jäteliete (Ga, harvinaiset maametallit, Ti, V). Ihmisperäisistä jätteistä selkeästi tärkeimpiä ovat erilaiset elektroniikkajätteet, esimerkiksi LCD paneelit ja loisteputket. Yleisesti elektroniikkajätteistä talteen otettavia metalleja ovat mm. Ag, Au, Cu, Pd ja Pt. LCD paneeleista voidaan ottaa talteen indiumia ja loisteputkista harvinaisia maametalleja.

Hydrometallurgiset prosessit ovat erityisen sopivia monimutkaisten ja/tai metallipitoisuuksiltaan köyhien, jollaisia sekundääriset raaka-aineet usein ovat, käsittelyyn. Nämä kiinteät ja nestemäiset raaka-aineet sisältävät monesti suuria määriä esimerkiksi perusmetalleja. Näin ollen arvokkaiden metallien, joiden pitoisuudet ovat pieniä, talteenottoon tarvitaan erittäin selektiivisiä erotusmenetelmiä, jollaisia hydrometallurgiset menetelmät ovat. Lisäksi hydrometallurgiset menetelmät ovat pyrometallurgisia ympäristöystävällisempiä sekä kuluttavat vähemmän energiaa.

Tässä väitöskirjassa neste-neste uutto ja ioninvaihto ovat tärkeimmät tutkitut menetelmät. Neste-neste uutto on metallurgiassa erittäin yleinen yksikköprosessi kaikenlaisten metallien tuotannossa. Sen sijaan ioninvaihdon käyttö metallurgisessa teollisuudessa on vähäistä, mutta sen tiedetään olevan erityisen sopiva sekä laimeille että monimutkaisille syöttöliuoksille.

Arvokkaiden metallien talteenottoa tutkittiin viidellä erilaisella sekundäärisellä raaka-aineella, jotka sisälsivät nestemäisiä ja kiinteitä sivuvirtoja metallurgisesta teollisuudesta, sekä elektroniikkajätteitä. LCD paneeleista saatiin otettua talteen erittäin puhdasta (99,7 %) In:a

liuottamalla paneelista saatua lasimurskaa  $H_2SO_4$ :lla, uuttamalla In ja Sn D2EHPA:oon ja takaisin uuttamalla In selektiivisesti HCl:oon. Uuttoprosessissa In saatiin myös väkevöityä 44 mg/L:sta 6,5 g/L:aan.

Germaniumin talteenottoa sivutuotteena tutkittiin kahdesta eri perusmetalliprosessin liuksesta kelatoivalla N-metyyliglukamiini hartsilla (IRA-743). Tälle verrattain monimutkaiselle adsorptioprosessille konstruointiin mekanismi perustuen ioninvaihdon tasapainon ja kolonnidynamiikan mallinnukseen.

Europiumia ja yttriumia saatiin liotettua jätteenkäsittelylaitoksen loisteputkiprosessin sakasta 2 M  $H_2SO_4$ :oon hyvillä saannoilla (91 ja 83 %). Raaka-aine sisälsi merkittäviä määriä myös muita harvinaisia maametalleja kuten gadoliniumia ja terbiumia, mutta ne eivät liuenneet merkittävässä määrin tavallisiin mineraalihappoihin huoneenlämmössä ja normaalipaineessa.

Terästeollisuuden pölyistä saatiin sinkki liotettua selektiivisesti raudan suhteen kontrolloidulla happoliuotuksella, joka tarkoitti sitä että pH pidettiin mahdollisimman lähellä 3:a menemättä kuitenkaan sen alle. Toisesta tutkitusta pölystä löydettiin myös molybdeeniä, joka liukeni paremmin vedellä kuin käytetyillä happoliuotusmenetelmillä. Saaduista liuksista Zn saatiin uutettua selektiivisesti D2EHPA:lla muiden metallien paitsi Fe:n suhteen. Tämän vuoksi täytyy käyttää joko edellä mainittua selektiivistä liuotusmenetelmää tai Fe täytyy saostaa ennen uutovaihetta. Kvaternäärisellä ammoniumsuolalla (Aliquat 336) saatiin pH:ta säätämättä (pH 13,7) uutettua 100 % puhdasta Mo/Cr seosta suoraan Mo:a sisältäneen pölyn vesiliuksesta. Mo/Cr seosta saatiin myös ko. pölyn  $H_2SO_4$  liuksista hydroksioksiimi LIX 84-I:llä ja trioktyyliamiinilla (TOA), mutta puhtaudet olivat vain 70 %:n luokkaa. Aliquat 336:lla saatiin tästäkin liuksesta 99 % puhdasta Mo/Cr seosta. Millään tutkituista reagensseista ei kuitenkaan saatu uutettua puhdasta Mo:a.

Ag-NaCl liuos saatiin puhdistettua kahden arvoisista epäpuhtausmetalleista aminometyylifosfonaatti hartsilla (Lewatit TP-260). Erotusprosessissa käytettiin uutta hartsin esikäsitelymenetelmää, kontrolloitua osittaisneutralointia, jonka avulla voitiin kontrolloida ioninvaihtokolonnin sisällä olevaa pH:ta erotuksen aikana. Osittaisneutralointi tehdään heikkojen orgaanisten happojen suoloilla, ja sen avulla vältetään saostumien muodostusta ja ioninvaihtokapasiteetin alenemista. Tässä erotustapauksessa osoitettiin myös että vastavirtaperiaatteella toimiva simuloitu liikkuvapeti (SMB) prosessikonfiguraatio on tehokkaampi kuin panoserotus kolonnissa tai yleensä metallurgisilla laitoksilla käytettävä ristivirtakonfiguraatio.

Työssä käytettyjä sekundäärisiä raaka-aineita vertailtiin myös taloudelliselta kannalta, ja jätteenkäsittelylaitoksen loisteputkisakka osoittautui selvästi lupaavimmaksi.

Avainsanat: Sekundäärinen raaka-aine, Elektroniikkajäte, Hydrometallurgia, Neste-neste uutto, Ioninvaihto

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## **FOREWORD**

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**Sami Virolainen**

## CONTENTS

|   |  |    |
|---|--|----|
| 1 | INTRODUCTION   | 13 |
| 2 | OVERVIEW OF POTENTIAL HYDROMETALLURGICAL SEPARATION METHODS FOR SECONDARY RAW MATERIALS                            | 15 |
|   | 2.1 Leaching   | 16 |
|   | 2.2 Precipitation and cementation  | 18 |
|   | 2.3 Solvent extraction   | 19 |
|   | 2.4 Ion exchange   | 25 |
| 3 | WASTES AND SIDE STREAMS IN MINING INDUSTRY SUITABLE FOR VALUABLE METALS RECOVERY                                   | 31 |
|   | 3.1 Steelmaking dusts  | 31 |
|   | 3.2 Zinc plant residues  | 32 |
|   | 3.3 Spent Bayer liquor and red mud from alumina production   | 33 |
|   | 3.4 Residues from the copper industry  | 36 |
| 4 | WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)   | 41 |
|   | 4.1 Overview of metals recovery from WEEE  | 41 |
|   | 4.2 LCD panels   | 45 |
|   | 4.3 Fluorescent lamps  | 47 |
| 5 | EXPERIMENTAL   | 49 |
|   | 5.1 Recovery of indium from LCD screens (Publication I)  | 49 |
|   | 5.2 Ion exchange recovery of germanium as a by-product from sulfate process solutions (Publication II)             | 50 |
|   | 5.3 Characterization and leaching of fluorescent lamp wastes   | 50 |
|   | 5.4 Recovery of zinc and molybdenum from steelmaking dusts (Publication IV)  | 51 |
|   | 5.5 Purification of Ag-NaCl solution by normal column operation and simulated moving beds (Publications III and V) | 51 |
| 6 | RESULTS AND DISCUSSION   | 53 |
|   | 6.1 Recovery of indium from LCD screens (Publication I)  | 53 |
|   | 6.2 Ion exchange recovery of germanium as a by-product from sulfate process solutions (Publication II)             | 57 |
|   | 6.3 Characterization and leaching of fluorescent lamp waste  | 62 |
|   | 6.4 Recovery of zinc and molybdenum from steelmaking dusts (Publication IV)  | 65 |
|   | 6.5 Purification of Ag-NaCl solution by normal column operation and simulated moving beds (Publications III and V) | 71 |
| 7 | CONCLUSIONS  | 75 |
|   | REFERENCES   | 77 |



## LIST OF PUBLICATIONS

- I Virolainen, S., Ibana, D. and Paatero, E., Recovery of indium from indium tin oxide by solvent extraction, *Hydrometallurgy*, 107 (2011), pp. 56-61
- II Virolainen, S., Heinonen, J., Paatero, E., Selective recovery of germanium with N-methylglucamine functional resin from sulfate solutions, *Separation and Purification Technology*, 104 (2013), pp. 193–199
- III Virolainen, S., Suppala, I. and Sainio, T., Controlled partial neutralization of amphoteric ion exchange resin for improved metals separation, *Reactive and Functional Polymers*, 73 (2013), pp. 647-652
- IV Virolainen, S., Salmimies, R., Hasan, M., Häkkinen, A., Sainio, T., Recovery of valuable metals from argon oxygen decarburization (AOD) dusts by leaching, filtration and solvent extraction, *Hydrometallurgy*, 140 (2013), pp. 181-189
- V Virolainen, S., Suppala, I. and Sainio, T., Continuous ion exchange for hydrometallurgy: purification of Ag(I)-NaCl from divalent metals with aminomethylphosphonic resin using counter-current and cross-current operation, *Submitted*

## AUTHOR'S CONTRIBUTION

The author of this thesis is the first author in all listed publications. In detail, the author's contribution to each publication was as follows:

- I Design of experimental work. Execution of the major part of the experiments. Interpretation of the data. Preparation of manuscript.
- II Design of experimental work. Interpretation of the data. Modeling and data fitting. Preparation of manuscript.
- III Design of experimental work. Interpretation of the data. Preparation of manuscript.
- IV Design of experimental work, except for the filtration tests. Interpretation of the data (except filtration). Modeling. Preparation of manuscript, with the exception of the filtration sections.
- V Design of experimental work. Interpretation of the data. Preparation of manuscript.

## NOMENCLATURE

### Symbols

|                          |   |
|--------------------------|---|
| $\alpha_{i,j}$           | separation factor between components i and j, -                                       |
| $\beta_{i,j}$            | ratio of fractions extracted between components i and j, -                            |
| A, B                     | ions  |
| $c^0$                    | initial concentration, mol/L  |
| $c_i$                    | concentration in the aqueous phase for component i, mol/L                             |
| $D_i$                    | distribution ratio for component i, -   |
| $D_{L,i}$                | axial dispersion coefficient, m <sup>2</sup> L/s mol                                  |
| $D_{s,i}$                | diffusion coefficient in resin pore, m <sup>2</sup> /s                                |
| $E_i$                    | fraction extracted for component i in solvent extraction, -                           |
| $F$                      | phase ratio between liquid and solid phases, -  |
| Gluc                     | glucose group in N-methylglucamine functional resin (IRA-743)                         |
| $\overline{\text{HA}}$   | acidic solvent extraction reagent   |
| $K_i$                    | affinity parameter in ion exchange, L/mol   |
| $k_L$                    | mass transfer coefficient, 1/s  |
| $\text{M}^{n+}$          | metal cation with charge n+   |
| $\text{MA}^{n-}$         | anionic complex of metal M with charge n-   |
| $\overline{\text{MA}}_n$ | metal complex of acidic solvent extraction reagent                                    |
| $n_i$                    | non-ideality parameter, -   |
| $Q$                      | amount of functional groups in resin, eq/L resin                                      |
| $q_{\text{eq},i}$        | equilibrium concentration in solid phase,   |
| $q_i$                    | concentration in resin phase for component i, mol/L resin                             |
| R                        | alkyl group in solvent extraction reagent<br>or resin matrix of an ion exchange resin |
| $R_p$                    | mean radius of resin particle, m  |
| $u$                      | velocity of liquid phase, m/s   |
| $V$                      | volume, L   |
| $\text{X}^-$             | univalent anion   |
| $z$                      | axial coordinate in ion exchange column, m  |

*Note: These definitions and/or symbols apply to the summary part of the thesis, and different symbols or definitions may be used in the attached publications.*

## Abbreviations

|        |   |
|--------|---|
| AOD    | argon oxygen decarburization              |
| APC    | aminopolycarboxylate chelant              |
| BV     | bed volumes (in ion exchange)             |
| EEE    | electrical and electronic equipment       |
| EPR    | extended producer responsibility          |
| EoL    | end-of-life                               |
| EoW    | end-of-waste                              |
| FLW    | fluorescent lamp waste                    |
| ITO    | indium tin oxide                          |
| LCD    | liquid crystal display                    |
| PS-DVB | polystyrene divinylbenzene                |
| REE    | rare earth element(s)                     |
| REO    | rare earth oxide                          |
| RIP    | resin in pulp                             |
| SMB    | simulated moving bed                      |
| UNEP   | United Nations Environment Programme      |
| WEEE   | waste electrical and electronic equipment |



## 1 INTRODUCTION

The term 'Secondary raw material' is not defined in the EU's, or in any national, legislation, but it is widely used to describe a waste that has become a possible raw material [1,2]. However there is an official reverse term known as the end-of-waste (EoW) or EoW criteria. EoW is defined within the EU Waste Framework Directive 2008/98/EC [3], such that a material is no longer a waste when it has gone through a recovery operation in certain legal conditions. After this, some material formerly defined as waste is defined as a product or secondary raw material. The EoW criteria are defined separately for different wastes. The purpose of the directive in the big picture is to guide society towards recycling, so that different wastes should be seen more as possible raw materials than a useless burden [4].

Today, hydrometallurgical separation methods are an essential part of extractive metallurgy, and utilized in various metal refining plants throughout the world. As rich ores for metals refining become scarce, the metallurgical industry has been turning to lower grade ores, solid and liquid side and waste streams in metal refining plants, and other forms of waste. For all of these potential sources of raw materials, hydrometallurgical separation methods are very suitable. They are known to be flexible, highly selective and environmentally friendly methods for the treatment of raw materials with varying amounts and compositions. Their energy consumption is also lower, compared to more conventional pyrometallurgical methods. It is often stated that hydrometallurgical methods have a large potential for resolving the future challenges in producing essential metals through environmentally and economically sustainable practices.

In principle, any object containing metals may be suitable as a raw material. In practice, the price of the obtainable metal together with the quantity and quality of the material define the viability of recovery. Some of the most important secondary raw materials for metals are presented more closely in Sections 3 and 4. They include, for example, side streams and wastes (both solid and liquid) from the mining industry, waste electrical and electronic equipment (WEEE) – including liquid crystal display (LCD) panels and fluorescent lamps, batteries, etc. – and used catalysts. The valuable metals in these include, for example, minor metals (Ge, In, Mo, Re), noble and precious metals (Ag, Au, Pd, Pt), valuable base metals (Co, Cu, Ni) and rare earth elements (REE). Currently end-of-life (EoL) recycling rates of these metals, according to a United Nations Environment Programme (UNEP) report by Graedel et al. [5] are: Ge < 1%, In < 1%, Mo = 30%, Re > 50%, Ag = 30-50%, Au = 15-20%, Pd = 60-70%, Pt = 60-70%, Co = 68%, Cu = 43-53%, Ni = 57-63%, REE < 1%. This clearly shows the potential of secondary raw materials as a source for many different metals.

As the world's population increases and people use more high-tech products, the usage of various natural resources in the coming decades requires more and more attention. In particular, the depletion of oil resources has been discussed widely. With metal resources, the situation is generally not as acute, but, ultimately, they are not inexhaustible. It has been stated in a UNEP report concerning metal recycling by Reuter et al. [6] that the global

demand of metals could increase up to ninefold when developing countries reach the same standard of living as developed countries. The EU produced a list of 14 critical raw materials in 2010 [7], highlighting uncertainty in the balance of demand and supply for certain elements. As a consequence EU is studying a possibility of stockpiling these raw materials [8], which include: antimony (Sb), beryllium (Be), cobalt (Co), fluorspar (CaF<sub>2</sub>), gallium (Ga), germanium (Ge), graphite (C), indium (In), niobium (Nb), platinum group metals (PGMs), rare earth elements (REEs), tantalum (Ta) and tungsten (W).

At the same time the use of metals is increasing, the primary ore deposits that are utilized become ever more low grade. Thus utilizing new primary metal deposits may require larger investment, in many forms, for example in the field of technology. Therefore, it makes sense to increase the recovery of metals from secondary raw materials, which in point of fact may be of a much higher grade than primary ores, or at least the raw material is more readily obtainable. Despite being seen as a promising metal resource, there are many practical difficulties in utilizing secondary raw materials, concerning mainly economics, logistics, technology and complexity of raw materials. Today, the recovery rates for metals in secondary raw materials vary from a few percent up to 75%, depending on the metal, the raw material and the processing route used [6].

Currently a widely-used term, 'Urban Mining' simply means the utilization of anthropogenic wastes as metal resources. Jesse Stallone, an expert in the field of Urban Mining, gives a broader definition [9]: "*The process of reclaiming compounds and elements from products, building and waste.*" The phrase 'Urban Mine' itself is an Australian trademark [6]. In addition to economic viability, metal recycling is also environmentally friendly, as many of the metals are categorized as hazardous waste and cannot be landfilled. The energy consumption, and therefore greenhouse gas emissions, of metals produced by recycling is also often lower than in primary production [6]. Due to the environmental risks, legislation concerning metal-containing waste, especially in developed countries, is tightening continuously; this is also a driving force for metal recycling. An approach called extended producer responsibility (EPR), introduced by the OECD in 2001 [10], has become an important tool for controlling the end-of-life (EoL) processing of many waste devices, for example vehicles and waste electrical and electronic equipment (WEEE) [11]. EPR means that manufacturers are responsible for their products being disposed of appropriately when they become waste. EPR is especially followed in the EU countries, Switzerland and Japan. In the United States and Canada, it is applied in only some states and provinces [12]. To force environmentally sustainable manufacturing and EoL processing of electrical and electronic equipment (EEE), the EU launched two directives in January 2003. The first prevents the use of certain hazardous substances in EEE [13] and the other, which was recast in 2012, deals with EPR [14,15]. In Switzerland and Japan there are also several laws and directives concerning EPR, and in India and Thailand, for example, there are proposals to change the legislation towards EPR in WEEE management [12].

This thesis focuses primarily on the hydrometallurgical separation methods needed in order to recover metals from secondary raw materials. The two main methods studied are solvent extraction and ion exchange; and along with these, (selective) leaching is also studied. The purpose is also to enhance knowledge of the secondary raw materials that are suitable as valuable metal sources, from economic, environmental and social points of view. In order to give background to these objectives, the valuable metals themselves are also studied; for example their aqueous chemistry, geology and markets.

## **2 OVERVIEW OF POTENTIAL HYDROMETALLURGICAL SEPARATION METHODS FOR SECONDARY RAW MATERIALS**

As can be inferred from the word, hydrometallurgy is defined as a field of metal processing that is connected to water [16]. Thus hydrometallurgical separation methods are those in which one, or more, of the phases related to the process is aqueous. The cyanide process for gold recovery and Bayer process for aluminum recovery from Bauxite started so-called modern hydrometallurgy in the 19<sup>th</sup> century [16].

Hydrometallurgical solutions are typically generated by dissolving metals present in the raw materials in acids or bases. Metals can be, and usually more-or-less are, separated already in the dissolution step when one or more of the metals are not soluble in the solvent used. The reverse process, precipitation (including cementation), is also widely used as a separation method. Alongside these, hydrometallurgical separation is also often performed by solvent extraction or by means of solid ion exchangers. These methods were first used for the separation of rare earth elements (REE) and actinides, but soon their application spread to all kinds of metals [17]. Other hydrometallurgical separation methods include, for example, separation with ionic liquids, membrane separation, and adsorption onto activated carbon or other natural materials. Once the metals have been separated from each other, pure metal can be produced for example by precipitation, cementation or electrolytically. By electrochemical methods metals may also be purified further if necessary.

Biohydrometallurgy is a widely studied area of hydrometallurgy today, but the industrial utilization of bioleaching started already in the 1950s [18]. In addition to bioleaching, biohydrometallurgy can also be used in the treatment of effluents at mines and plants [19–22], and metal recovery from secondary raw materials [23,24].

Hydrometallurgy has become an ever increasingly viable option for pyrometallurgy since the mid 20<sup>th</sup> century. This is due to the fact that primary ores for metal refining have become more and more low grade, for which hydrometallurgical methods are often more suitable. As the concentrations of metals in secondary raw materials are often small, and also highly variable, hydrometallurgical recovery methods are extremely suitable for the treatment of such materials because they are much more adjustable than pyrometallurgical methods. Hydrometallurgical methods also have features and applications that can have significant positive effects on the environmental aspects of metallurgical plants [22]. Hydro- and

pyrometallurgical methods are compared in Table 1, based on some typical considerations in extractive metallurgy.

Table 1. Comparison of hydro- and pyrometallurgy.

| Feature  | Hydrometallurgy | Pyrometallurgy |
|--|-----------------|----------------|
| Sulfur dioxide generation                        | +               | -              |
| Gaseous emissions to atmosphere                  | +               | -              |
| Aqueous emissions to environment                 | -               | +              |
| Energy consumption                               | +               | -              |
| Treatment of low grade and complex raw materials | +               | -              |
| Treatment of high grade ores                     | -               | +              |
| Capital costs                                    | +               | -              |
| Operation costs                                  | -               | +              |
| Emission control                                 | +               | -              |
| Scale of operation                               | -               | +              |
| Selectivity/Product purity                       | +               | -              |

## 2.1 Leaching

Leaching and precipitation were the first methods used in hydrometallurgy [16]. They are opposite unit processes; in leaching, the thermodynamic conditions in which a mineral is dissolved, are utilized. On the contrary, in precipitation, the conditions in which the metal or metals are insoluble are used. Typical leaching reagents include water, acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , etc.), bases ( $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ ), salt solutions and combinations of these. Processes may be enhanced by the addition of oxidizing ( $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{HClO}$ ,  $\text{NaClO}$ ) or reducing ( $\text{Fe}^{2+}$ ,  $\text{SO}_2$ ) agents. Equilibrium and kinetics of leaching are often favored by more aggressive conditions, compared to NTP, and thus elevated temperature and/or pressure is commonly used. Several methods to perform the leaching process exist, including: heap leaching (Fig. 1), dump leaching (heap without crushing), reactor leaching, vat leaching, autoclave leaching (high pressure and temperature) and in-situ leaching (leachate pumped in the ore deposit).

Microorganisms can have an effect on the structure of the rocks. This feature is used in heap and dump leaching of, especially, sulfide ores of gold and copper, in a process called bioleaching [19,25,26]. Talvivaara mine in Sotkamo, Finland, exploits bioleaching, producing nickel zinc, copper and cobalt in arctic conditions [27]. In bioleaching, bacteria oxidizes  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , which then oxidizes the minerals [28]. Bioleaching is expected to reduce investment and operating costs compared to conventional leaching processes. It is also often seen as more environmentally sensitive process, since the use of strong chemicals, energy and aggressive conditions are reduced lowered [19,25,26]. Other methods that have been studied for improving the performance of conventional leaching are for, example, microwave [29,30] and ultrasound [31,32] treatments, but no industrial applications for these have been reported. Ultrasound treatment in particular has been mentioned in many cases related to the leaching



of waste materials and/or precious metals [32], but economic considerations have prevented, and will likely continue to prevent, industrial application in the near future.

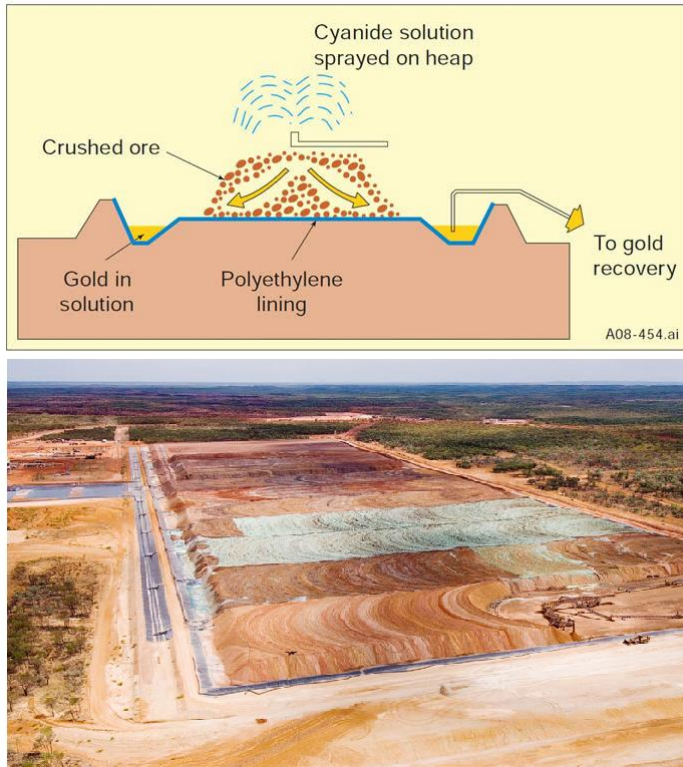


Figure 1. Schematic of the principle of gold heap leaching (upper), and a picture of a copper heap leach pad (lower) [33,34].

## 2.2 Precipitation and cementation

Precipitation is an essential unit process in the hydrometallurgical industry. It is based on the solubility, or actually the lack of it, of the product. In practice, precipitation is done by hydroxide (CaO or Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, NaOH, NH<sub>4</sub>OH) [35], sulfide (FeS, CaS, Na<sub>2</sub>S, NaHS, NH<sub>4</sub>S, H<sub>2</sub>S, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) [36] or carbonate [37]. Precipitation with all of these alternatives is pH dependent, so the process is controlled by monitoring and adjusting pH (Fig. 2) [36,37].

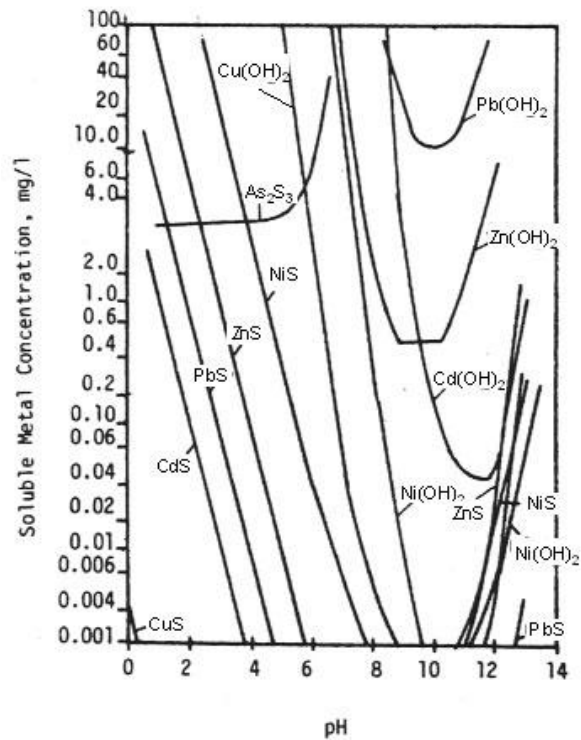


Figure 2. Solubility of some metal sulfides and hydroxides as function of pH [38].

Cementation is an electrochemical process, in which a metal in the aqueous solution is reduced to its elemental form by some more electropositive metal in solid form (Fig. 3). The general reaction equation for cementation is thus:



Zn powder is often used as a cementation reagent, because it is more electropositive than many metals. Other cementation reagents are, for example, aluminum, copper and iron. In industrial hydrometallurgy, cementation was used until the 1970s as a mainstream unit

operation, and is also widely used today, in the recovery of gold and silver from cyanide solutions (the Merrill-Crowe process) [39].

Currently new Au leachates, for example thiosulfate, are being investigated to replace hazardous cyanide, and large scale operation with ion exchange as separation method has been launched in Barrick's Goldstrike mine in Nevada [40]. Cementation is also seen as a possible recovery method from such solutions, since carbon adsorption – currently a mainstream industrial unit process – is not suitable for thiosulfate solutions [41,42]. Copper is cemented – often with scrap iron – from various solutions, but industrial use has diminished recently [43]. Zn sulfate solutions are often purified in industrial processes before electrowinning by cementation with Zn powder and some activators [44].

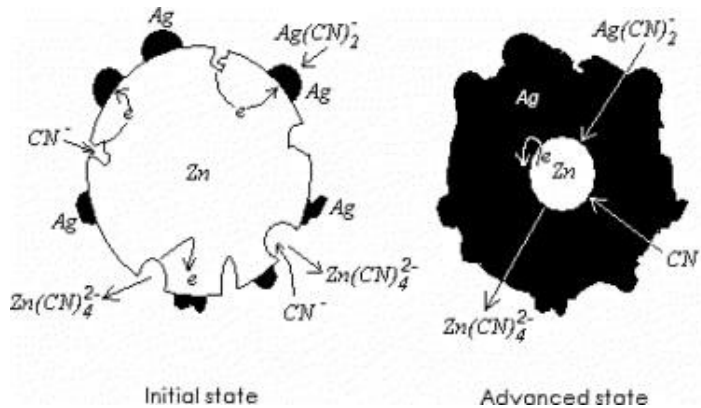


Figure 3. Cementation of Ag from cyanide solution [45].

### 2.3 Solvent extraction

Industrial utilization of solvent extraction in hydrometallurgy began with the Manhattan project in the 1940s [17]. To the present day, solvent extraction has been applied to separate almost every element in the periodic table [46]. It is also applied widely in the separation of organic compounds [47,48]. In solvent extraction, metals are extracted with a suitable reagent to a water-insoluble organic phase, which is typically, for example, a kerosene-based hydrocarbon solvent. While mixing, one of the phases is dispersed within the other one creating large surface area, over which the extractable species moves to the other phase (Fig. 4).

The following three fundamental quantities are used to describe the efficacy of the solvent extraction process: the Distribution ratio,  $D_i$ , is defined with analytical concentrations of the component  $i$ . Fraction extracted,  $E_i$ , describes the extent of extraction and may also be presented as a percentage. The separation factor,  $\alpha_{i,j}$ , describes selectivity between two components, and is by definition written so that it is larger than unity [49]:

$$\begin{aligned}
 D_i &= \frac{\bar{c}_i}{c_i} \\
 E_i &= \frac{D_i}{D_i + \frac{V}{V}}, \\
 \alpha_{ij} &= \frac{D_i}{D_j}
 \end{aligned}
 \tag{2}$$

where bars above the symbols refer to the organic phase.

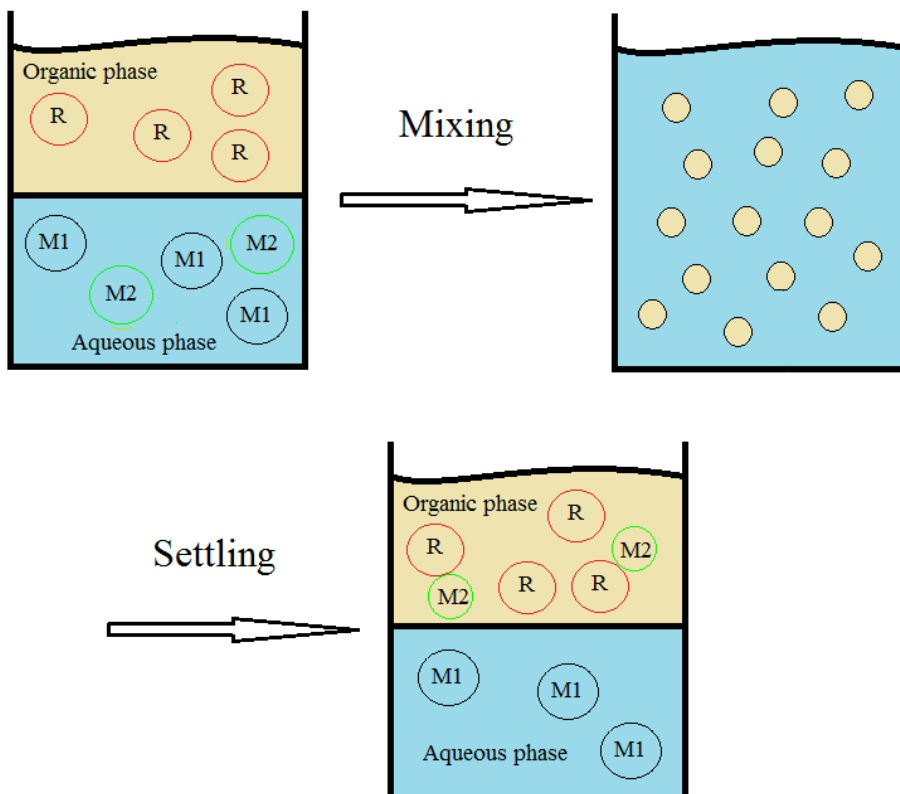


Figure 4. Principle of solvent extraction. Symbols: R = Reagent, M1 and M2 are different metals.

In the author's own opinion, the separation factor describes well the relations of metals' theoretical affinities to the phases. Consider, for example, two metals  $i$  and  $j$  with equal total concentrations in a system, with fractions extracted of 99.9% and 90% respectively. For this kind of equilibrium to take place,  $i$  needs to have a lot higher affinity to the target (organic)

phase and thus the value of the separation factor (=1000) describes the ratio of affinities well. However, if we consider practical application, the selectivity is not good and the purity of i in the organic phase is only 53%. Thus, in the author's opinion, purities describe the selectivities better. Or then ratio of fractions extracted, symbol  $\beta_{i,j}$  used in this thesis in Section 6.1, may be calculated and used as a quantity of selectivity:

$$\beta_{i,j} = \frac{E_i}{E_j} \quad (3)$$

According to Ritcey [50], solvent extraction reagents are divided into three categories, based on their extracting mechanism:

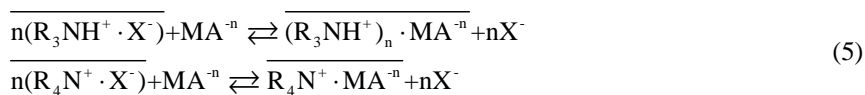
1. Extractants involving compound formation. This mechanism is involved in Publications I and IV.



Where  $M^{n+}$  metal cation with charge n+  
 $\overline{HA}$  extractant  
 $\overline{MA_n}$  metal complex of extractant

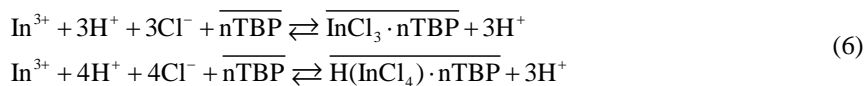
Bars refer to the organic phase.

2. Extractants involving ion association. This mechanism is involved in Publication IV.



Where  $R_3N$  tertiary amine  
 $R_4N^+$  quaternary amine  
 $MA^{-n}$  anionic complex of metal M with charge n-

3. Extractants involving solvation. The mechanism cannot be generalized for a simple reaction equation, but, as an example, reaction equations for In extraction from HCl by TBP are given [51]. This mechanism is involved in Publication I.



The first group consists of acidic extractants that extract metals either by chelating or a cation exchange mechanism, and includes organophosphoric acid derivatives, carboxylic acids and hydroxyoximes. The second group consists of amine extractants, which are either strong (quaternary amines) or weak (secondary and tertiary amines) anion exchangers. The mechanism in Eq. 5 is given for a univalent counter ion. The third group includes ethers, esters, ketones, aldehydes and alcohols, together with organophosphoric acid derivatives with oxygen or sulfur as an electron donor atom. The mechanism is solvation of neutral inorganic molecules or complexes [50]. Examples of the reagents, with their practical applications in hydrometallurgy, are given in Table 2. From these, D2EHPA and TBP are used in Publication I, and D2EHPA, LIX<sup>®</sup>84-I, trioctylamine and Aliquat<sup>®</sup>336 in Publication IV.

Although nowadays there is a wide range of equipment available for solvent extraction in hydrometallurgy [47,50], the most common form is still a simple mixer-settler (Fig. 5 a) and c)), in which the actual reaction takes place in a continuous mixing unit. After the mixer is much larger settler unit, in which the phases are separated from each other. Another industrially important type of solvent extraction equipment is the column extractor (Fig. 5 b) and d)), of which there are several variations available [50].

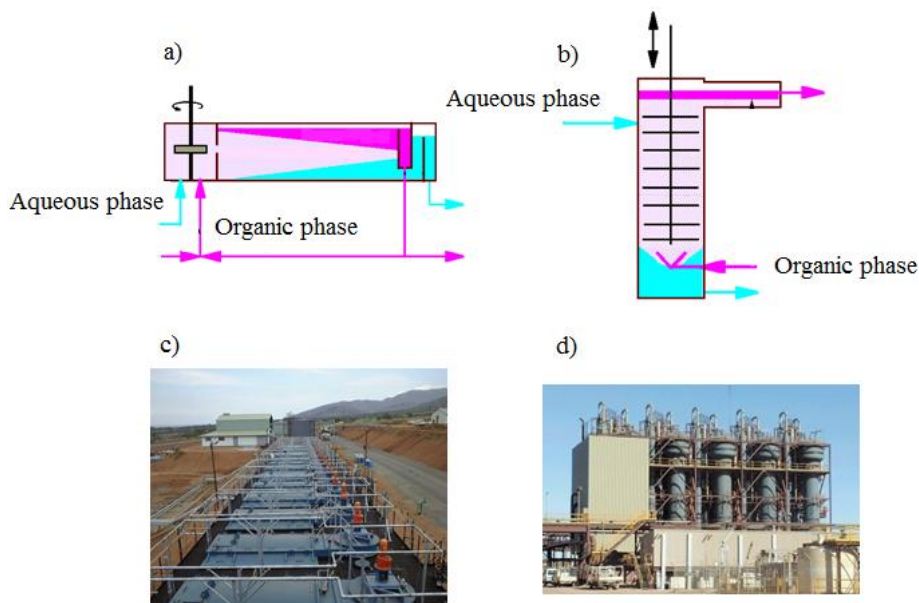


Figure 5. Schematics of a) a mixer-settler unit [52] and b) a column extractor [52]. c) and d) are respectively real life photos of those from Kasese Cobalt Company Limited (KCCL) [53], Uganda and Olympic Dam, Australia [54].

Table 2. Some industrially important and commercially available solvent extraction reagents [50,55–61].

| Group            | Commercial name                                      | Chemical name (active compound)             | Structure                              | Manufacturer                               | Applications                |
|------------------|--|---|--|--|-----------------------------|
| Compound forming | D2EHPA   | Di-(2-ethylhexyl) phosphoric acid           | <p>R = 2-ethylhexyl</p>                | Several                                    | Zn, U, Mo, In, REE          |
|                  | Cyanex <sup>®</sup> 272<br>Ionquest <sup>®</sup> 290 | Bis-(2,4,4-trimethylpentyl) phosphinic acid | <p>R = 2,4,4-trimethylpentyl</p>       | Cytec<br>Rhodia                            | Co/Ni separation, REE,<br>V |
|                  | LIX <sup>®</sup> 84-I                                | 2-hydroxy-5-nonylaceto-phenone oxime        | <p>R = C<sub>9</sub>H<sub>19</sub></p> | BASF                                       | Cu                          |
|                  | Versatic <sup>™</sup> 10                             | Neodecanoic acid                            | <p>R = alkyl group</p>                 | Resolution<br>Performance<br>Products Ltd. | Cu, Co, Ni, Fe              |

Table 2. Continued.

| Group                  | Commercial name               | Chemical name<br>(active compound) | Structure   | Manufacturer | Applications                 |
|------------------------|-------------------------------|------------------------------------|-------------|--------------|------------------------------|
| <b>Ion associating</b> | E.g. Alamine <sup>®</sup> 336 | Tri-n-octylamine                   |             | BASF         | U, V, W, Mo                  |
|                        |                               |                                    | R = n-octyl |              |                              |
|                        | Aliquat <sup>®</sup> 336      | Quaternary ammonium salt           |             | BASF         | U, V, W, Mo                  |
|                        |                               |                                    | R = octyl   |              |                              |
| <b>Solvating</b>       | TBP                           | Tri-n-butylphosphate               |             | Several      | U, V, Mo, Nb/Ta              |
|                        |                               |                                    | R = n-butyl |              |                              |
|                        | Cyanex <sup>®</sup> 921       | Trioctylphosphineoxide             |             | Cytec        | U, Nb/Ta separation, Re, REE |
|                        |                               |                                    | R = octyl   |              |                              |



## 2.4 Ion exchange

During the 1800s and early 1900s, research was conducted with ion exchange, but, as with solvent extraction, practical application began with the Manhattan project in the 1940s [17,62]. In ion exchange, an ion, which is associated with the fixed charge in the ion exchange material, is replaced by another ion. The process is stoichiometric (Fig. 6). The process in which adsorbent, which can also be an ion exchanger, takes some species from solution is not, by definition, ion exchange, but sorption [62]. Despite that, generally when people talk about ion exchange as a separation method, the term usually covers both mechanisms and only solid separation materials. And because the ion exchange process often involves sorption of electrolytes etc., and vice versa, sorption processes may be accompanied with ion exchange [62].

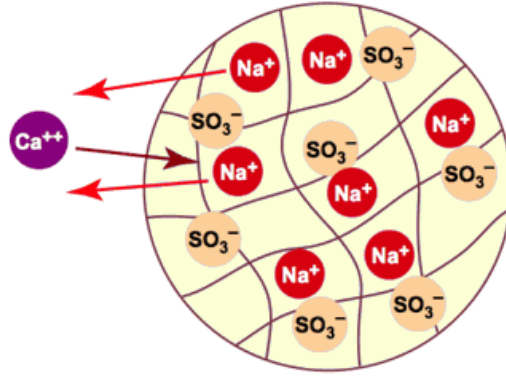


Figure 6. Principle of ion exchange [63].

As with solvent extraction, the distribution ratio,  $D_i$ , in ion exchange is defined with analytical concentrations of the component  $i$  and the separation factor,  $\alpha_{i,j}$ , as a ratio of the distribution ratios. The selectivity coefficient,  $k_{i,j}$ , is corrected with the valences of the metals [64]:

$$\begin{aligned}
 D_i &= \frac{q_i}{c_i} \\
 \alpha_{i,j} &= \frac{D_i}{D_j} \quad , \\
 k_{i,j} &= \frac{q_i^{|z_j|} c_j^{|z_i|}}{q_j^{|z_i|} c_i^{|z_j|}}
 \end{aligned} \tag{7}$$

where  $q_i$  is the concentration of component  $i$  in the resin phase.

Ion exchangers are based on many different materials which include for example: minerals, synthetic inorganic materials, ion exchange resins, ion exchange coals (activated carbon), liquid ion exchangers (solvent extraction reagents and ionic liquids), ion exchange membranes and cellulose ion exchangers [62,65]. Industrially, the most important group of these, excluding liquid ion exchangers, is ion exchange resins [65]. In the resins, as in solid ion exchangers in general, the reactive functional groups are attached to a matrix, which does not usually take part in the ion exchange process. The matrix is usually a polystyrene divinylbenzene copolymer (PS-DVB) or acrylic. Depending on the matrix material and fraction of the crosslinker (DVB), the physical structure of the resin may either be macroporous or a gel. In macroporous resin, the matrix has pores in which the solution can enter, while the gel type resin can be considered as a homogenous gel [62,65]. The resins are hydrophobic in nature, with the exception of their functional groups. Based on their functional groups, ion exchange resins can be divided into four groups. General reaction equations written for univalent ions (except for chelating resins) are also given for each group in the following list:

1. Strong cation exchangers



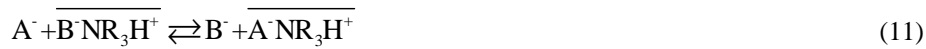
2. Weak cation exchangers



3. Strong anion exchangers



4. Weak anion exchangers



5. Chelating resins



In Eq. (9) the proton is marked as another cation, in order to highlight the fact that weak cation exchangers typically have good affinity to them, and thus they function better at higher pH than in very acidic solutions. Anion exchangers are not exclusively amines, but they are by far the most common ones in practice. Chelating resins act as multidentate ligands for polyvalent cations and often have good selectivity towards a certain metal because of the favorable structure of the cyclic complex that the functional groups form with the metal. Chelating resins are often weak cation exchangers. Examples of some practically important commercial resins are given in Table 3. It should be noted that the applications given are those ones provided by the manufacturer, and all of these resins have potential in hydrometallurgical separations.

In practical applications, ion exchange is usually done in columns (Fig. 7 a) and b)). After the resin has been saturated with the desired metal(s) taken from the feed solution, the adsorbed metals are eluted. Finally the resin is converted to the desired ion form, if needed, by acid, base or salt solution. Between these process steps the resin bed is usually washed with water or some salt solution because the feed, elution and regeneration solutions preferably should not be mixed. Ion exchange can be also done so that there are continuous raffinate and eluent flows coming out from the process [62,65]. In this multicolumn, so called simulated moving bed (SMB), setup the locations of the ingoing (and out coming) solutions are changed periodically, either by valves or by moving the columns (Fig. 7 c)). This setup is used in Publication V for the purification of Ag-NaCl solution. SMB operation allows more efficient utilization of the resin and eluent consumption is reduced [66]. In the hydrometallurgical industry, one increasingly prevalent setup in ion exchange is the so-called resin in pulp (RIP) process, in which the resin is mixed with the leaching slurry, thus reducing the number of process steps [67].

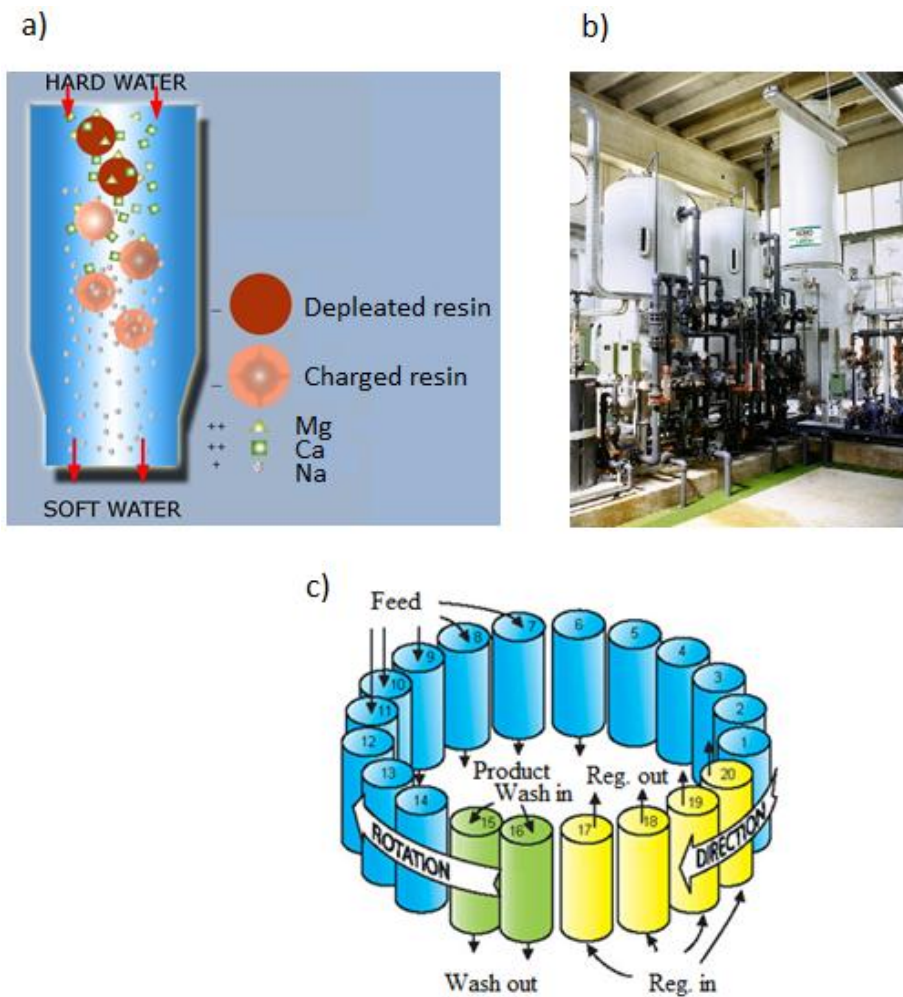


Figure 7. Ion exchange equipment: a) Schematic of ion exchange column [68], b) real ion exchange columns [69] and c) schematic of SMB set-up [70].

Table 3. Some industrially important and commercially available ion exchange resins [67,71–77]. Amberlite™ IRA-743 has been used in Publication II, and Lewatit® TP-260 in Publications III and V.

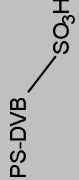
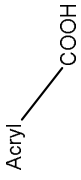
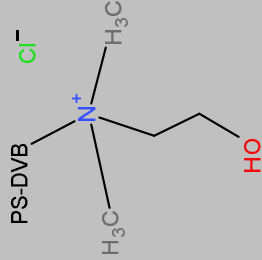
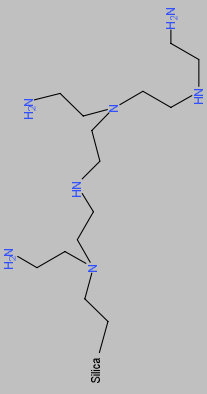
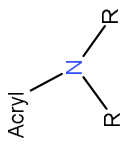
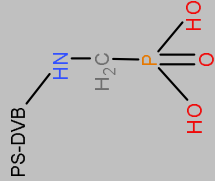
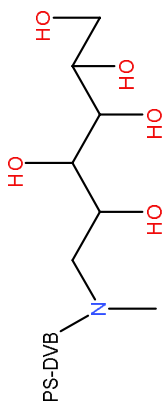
| Group                           | Commercial name   | Functional group    | Structure  | Manufacturer | Applications                       |
|---------------------------------|-------------------|---------------------|--|--------------|------------------------------------|
| <b>Strong cation exchangers</b> | Dowex™ 50         | Sulfonic acid       |  | Dow          | Food processing                    |
|                                 | Purolite® C-104   | Carboxylic acid     |  | Purolite     | Water treatment, transition metals |
| <b>Strong anion exchangers</b>  | Amberlite™ IRA410 | Quaternary ammonium |  | Rohm&Haas    | Water treatment                    |

Table 3. Continued.

| Group                 | Commercial name                        | Functional group           | Structure   | Manufacturer        | Applications                    |
|-----------------------|--|----------------------------|---|---------------------|---------------------------------|
| Weak anion exchangers | WPGM <sup>®</sup> (WP-1 <sup>®</sup> ) | Polyamine                  |   | Purity Systems Inc. | Cu, and variety of other metals |
|                       | Amberlite <sup>™</sup> IRA-67          | Tertiary amine             |  | Rohm&Haas           | Water treatment                 |
| Chelating resins      | Lewatit <sup>®</sup> TP-260            | Aminomethylphosphonic acid |   | Lanxess             | Cu/Co, Zn/Co, U, Ti             |
|                       | Amberlite <sup>™</sup> IRA-743         | N-methylglucamine          |  | Rohm&Haas           | B, Ge                           |

### **3 WASTES AND SIDE STREAMS IN MINING INDUSTRY SUITABLE FOR VALUABLE METALS RECOVERY**

Liquid and solid side streams and wastes in metallurgical industry are further possible secondary raw materials. Some of the most important of these are listed in this Section. It should also be noted that these residues always contain significant amounts of the primary metal itself, and recovery of this can also be the target, if economic, legislation and/or technical aspects develop in this direction.

#### **3.1 Steelmaking dusts**

The author's own data, together with a detailed discussion about the recovery of metals from steelmaking dusts are presented in Section 6.4 and Publication IV. Steelmaking dusts, which are formed at a rate of approximately 15-30 kg/ton of steel produced [78], contain several metals which can be seen as a target metals in secondary processing. The main compounds in steelmaking dusts are Fe, Zn and Ca. The concentration of Zn varies, depending on the dust, from a few percentage to tens of percentage, while in Zn minerals, the content is typically 5-15% [79]. Typical minor compounds (concentration 0.01-10 wt.%) in these dusts include Cr, Mg, Mn, Ni and Pb [80-87]. The presence of Mo has been reported by Henderson and Roddis [88], Neumeier and Adam [82], Nogueron and Espi [89], Shimakage et al. [90], and Stefanova et al. [87].

Preferably the steelmaking dusts are recycled back to the pyrometallurgical process. However, the composition of the dust may be unsuitable for recycling and, if this is the case, then hydrometallurgical processing becomes attractive. Also, if the dust contains sufficient amounts of some high value metals, then end products will have to be produced through hydrometallurgical processing.

In hydrometallurgical recovery processes for steelmaking dust, the most common target is Zn. Though the leaching yield of Zn with  $H_2SO_4$  is good, Fe is also leached if pH is not controlled [86,91]. The use of HCl [91,92] or NaOH [87] has been proposed to overcome this problem. Precipitation [90,93-96] and solvent extraction have been the most widely used separation methods for dust leachates. D2EHPA, due to its well-known good affinity towards Zn, has been the most applied solvent extraction reagent [95,97,98], though other reagents have been also used with good results [93,98,99]. In this thesis (See Section 6.4 and Publication IV),  $H_2SO_4$  or water leaching and solvent extraction recovery of Zn and Mo are studied, and suggested as potential recovery methods for argon oxygen decarburization (AOD) dusts. Filtration of the slurry, an essential step in the recovery process, is also discussed in Publication IV.

### 3.2 Zinc plant residues

In zinc refineries solid wastes, for example jarosite, goethite and neutral leach residue, are suitable secondary raw materials for other metals. Valuable metals in these residues are for example Ag, Au, Co, In, Ge, Sb and Tl [6,100]. The Zn and Fe concentrations are similar to the steelmaking dusts, and Pb is present as a major impurity, with a typical concentration of a few percentage [6,101]. Ag concentrations are usually less than 100 mg/kg, but can be much higher in individual cases [100]. From other possible target metals, concentrations of In vary up to 150 mg/kg [102] and concentrations of Ge vary from a few mg/kg up to 5000 mg/kg [103]. Metals have been removed from the aforementioned residues for both, economic and environmental reasons [6,104].

Pyrometallurgical processes are conventionally used for the enrichment of by-product metals from Zn plant residues. Hydrometallurgical methods, on the other hand, have proven to be suitable for producing high purity end products. Rosato et al. [105] used thiourea leaching and carbon adsorption for Ag and Au recovery from a neutral leach residue. In the work of Berezowsky et al. [106], cyanide leaching did not give good yield for Ag from a similar raw material until the starting material was roasted with lime. On the other hand thiocyanate and thiosulfate have been reported to leach Ag without pretreatment. The strong anion exchanger, AV-17-10P, among a variety of tested resins, and one activated carbon adsorbent, were found to be suitable for further purification [107]. Ju et al. [108] leached heavy metals and Ag with good yields from a jarosite residue with 6 M  $\text{NH}_4\text{Cl}$  solution, but did not present any method for the separation of valuable metals from these leachates.

Generally  $\text{H}_2\text{SO}_4$ , possibly with added oxidants, has been used for Ge, Ga and In leaching from Zn plant residues, and oxidants such as  $\text{NaClO}_3$  may be used to improve the yields [109]. Demarthe et al. [103] reviewed, in 1990, used and possible separation methods for Ge and In recovery in Zn plants, and concluded that, at that time, solvent extraction was the most popular separation method for both of these metals. Hydroxyoxime LIX<sup>®</sup>63 or 8-hydroxyquinoline Kelex 100 had been used for selective Ge recovery from sulfate solutions, and TBP for In recovery from chloride solutions. As stated in Publication I, D2EHPA is generally the most suitable reagent for In separation, and it has been reported to be suitable for both sulfate [110,111] and chloride solutions [112] from Zn plant residues. Ga may also be recovered by D2EHPA alongside In [112]. Huang [113] reported recovery of In, Ge and Ga by solvent extraction from sulfate solution, and recovery of Tl from NaOH leachate by precipitation at the Zhuzhou smelter. Hydroxamic acid YW100, D2EHPA and N,N'-di(1-methyl-heptyl)acetamide N503 were used as reagents for Ge and Ga extraction [113]. Wang et al. [114] used G315 extractant, which was developed for Ga and Ge extraction, but the structure remains unknown to the author at present. For sulfate solutions, ion exchange with anion exchangers and chelating resins has been used in many cases for Ge recovery, and it has been stated to function also for concentrated Zn solutions [115]. Fortes et al. [116,117] found that iminodiacetic acid functional resin is the best choice for ion exchange recovery of In from



simulated zinc residue leachate. In Publication II of this thesis, a chelating resin was successfully used to recover Ge from concentrated ZnSO<sub>4</sub> solution.

### 3.3 Spent Bayer liquor and red mud from alumina production

Spent Bayer liquor, an aqueous alkaline waste from the production of alumina from Bauxite by the Bayer process, is globally the major raw material for gallium production (273 tons in 2012) [118]. The current price for Ga is 300 USD/kg [119]. Bauxite ore contains 20-80 mg/kg of Ga, which is concentrated during the process to 100-200 mg/kg in the aqueous solution [120]. Other metals of interest include REEs, vanadium and titanium.

There are four ways to recover Ga from spent Bayer liquors: precipitation, an electrochemical route, solvent extraction, and ion exchange. In precipitation methods, Ga and Al are precipitated by CO<sub>2</sub>, which enriches Ga in relation to Al. The process may contain lime precipitation as an additional purification step. The final Ga product is produced from the Ga-Al solution by electrolysis. The precipitation method is industrially widely used in the present day, and usually operated without the lime precipitation step. The electrochemical route is based on two electrolysis steps. Firstly Ga amalgam is produced from spent Bayer liquor by using a Hg anode. Many cationic impurities, for example V, are deposited at the cathode. In the secondary electrolysis, pure Ga metal is produced from a NaOH solution of Ga. The electrolytic method is still industrially in use, though it has been closed in many facilities because of the toxicity of Hg. The first electrolysis step with Hg may also be replaced by cementation with Al powder or an alloy of Ga and Al. Both, the precipitation and electrochemical methods have also a sulfide precipitation as an additional purification step [121].

Solvent extraction recovery of Ga from spent Bayer liquor was patented in the 1970s [122], but has not been used industrially [121]. 8-hydroxyquinoline Kelex 100 is the best known reagent, and it extracts Ga through a cation exchange mechanism. The extraction is not fully selective over Al and Na, but these can be scrubbed from the organic phase. After scrubbing, the Ga is stripped with ca. 1.5-2.0 M HCl, and may be purified further with a quaternary ammonium salt reagent (Aliquat<sup>®</sup>336) [123]. The solvent extraction of Ga from Bayer liquor has slow kinetics, which can be improved through the choice of diluent and modifier, ultrasound, or formation of a microemulsion [124–128]. In addition to slow kinetics, another reason for the industrial unpopularity of solvent extraction recovery is reagent loss due to solubility and degradation [121].

Ion exchange is currently the most popular method for Ga recovery from spent Bayer liquors. New installations in particular are based on the ion exchange method [121], which was first patented by Hirose et al. [129] in 1984. A bifunctional resin, having an oxime group and some other N, S or P atom containing functional group, which are capable of forming a complex with Ga, was used. Resins, synthesized by Hirose et al. [129], were compared with a strong base anion exchanger, another type of chelating resin and Kelex 100 extractant, and they

showed better performance. Today amidoxime functional Duolite ES-346 resin, for example, is often used in operation. In ion exchange processes the resulting solution may also be purified of heavy metals by sulfide precipitation, and the final product is made electrolytically. Advantages of the ion exchange operation, compared to the other hydrometallurgical separation methods, are minimal effects on the main alumina processing, good yield and selectivity, low energy consumption and low reagent losses. The drawbacks are degradation of the amidoxime group, in certain conditions, and co-extraction of V. The whole Ga recovery process by ion exchange is presented in Fig. 8 [121].

Red mud, the solid waste of the Bayer process, may contain relatively large amounts (50-200 mg/kg) of scandium, Sc, a highly valuable metal with a current price of 15500 USD/kg [130–132]. In addition to Sc, red mud produced from Jamaican bauxite is known to contain large amounts (~3000 mg/kg as oxides) of other REEs [132]. Wang et al. [130] studied leaching of Sc from red mud with mineral acids, and observed that H<sub>2</sub>SO<sub>4</sub> was the most efficient leachate. The best achieved yield was only 48%, but the authors indicated that, with optimization, a better yield could be achieved. Different kinds of solvent extraction reagents were tested for selective Sc recovery and D2EHPA, modified with TPB, gave the best selectivity at pH 0.25. AFI21 and AFI22 ion exchange resins were found by Smirnov and Molchanova [133] to be the best-performing, among a variety of resins, when used to recover Sc and U from H<sub>2</sub>SO<sub>4</sub> solutions of red mud. The resins contain N and P atoms in functional groups, but the authors did not describe the structure in more detail.

Ochsenkun-Petropulu et al. [134] studied the selective leaching of REEs, whose total concentration in Greek red mud may be up to 1%, which is only slightly lower than in low grade REE ores [135]. Among mineral acids, HNO<sub>3</sub> was the best leachate in terms of yield and selectivity over Fe. The best yields were achieved when the equilibrium pH was close to 0. Ochsenkun-Petropulu et al. [134] also claim that solvent extraction separation would be more efficient from HNO<sub>3</sub> media compared to HCl or H<sub>2</sub>SO<sub>4</sub>.

Bauxite contains 100-1400 mg/kg of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) [136–138], which has a current price of 12 USD/kg [131]. It may be recovered or enriched from red mud and/or Bayer liquor either by pyro- [139] or hydrometallurgical methods. Ion exchange with a strong basic anion exchanger (201x7) has been used for pure V<sub>2</sub>O<sub>5</sub> production from Bayer liquor, after precipitating and leaching with NaHCO<sub>3</sub> [136]. Mukherjee et al. [137] utilized carbon adsorption after hot water leaching of sludge from the Bayer process with a high V<sub>2</sub>O<sub>5</sub> content. However, the most practical separation methods, according to Mukherjee and Gupta [138], are crystallization and precipitation, since the V solutions are often reasonably concentrated (~20 g/L).

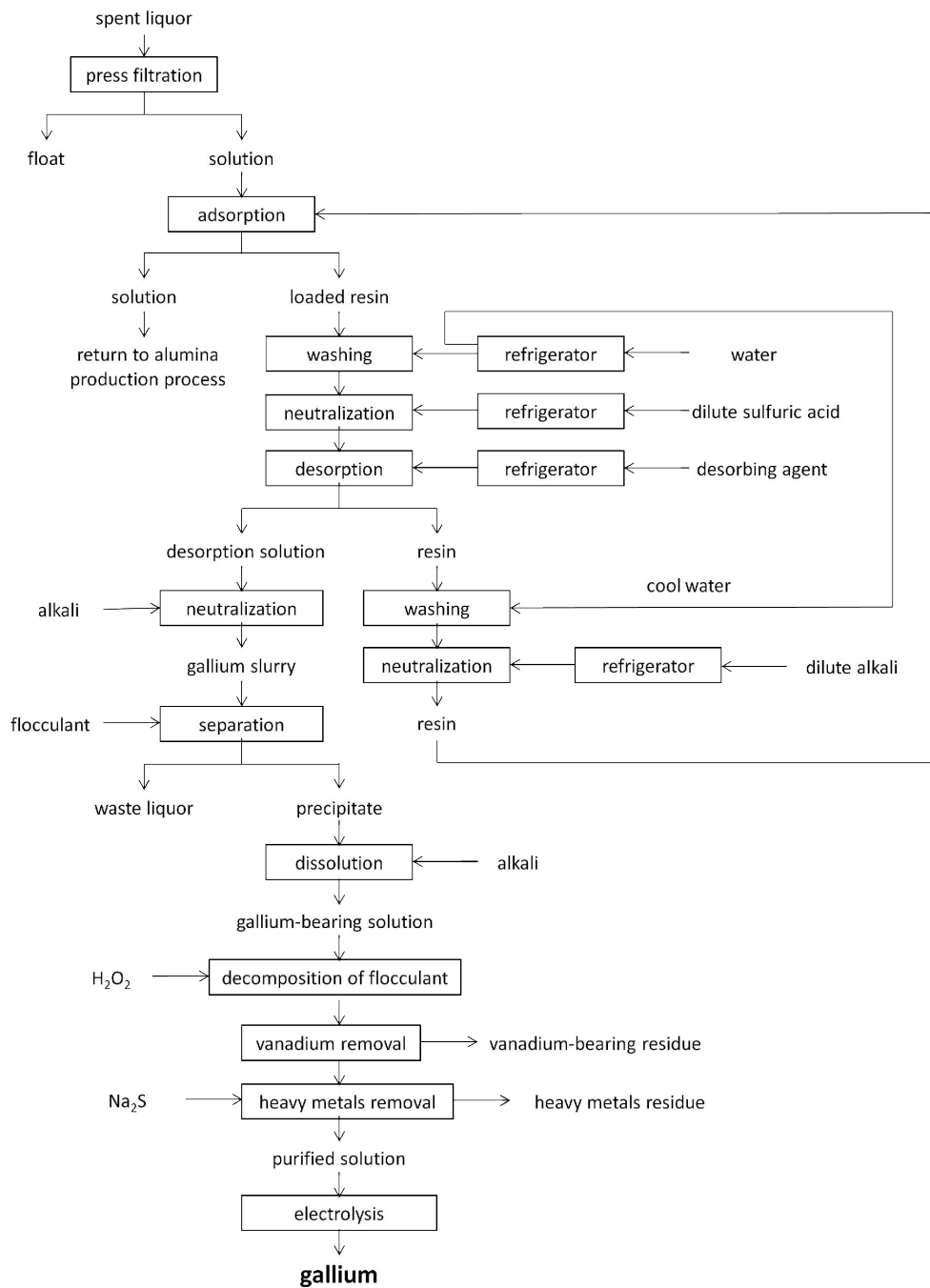


Figure 8. Flow sheet of a recovery process for gallium from spent Bayer liquor by ion exchange [121].

Like V, titanium may also be recovered from red mud by either pyro- or hydrometallurgical methods [140]. The  $\text{TiO}_2$  content in red mud varies between 4.8 and 7.1% [140–142], and the current price for pure Ti is 11 USD/kg [143]. It may be leached with  $\text{H}_2\text{SO}_4$ , but the leaching is not selective over Fe or Al, and the yield is also low (65–86%) [140,144], although this may be enhanced with ultrasound [141]. Deep et al. [145] discovered that Ti can be separated from HCl solutions of red mud by solvent extraction with bis-(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex<sup>®</sup>302) and bis-(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex<sup>®</sup>301). From  $\text{H}_2\text{SO}_4$  solution, Cyanex<sup>®</sup>272 is selective over Fe and Al, and the Ti may also be stripped with HCl, thus avoiding the use of  $\text{H}_2\text{O}_2$  [146], which forms a stable complex with Ti. D2EHPA and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) are seen as promising extractants for the selective recovery of Ti from red mud perchlorate solutions. Selectivity over some essential metals in red mud is achieved, but for stripping, concentrated acids and/or oxidants are needed according to Singh and Dhadke [147]. Though in a suggested Ti recovery process from smelting slag of red mud and Bauxite by Logomerac [148], D2EHPA modified with 2-ethylhexanol is stripped with  $\text{Na}_2\text{CO}_3$ . Silica gel impregnated with Cyanex<sup>®</sup>301 has been proven to yield pure Ti with a high yield from a HCl solution of red mud. Adsorption is selective over all other metals generally present in red mud, except Fe(III), Zr and Th. Ti was eluted with  $\text{H}_2\text{SO}_4$  with some added  $\text{H}_2\text{O}_2$ , and the other three metals adsorbed were eluted with oxalic acid [149]. Ion exchange membranes utilizing Donnan dialysis have been studied, but the process, though it is seen as a potential option, is far from industrial application [142,150].

### 3.4 Residues from the copper industry

The copper industry produces various solid wastes, such as slags, slimes and dusts, which have potential for secondary metal recovery. The earliest patents and articles about the recovery of metals from Cu industry residues date back to the 1960s. Usually at Cu plants the aim is to recycle residues, especially dusts, back to the pyrometallurgical process. The motives for using hydrometallurgical processing are the same as with, for example, steelmaking dusts and Zn plant residues discussed previously in this thesis; the composition of a residue may demand hydrometallurgical processing, especially if some valuable high purity end products are desired.

In pyrometallurgical Cu refining, the concentrate is smelted to produce a Cu-rich (over 70%) matte [151]. At this stage a slag phase is produced at a rate of approximately 2.2 tons per ton of Cu produced [152]. The main constituent of slag is crystalline fayalite  $\text{Fe}_2\text{SiO}_4$ . Table 4 gives production rates and chemical compositions of Chilean, Finnish and Congolese slags. Generally, the main metals are Fe (with an over 30% share) and Co, Cu, Pb and Zn with up to few percent share. Chilean slag has a relatively high Mo content, Congolese slag from Kinshasa has a high Co content, and Congolese slag from Lubumbashi has a high content of Zn. All of these are assigned as target metals, the recovery of which has been studied.

Table 4. Production rates and compositions of some copper smelter slags [153–155].

| Slag                          | Production rate, Mt/year | Fe, % | Cu, % | Co, % | Zn, % | Mo, % |
|-------------------------------|--------------------------|-------|-------|-------|-------|-------|
| <b>Chilean (Total)</b>        | 5                        | 43    | 1.1   | NA    | NA    | 0.3   |
| <b>Finnish (Total)</b>        | 0.35                     | 41    | 0.35  | NA    | 1.7   | NA    |
| <b>Congolese (Kinshasa)</b>   | 0.01                     | 28    | 1.35  | 4.09  | 1.7   | 0.01  |
| <b>Congolese (Lubumbashi)</b> | NA                       | 21    | 1.43  | 0.72  | 8.9   | NA    |

Sulfuric acid is, by far, the most widely used leachate for metals recovery from Cu slags. The difficulty is in achieving good selectivity for target metals over Si and Fe; their presence in leachates is not desired because they are harmful to downstream processing. With direct H<sub>2</sub>SO<sub>4</sub> leaching, 78 and 90% yields, respectively, for Cu and Co are obtained [156]. H<sub>2</sub>SO<sub>4</sub> roasting of Cu slag, followed by water leaching was patented by Lindblad and Dufresne in 1975 [157]. Later the method has been used by many authors [158–160] and yields for the main metals have been: Cu 88-95%, Co 87-95%, Zn 93%, Fe 83%, Ni 90%. HCl may also be used for roasting, and calcination has been reported to increase the yields for all metals to over 97% [161]. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as an oxidant has been reported to increase the yield of Cu to over 99% [162]. Ziyadanogullari [163] used sulfide roasting and achieved yields of over 96% for Co and Cu with perfect selectivity over Fe.

In order to avoid the roasting, Zhang et al. [155] used high temperature and NaClO<sub>3</sub> oxidant with H<sub>2</sub>SO<sub>4</sub> to leach Co, Cu and Zn selectively over Fe and Si. Pressure leaching with dilute H<sub>2</sub>SO<sub>4</sub> was studied by Anand et al. [164], and the yields for Co, Cu and Ni were over 95%, while the Fe remained in the solid phase. Rudnik et al. [165] used electrolytic NH<sub>3</sub>+NH<sub>4</sub>Cl dissolution followed by NH<sub>3</sub>+NH<sub>4</sub>Cl leaching and electrolysis to produce pure Cu and 92% Co. HCl is reported to enhance Zn selectivity and ammonia Cu selectivity [166]. Acma et al. [167] leached Co and Fe selectively over Cu with H<sub>2</sub>SO<sub>4</sub> by first reducing the converter slag with coke. After similar reduction, FeCl<sub>3</sub> can be used as a leachate to obtain over 92% yields for Co, Cu and Ni [168]. Satapathy et al. [169] patented a method in which the slag is treated with chloride and solid reductant to selectively leach Cu with NH<sub>4</sub>OH and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and subsequently Co and Ni with H<sub>2</sub>SO<sub>4</sub>.

When Mo is the target metal, the slag is most commonly roasted prior to leaching. The method was patented in 1972 by Ammann [170]. Recently Parada et al. [171] used roasting and H<sub>2</sub>SO<sub>4</sub> leaching for the recovery of Mo, with an 80% yield. Zimmerley and Beck patented, in 1967, a complicated method with several leaching steps, though the Mo yield was reported to be 92% and purity high. Sanchez and Palacios [172] concluded that roasting oxidizes the Mo to a soluble form and Fe to an insoluble form, thus improving the yield and selectivity of Mo.

Compared with leaching, chemical separation methods are not studied nearly as often in relation to metals recovery from Cu slags. Banza et al. [173] reported the use of solvent extraction, with hydroxyoxime LIX 984, to separate Cu, and D2EHPA to separate Co and Zn from H<sub>2</sub>SO<sub>4</sub> leachate of Cu slag. H<sub>2</sub>O<sub>2</sub> was used in leaching to improve selectivity over Fe and silica (which is known to be harmful in filtration, because of its effect on viscosity, and solvent extraction, because of crud formation). Overall recoveries for the metals were: Co 90%, Cu 80% and Zn 90%. Cu and Co were cemented from H<sub>2</sub>SO<sub>4</sub> leachate by Deng et al. [158], though purities were not reported. Kaksonen et al. [154] precipitated, selectively, Cu and Zn from Cu slag leachate of Cu, Fe, Ni and Zn. In this research bioleaching with H<sub>2</sub>SO<sub>4</sub> was used, but yields obtained were only 41-62% for all of the metals.

Anode slimes from primary and secondary electrolytic Cu refineries are potentially important sources of many metals, because valuable metals and metalloids are deposited in the Cu blister during the smelting of raw materials (Cu matte, scrap, wastes) for electrorefining. Globally, these slimes are generated at a rate of 55000 tons/year (3-5 kg/ton of anode) [174]. They are an especially important raw material for selenium, Se, and tellurium, Te, since the recovery of these metals from ores is difficult. Current prices of Se and Te are, respectively, 64 and 110 USD/kg [143].

The mineralogical composition of anode slimes is complicated, containing metals as mixed phases, both crystalline and amorphous [175]. Kilic et al. [176] produced a good summary of the composition of Cu anode slimes in their recent article. The most valuable components are Ag, Au and PGMs. Other recoverable metals, besides Cu, include As, Bi, Co, Ni, Pb, Sb, Se, Sn, Te and Zn. As an example, the previously mentioned authors' own anode slime sample (Sarkuysan Copper, Turkey) had the following composition: Cu 26%, Pb 13%, Sn 8.1%, Se 4.7%, As 3.9, Ag 2.8%. A two-step oxidative leaching process for the recovery of Cu and Se was suggested: first Cu is leached with H<sub>2</sub>SO<sub>4</sub> (97% yield), and secondly Se is leached with concentrated NaOH (87% yield). Yavuz and Ziyadanogullari [177] reported high Ag and Au contents (7.9% and 0.37% respectively) in a Turkish brass factory (Kirikkale) sample. Leaching was studied successfully (Ag yield over 80%, Au yield 100%) by thiourea leaching with Fe<sup>3+</sup> as an oxidant after leaching Cu with H<sub>2</sub>SO<sub>4</sub>, Se and Te with Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S, and Ag<sub>2</sub>Se phase with H<sub>2</sub>SO<sub>4</sub> and NH<sub>3</sub>. Amer [178] gave the following composition for an Egyptian Cu anode slime: Cu 18.6%, Pb 15.3%, Sn 9.8%, Fe 1.72%, Sb 1.30%, Ni 0.94%, Ag 0.46%. The suggested leaching process for recovering Cu and Ag was similar to the Turkish brass factory slime example. Yields for both metals were over 90%.

Fernandez et al. [179] give a comprehensive flowsheet for Cu anode slime treatment. As (yield 85%) and Sb (80%) are leached with KOH, and sulfide precipitation is suggested for further recovery. Then, Se (98%) is leached with water, after carbonate roasting, and recovered by reducing with hydrazine dichlorohydrate. Then H<sub>2</sub>SO<sub>4</sub> is used to leach Cu (85%) and Te (18%). It is suggested to purify Cu with solvent extraction, although details are not given. The remaining Te is leached with HCl and reduced with metallic Cu. Residual slime is smelted in order to obtain bullion rich with Ag and Au.

In a patent by Wang et al. [180] from 1981, a detailed process for recovering valuable metals from Cu anode slimes is described. First Ag, Se, Te and Cu are leached with HNO<sub>3</sub> and Ag is precipitated with HCl. At this point the media of the leachate is changed from HNO<sub>3</sub> to HCl by extracting HNO<sub>3</sub> to tributylphosphate (TBP) and introducing HCl. Se and Cu are separated from Te with TBP and Se is recovered with SO<sub>2</sub>. From the HNO<sub>3</sub> leaching residue, Au is leached with aqua regia and purified by solvent extraction with dibutyl carbitol. Pure (99.9%) Au is recovered by oxalic acid. Yields for the metals are: Ag 95%, Se 96%, Te 75% and Au over 99%. Carbon adsorption, known from primary Au refining, has also been suggested as a separation method for chlorinated leachate of Cu anode slime. In this patent Ag is recovered as a (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-AgCl complex with mixture of NH<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> [181].

A review paper by Hait et al. [174] provides a flowsheet for Au, Ag, Cu, Ni, Se and Te recovery from anode slime. The leaching of Au, Cu, Se and Te is accomplished with H<sub>2</sub>SO<sub>4</sub>+NaCl+MnO<sub>2</sub>. Solvent extraction with binary dialkyldithiophosphoric acids is used for Au and Cu extraction. Cu is stripped with NH<sub>3</sub> and Au with thiourea. Se and Te are extracted with TBP. Ag is leached with NH<sub>3</sub> and Ni with pure H<sub>2</sub>SO<sub>4</sub>.

In a patent by Soldenhoff [182], Au is leached to HCl containing H<sub>2</sub>O<sub>2</sub>. Solvent extraction with alcohol (2-ethylhexanol) or phosphine sulfide Cyanex 471X [183] is used for purification. Chlorinating water leaching of Au and PGMs has been used by many authors. Selective leaching of Au, followed by cementation, with an overall yield of 90%, was reported by Donmez [184]. PGMs, Au and Se can also be selectively recovered from chlorinating leachate by reduction with SO<sub>2</sub>. The method is based on the catalytic effect of elemental Se on the reduction of PGMs and Au [185]. Pd+Pt concentrate may also be obtained by cementation with Zn [186,187]. Feng and Wang [186] reported bench scale and pilot solvent extraction tests made in the Daye Copper smelter for separating Au, Pd and Pt from chlorinated leachate. Au may be extracted with dibutyl carbitol or TBP, from which TBP is preferred. An unspecified S201 reagent can extract Au and Pd selectively. Pt can be extracted with petroleum sulfoxide, but only from high HCl concentrations. Thus looking for an alternative extractant is preferred in order to minimize the cost of recovering small Pt amounts. Selective Au leaching with sulfite followed by selective Ag leaching with HNO<sub>3</sub> has been used by Tarasov et al. [188]. It has been stated in many references that the Ag is recovered as AgCl if chloride (e.g. NaCl) is added to the leachate [189].

A mixture of H<sub>2</sub>SiF<sub>6</sub> and HNO<sub>3</sub> dissolves from anode slime everything, with the exception of Au, with over 85% efficiency [175], although NaCl, instead of H<sub>2</sub>SiF<sub>6</sub>, may be used with HNO<sub>3</sub> to leach Au, Pd and Pt [190]. Recovery of Sn from Cu anode slime has been reported by alkali fusion [191]. If the Ni content in a slime is high, it may be recovered with H<sub>2</sub>SO<sub>4</sub> in an autoclave without oxidizing agents, and in the same treatment, Te is leached after oxygen is added [192].

Conventional hydrometallurgical separation methods, for example precipitation and solvent extraction, have been mainly used within the separation stages in the treatment of solid

residues from Cu refineries. However, the author suspects that there is significant development potential with, for instance, ion exchange, possibly with simulated moving beds (SMB). As an example, based on the experiments of Hubicki et al. [193,194] with synthetic chloride and nitrate solutions that resembled Cu anode slime leachates, Pd could be selectively adsorbed with strong anion exchangers, iminodiacetate resins and amidoxime resins.



## 4 WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)

In this Section, some practically important waste electrical and electronic equipment (WEEE) for metals recovery are described in detail from chemical engineering, economic, environmental and social points of view. This Section is based on a literature survey, while experimental results, with discussion, are presented in Section 6.

In addition to the materials discussed in this and previous Sections, the following wastes are potential resources for valuable metals: photovoltaic cells, vehicles, hard metal scrap, catalysts from the petrochemical industry, solid waste from thermal power plants, batteries and fly ashes.

### 4.1 Overview of metals recovery from WEEE

The EU directive for the handling of waste electrical and electronic equipment (WEEE) defines these as equipment that either are concerned with the electrical network or need electricity to function [14]. According to Bushehri [195], 25-50 million tons of WEEE were generated annually worldwide in 2006, while in the EU, the estimated annual amount today is 10 million tons [15], which is expected to grow at 2.5-2.7% annually [196]. In total, about 60% of WEEE is metal, mostly iron and steel [197]. Feng *et al.* analyzed 24 different WEEE samples from Europe, Japan, Korea and North America [198], and mean concentrations of major metals were; Cu (7200 mg/kg), Zn (2800 mg/kg), Pb (2000 mg/kg), Ba (1800 mg/kg), Cr (370 mg/kg) and Ni (240 mg/kg). Cd, Ag, Hg and As were found in smaller quantities. These values may vary significantly and, for example, Widmer *et al.* [197], referring to the report of European Topic Centre on Resource and Waste Management, stated in 2005 that 7% of WEEE is composed of Cu. It is known that circuit boards contain notable amounts of noble and platinum group metals. Tuncuk *et al.* [199] gathered chemical analyses of two printed circuit board wastes, two TV board wastes and one mobile phone waste, and multiplied the concentrations of metals by their monetary value thus revealing the economic potential of each metal in certain waste batches. The results show that Cu, Au, Ag and Pd are economically the most interesting metals to be recovered. Their concentrations were respectively 9.2-20%, 3-350 mg/kg, 86-1380 mg/kg and 3.7-309 mg/kg, from which the upper limits are approximately in the range of primary ores for the metals. Generally, mobile phone waste was the richest in terms of precious metal content [199]. Cui and Zhang [200] made similar analyses and also concluded that the precious metals are the most interesting from an economic point of view. Also Zn and Pb are interesting, since their concentrations are in the range of typical primary ores for these metals. Substantial amounts of metals are already recovered from WEEE. For example in Taizhou, the largest WEEE recycling center of China, one million tons of scrap copper and 0.6 million tons of scrap aluminum were recovered in 2011 [198].

A large proportion of the WEEE from developed countries is transported to Africa and the Far East (Fig. 9). In the United States, the portion was estimated to be 50-80% in 2002 [201]. In

Africa, WEEE are often reused and in the Far East they are recycled for their valuable components [12]. In China, the major part of the WEEE was recycled by the non-regulated sector in 2005. This is because of the high disposal costs and valuable substances in the material. There is also a lack of awareness in the safety, health and environmental hazards of WEEEs and their recycling by primitive methods [202]; this is why the Chinese government has proposed regulations which will prohibit these “backyard workshops” [198]. Also, even handling the WEEE by more sophisticated and controlled methods has been reported to cause serious health and environmental problems in the big recycling centers of China [198,201].

Recovery of valuable metals from WEEE, in particular with hydrometallurgical methods, has been comprehensively reviewed by Tuncuk et al. [199] and Cui and Zhang [200]. Treatment of the WEEE starts with manual dismantling, and at that point the parts are divided into fractions such as metals, plastics, ceramics and various separate components (LCD, batteries). Next, the particle size is reduced by shredding and milling, and following this a physical separation step is performed by, for example, gravimetric, magnetic or electrostatic methods (Fig. 10) [199].

After the physical separation and pretreatment methods described in the previous paragraph, a hydro- or pyrometallurgical route is chosen (Fig. 10). As in the whole field of metallurgy, hydrometallurgical methods are currently challenging conventional pyrometallurgical processes. Pyrometallurgical methods for recovering a variety of metals from WEEE are being used industrially in the Noranda process (Quebec, Canada), Boliden smelters (Rönnskär, Sweden) and Umicore precious metals’ recovery process (Hoboken, Belgium) [200]. For hydrometallurgical methods, some pretreatment methods may also be necessary because the metallic parts are often encapsulated by plastics or ceramics. In WEEE, metals are usually found either in their native form or as alloys, meaning that oxidative leaching methods are required for leaching all the base and precious metals effectively.

Aqua regia, common mineral acids and ammonia, with some added oxidants have been used for leaching Cu. Autoclave leaching, with  $H_2SO_4$  generated in an autoclave from pyrite ( $FeS_2$ ) wastes, was recently reported to leach selectively Zn, Ni and Cr from WEEE, while leaving Ag, Au, Pd and Pt to the leaching residue [204]. For precious metals common complexing agents such as cyanide, thiosulfate, thiourea and halides are used to enhance the leaching [199,200]. Recently Yazici and Deveci published an article which described how Cu, Ni, Fe and Ag were efficiently leached from waste printed circuit boards using a mixture of  $H_2SO_4$ ,  $CuSO_4$  and NaCl. In particular, the concentration of  $Cu^{2+}$ , which acts as an oxidant in the presence of air or oxygen, was observed to have a positive effect on the leaching [205]. In addition, biohydrometallurgy is suggested to have potential for valuable metals’ recovery from WEEE in the future [200].



Figure 9. Global traffic of WEEE, according to Baker et al. [203].

For purification of the leaching solutions, a variety of chemical separation methods have been applied: cementation has been used by Quinet et al. [206] for Ag, Pd and Au; by Alam et al. [207] for Ag; and by Kamberovic et al. [208] for Ag and Au. Precipitation has been used by Sheng and Etsell [209] for Au, and by Quinet et al. [206] for Ag. Solvent extraction has been used by Alam et al. [207] for several metals (Co, Ni, Zn, etc.), by Le et al. for Cu, by Kinoshita et al. [210] for Cu, by Chmielewski et al. [211] and by Park and Frey [212] for Au. Activated carbon adsorption and ion exchange has been used by Quinet et al. [206] for Ag, Pd and Au. For ion exchange, many similar separation tasks comparable to WEEE leaching solutions in terms of aqueous media and metals have been successfully studied [200].

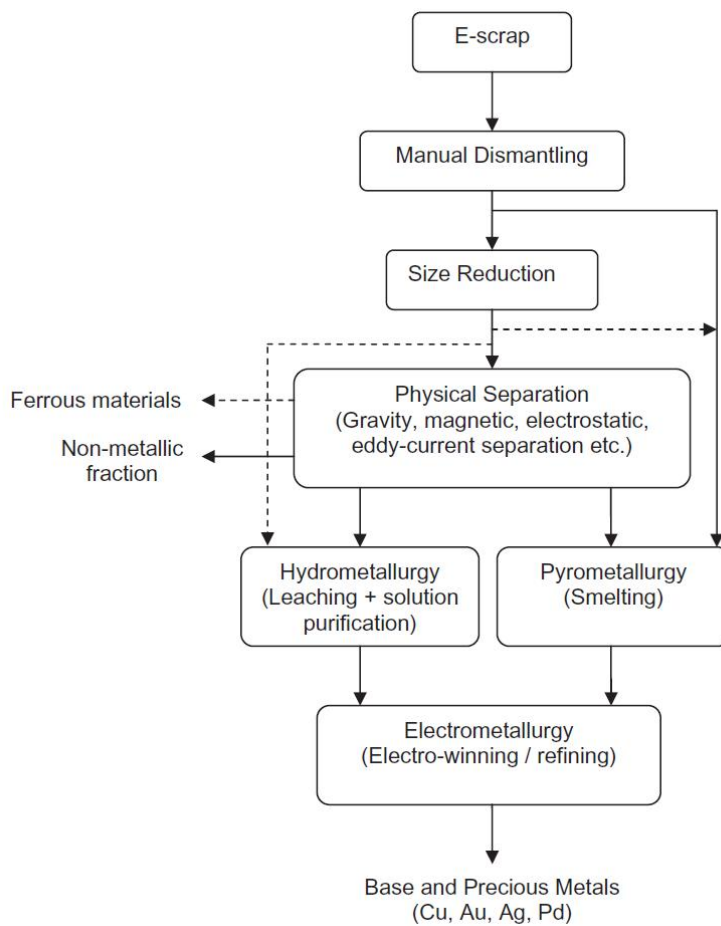


Figure 10. General flowsheet for recovery of valuable metals from WEEE [213].

## 4.2 LCD panels

LCD panels have a significant potential as a raw material for indium – a rare and valuable metal. The author's own contribution to the topic with experimental data is presented in a detailed manner in Section 6.1, and in Publication I. According to the author's own measurements, published in the Proceedings of International Solvent Extraction Conference 2011, in Santiago, Chile [214], one kg of LCD glass contains 220 mg of indium. This is in line with several literature references [215–218], which report contents between 102 and 410 mg/kg. Also theoretical calculation based on the thickness of the indium tin oxide (ITO) layer gives a value between 225 and 563 mg/kg. One exception is that Dodbiba et al. [219] obtained a leaching yield of 970 mg/kg glass, but there may be differences in the amount of ITO in different kinds of LCD panels. All of these values are higher than typical In content in Zn ores, a primary source if In, from which it is recovered as a side product [220].

In LCD panels, ITO is located at the surface of the glass plates that surround the liquid crystals (Fig. 11), which create the picture when they twist because of an applied electric current. ITO is a suitable material for the electrode on the glass, because it needs to be transparent and have suitable (semi)conducting properties.

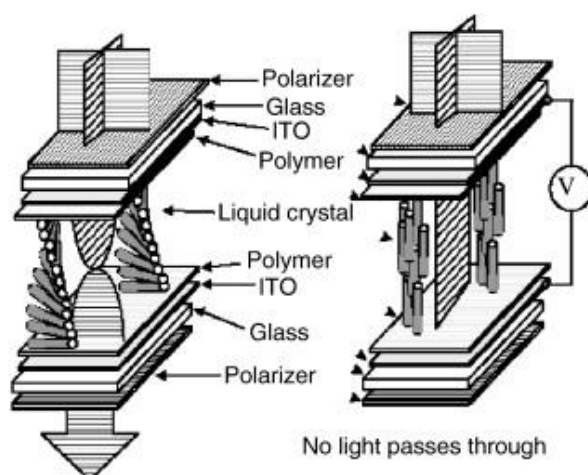


Figure 11. The structure of an LCD panel [221].

The earliest patent for recovering In from waste LCD panels is from 2000, by Shimofusa et al. [222]. In this method the indium is separated from heavy metals by solvent extraction from  $\text{HNO}_3$ . In 2003 and 2007, methods that included selective precipitation of indium were patented [223,224]. Recovering indium from waste LCD panels has been under intensive research in the very recent past, and many different methods, especially for the separation step have been proposed. Leaching coupled with solvent extraction was used by Felix et al. [216]. Pyrolysis of plastics to liquid and gaseous products, followed by  $\text{H}_2\text{SO}_4$  leaching of In was successfully utilized by Wang et al. [225]. Aminopolycarboxylate chelants (APC) were used to leach indium from LCD glass by Hasegava et al. [217,226], but an elevated temperature or

microwaves were needed to obtain effective leaching behavior. The previously mentioned high yield (970 mg/kg) for HCl leaching of In by Dodbiba et al. [219] was achieved by electrical disintegration of the LCD module. Homogenous liquid-liquid extraction recovers and concentrates the In well, according to Kato et al. [227]. Despite some other difficulties in these recovery processes, the major drawback in many of these studies and/or methods is that the selectivity for indium over tin is not satisfactory or is not studied at all. As an exception, Ma et al. [228] proposed the so called vacuum chlorinated method, in which  $\text{In}_2\text{O}_3$  is converted (98.02% yield) by  $\text{NH}_4\text{Cl}$  at an elevated temperature to volatile  $\text{InCl}_3$  with 99.05% purity.

Indium can be also recovered from the waste produced by the sputtering process by which the ITO film is introduced onto the glass. This sputtering waste is actually the more important secondary source of In, since only 30% of the indium is deposited on the glass in the sputtering process. This means that there is a significant amount of waste ITO, which is high grade in terms of In, and actually, since 2007, more In has been produced from secondary than from primary sources [229]. Ryoshi et al. [230] patented a method in 2008 in which scrap ITO is leached with HCl and In is then precipitated as an oxide with NaOH. Recently, Kang et al. [231] published a method in which high purity In (> 99.99%) is recovered from sputtering waste by solvent extraction and electrolytic refining.

In general, a significant amount of work has been done on the separation of indium by solvent extraction, and a review by Paiva [232] presents these studies in a detailed manner. Ion exchange is not nearly as studied as a separation method for In, though recently, for example, solvent impregnated resins have been synthesized for recovery by Li et al. [233].

In the authors own work (Section 6.1, Publication I) it is concluded that all common mineral acids are suitable for In recovery from ITO.  $\text{H}_2\text{SO}_4$  is suggested as a leachate because of its economic, environmental and practical suitability. D2EHPA is suggested as the solvent extraction reagent. It extracts both In and Sn, and In can then be selectively stripped with HCl. Recent work by Yang et al. [218] verified these conclusions after studying the common mineral acids for leaching and several organophosphorous reagents for solvent extraction.

### 4.3 Fluorescent lamps

By definition, fluorescent lamps belong to the waste electrical and electronic equipment (WEEE), but they are discussed in their own Section, due to their relevance for this thesis. Fluorescent lamps contain significant amounts of REEs, as oxides, in their luminescent or phosphorescent powders (Fig. 12). The author's own contribution to the topic is presented in more detail in Section 6.3, which reveals that, economically, the most interesting metals are europium, Eu, terbium, Tb, and yttrium, Y. The content of Y is very high, while Tb and Eu have high prices. These same metals, especially Eu and Y, are the most common target metals in the literature on the recovery of metals from luminescent powders.

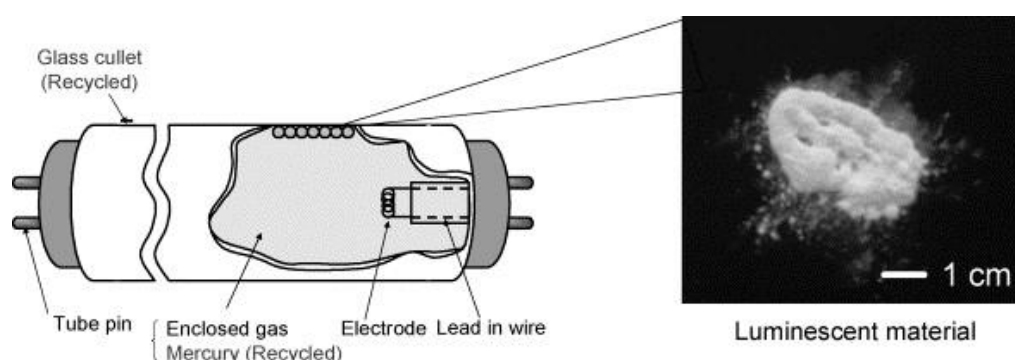


Figure 12. Structure of a fluorescent lamp [234].

All common mineral acids have been used for REE recovery from fluorescent lamps, and they do not differ significantly in terms of the leaching yields of the target metals. The factors that affect the choice of leachate are selectivity over matrix components, practical and environmental aspects and suitability of the leachate to downstream processing.

Rabah et al. [235] suggested a leaching-solvent extraction process for Y and Eu recovery. The Y and Eu are leached to a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , and then thiocyanate added, Y and Eu were extracted with trimethylbenzylammonium chloride to the organic phase, and back to the aqueous phase with  $\text{HNO}_3$ , containing TBP. For leaching and solvent extraction, over 90% yields were achieved for both metals, while for stripping a total yield of 99% was achieved. The leaching was performed in an autoclave and stripping was done at elevated temperature. TBP complexes of Y and Eu were also utilized by Shimizu et al. [234] by extracting them to supercritical  $\text{CO}_2$ . This method also gave yields of over 99% for recovery of both Y and Eu.

During recent years, De Michelis and Innocenzi et al. [236,237] studied a method for the recovery of Y from fluorescent lamps and cathode ray tubes in which Y is leached to  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  and then precipitated with oxalic acid.  $\text{H}_2\text{SO}_4$  was reported to be the better leachate, in terms of selectivity over calcium, which is the most concentrated impurity in the raw material. The oxalate produced was pure and the process simple. The total yield of Y for the suggested leaching and precipitation conditions was over 95%, also for a mixed raw material of

fluorescent lamp and cathode ray tube powders, though the conditions have to be carefully adjusted for each raw material. In 2007, Otto and Wojtalewicz [238] patented similar method, in which  $\text{HNO}_3$  is used as a leaching agent in two steps so that less soluble REE compounds are also dissolved.

Gruber [239] patented a method, in 2006, for selectively extracting Y and Eu from any common mineral acid solution of fluorescent powders by D2EHPA or a similar type of reagent. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester PC-88A has also been successfully used to selectively recover Eu, Tb and Y from such solutions [240], but it has been shown to be sensitive to impurities such as Al, Fe, Ti, V and Zn. Selectivity over these can be obtained with the ionic liquid N,N-dioctyldiglycol amic acid (DODGAA) [241].

There appears to be a lack of studies into the ion exchange recovery of REEs from leachates of fluorescent lamp powders, though it appears to be viable method for such separation tasks in order to produce high purity REEs. The only reference is by Takahashi et al. [242], who successfully used chelating resins to separate >90% pure rare earth oxides (REO).



## 5 EXPERIMENTAL

The experimental methods used in this thesis are complemented in this section with those that have not been given in the enclosed publications. This work consists of five different studies into the recovery of valuable metals from secondary raw materials, the background and aims of which are given briefly in this section. For Ag-NaCl purification, the configurations of cross-current and counter-current simulated moving bed experiments are described, since they are such an essential part of the case.

In all experiments, the metal contents of aqueous samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, device: IRIS Intrepid Duo, Thermo Electron Corporation). The aqueous chemistry of the solutions in the different cases has been modeled, and the results have been used in order to explain the experimentally-observed behavior of the separation processes. Equilibrium and dynamic models were constructed to describe the behavior of ion exchange recovery of germanium. Modeling of solvent extraction was not included in this work.

### 5.1 Recovery of indium from LCD screens (Publication I)

In this case, leaching studies using authentic crushed LCD glass were done. Solvent extraction was studied as a separation method for indium and tin in batch experiments.

As an authentic raw material, a 32" LCD TV was used. The screen was manually dismantled, the glass panels were crushed with a hammer mill and the powder was screened to a particle size of  $<710 \mu\text{m}$ .

Leaching experiments for synthetic ITO powder are described in Publication I and, based on those results, 1 M  $\text{H}_2\text{SO}_4$  was chosen as a leachate for crushed LCD powder. Leaching was performed in a 1 L glass reactor at ambient conditions with liquid to solid ratios of 3:1 and 10:1 mL/g. For reference, the glass powder was leached with 10 M HCl, giving contents of 246 mg/kg for In and 20.9 mg/kg for Sn.

Solvent extraction experiments for studying the selectivity between In and Sn are described in Publication I. Loading isotherm from 1 M  $\text{H}_2\text{SO}_4$  leachate of the glass powder to 20 wt.% D2EHPA, and subsequent stripping isotherm into 1.5 M HCl were made for McCabe-Thiele analysis of the separation process. These experiments were done at ambient conditions in separation funnels.

## **5.2 Ion exchange recovery of germanium as a by-product from sulfate process solutions (Publication II)**

Some process solutions, for example in cobalt or zinc plants, may contain recoverable amounts of germanium. Usually the Ge is separated after recovery of the main metal(s) by distillation of volatile  $\text{GeCl}_4$ . In this case study, ion exchange was investigated as an alternative method for the recovery of Ge from the mother solution, which has a high concentration of the base metals. In general, this is a typical, and challenging, separation task when utilizing base metal process solutions for valuable metals' recovery. Based upon preliminary screening experiments (see Publication II), made for different kinds of N-donor atom-containing ion exchange resins, N-methylglucamine functional IRA-743 was chosen for subsequent dynamic column adsorption studies.

The chemicals used, experimental procedures as well as feed solutions and operational parameters for each experiment are described in Publication II. Modeling was a crucial part of this work. Equilibrium and dynamic models, to give information about ion exchange mechanism, were constructed.

## **5.3 Characterization and leaching of fluorescent lamp wastes**

In this case study, two different fluorescent lamp based wastes, FLW1 and FLW2, were characterized. FLW1 waste was obtained by manually dismantling fluorescent lamps and crushing the glass parts, while FLW2 was a precipitate from a waste treatment plant's fluorescent lamp treatment process. Characterization of FLW1 was performed by an external laboratory using the EN 13656 standard digestion method, which is a microwave-assisted leaching method, using mixture of HCl,  $\text{HNO}_3$  and HF as a leachate. FLW2 was dissolved by  $\text{LiBO}_2$  fusion. The quantification of both leachates was done by ICP-OES.

Based on the characterization results, FLW2 was chosen as raw material for leaching experiments because of its high content of REEs. Leaching experiments were performed with three different leachates: HCl,  $\text{H}_2\text{SO}_4$  and a 3:1 mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . For these, 1 M, 2 M and 5 M (total) concentrations were used. Experiments were conducted in 250 mL separation funnels at ambient conditions for 24 hours. The samples were analyzed using ICP-AES. As a reference, some of these were also sent to an external laboratory, in which they were analyzed with ICP-MS. Results of this case study do not appear in the publications.

#### **5.4 Recovery of zinc and molybdenum from steelmaking dusts (Publication IV)**

Two argon oxygen decarburization (AOD) dusts (named AOD1 and AOD2) were studied for the recovery of valuable metals. After an economic evaluation of the dusts, leaching and solvent extraction were used as separation methods to recover Zn and Mo (with Cr) as final target metals. The dusts were obtained from the Outokumpu Tornio Works (Finland); the difference between them was that they were collected from different production lines. Qualitative mineralogical analysis is given in the paper of Stefanova et al. [87], but the key difference was that the AOD2 dust contained Zn in ZnO and ZnFe<sub>2</sub>O<sub>4</sub> phases, while AOD1 had only the ZnO phase.

Chemicals used and experimental methods are given in detail in Publication IV, but kinetics leaching experiments were done in a 4 L reactor and solvent extraction isotherms in a 1 L reactor by adjusting pH, either with ammonia or H<sub>2</sub>SO<sub>4</sub>. In the publication filtration of the slurry after leaching was also studied, but the results are not discussed in this summary, since the method is not in the key scope of the thesis (chemical separation methods).

#### **5.5 Purification of Ag-NaCl solution by normal column operation and simulated moving beds (Publications III and V)**

Silver is often present in base metal production process solutions and might be a viable by-product. Ion exchange has not often been used in practical applications for Ag recovery, since there appears to be a lack of sufficiently selective resins. In this case study, pure Ag-NaCl was the goal, which was approached by trying to adsorb all the other metals from the feed solution with aminomethylphosphonium functional resin Lewatit TP-260. Continuous cross-current and counter-current operations were explored for improving the efficiency of the separation process.

Within this separation task, a novel pretreatment step, termed controlled partial neutralization, was developed for aminomethylphosphonium functional resin. In this pretreatment, protons in the phosphonium group are neutralized with conjugate bases of weak organic acids, while the amino groups remain protonated. The pH of the feed solution in this case was in the neutral zone, and the resin used, aminomethylphosphonium functional Lewatit TP-260, has weakly acidic and basic properties. Thus the adsorption process is very sensitive to pH in two ways: 1. if the phosphonium groups are in the protonated form, the capacity of the resin decreases because of competition. And 2. if the amino groups are not protonated, they are capable of adsorbing protons and thus increasing the pH in the column, which may cause precipitation of some metals.

Details of the materials used, chemicals and experimental methods are given in Publications III and V. In Fig. 13, cross-current and counter-current SMB configurations, both having eight columns, are described. In cross-current operation, none of the columns were connected. Thus each of the beds went through a similar cycle, comparable to batch column operation, in

the following sequence: feed, wash, regeneration, controlled partial neutralization with washes. This is the conventional operation mode in hydrometallurgical plants. In counter current operation, the wash after the feed zone was connected to the feed zone, and the four feed columns were in series. Hence the switch time could be increased, and consequently the controlled partial neutralization with washes could be done in one column, releasing columns to the other zones.

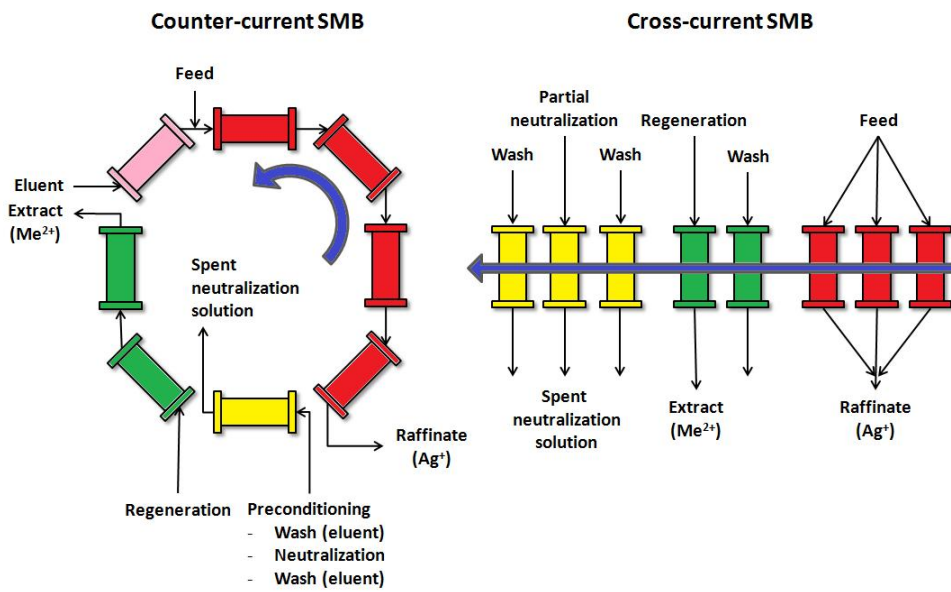


Figure 13. Schematic of cross-current and counter-current operations in purification of Ag-NaCl solution by aminomethylphosphonium functional resin Lewatit TP-260. Simulated solid phase flow is demonstrated with blue arrows.

## 6 RESULTS AND DISCUSSION

### 6.1 Recovery of indium from LCD screens (Publication I)

Yields of leaching indium and tin from crushed LCD screen glass with 1 M  $\text{H}_2\text{SO}_4$  under ambient conditions for 24 hours were only 51-52% and 66-71% respectively. They did not improve by increasing the liquids to solids ratio from 3:1 to 10:1, because there was only 246 and 20.9 mg/kg of In and Sn respectively in the glass powder, so there was enough acid to react with all of the available metal oxide in both cases (Fig. 14). According to the literature (see Section 4.2) the yields could be improved by increasing pressure and temperature, and also by using, for example, microwaves or electrical disintegration to enhance the leaching. A solution containing 44 mg/L of In and 4.9 mg/L of Sn was obtained with L/S = 3:1, which is at the lower end of technically possible operation, although, the leachate could be recirculated to increase concentration. The kinetics of leaching were slow, and it is possible that the system was not in equilibrium after 24 hours, when the experiment was stopped, meaning that better yields could potentially be achieved also under these ambient conditions. The value of In in the glass powder was 0.14 USD/kg and in the 3:1 leachate 25.1 USD/m<sup>3</sup>.

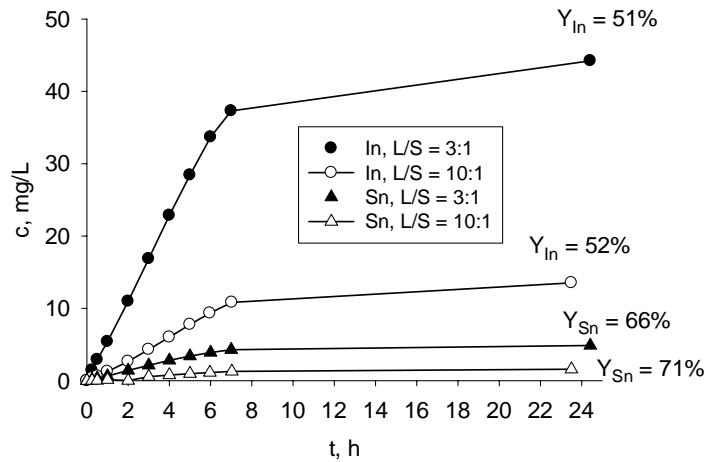


Figure 14. Leaching kinetics of crushed LCD glass powder with 1 M  $\text{H}_2\text{SO}_4$ .

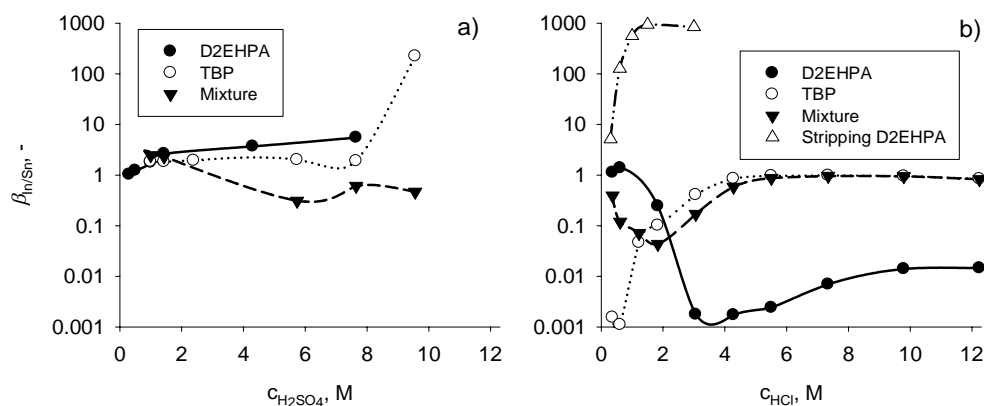


Figure 15. Solvent extraction selectivity of indium over tin from a)  $H_2SO_4$  and b)  $HCl$ . The figure has been also published in Proceedings of the 19<sup>th</sup> International Solvent Extraction Conference, 2011, in Santiago, Chile [214].  $\beta$  is used as a symbol for the ratio of fractions extracted for describing selectivity.

Selectivity of In over Sn was studied with 1.0 M D2EHPA, 1.0 M TBP and a 0.2 + 0.8 M mixture of these reagents. Stripping of In and Sn, loaded in 20 wt.% D2EHPA, was also studied. With D2EHPA, the selectivity was achieved with neither  $H_2SO_4$  nor  $HCl$  (Fig 15). With TBP and the mixture reagent the selectivity for Sn over In was achieved in  $HCl$  concentrations of respectively ca. 0.5-1.5 M and 1-2 M. Using these organic phases the separation task was fulfilled, but the In solution still required further concentration. On the other hand, stripping D2EHPA with  $>1.5$  M  $HCl$  recovered In selectively. Since D2EHPA is known to have a high capacity for In, the suggested solvent extraction scheme would be to extract In and Sn to D2EHPA from 1 M  $H_2SO_4$  and then to strip the In selectively to 1.5 M  $HCl$ .

As discussed in the introduction of Publication I, the solvent extraction mechanism of these metals is complicated, with the both reagents involving many different extracted species in the acid concentration range studied. In accordance with the theory, in the D2EHPA- $H_2SO_4$  system, the extraction proceeds by a cation exchange mechanism. Both metals are extracted strongly in lower acid concentrations and the extent of extraction decreases with increasing concentration. From  $HCl$ , Sn is extracted better in higher acid concentrations, indicating that the existing solvation mechanism is stronger than for In, which was not extracted at all. In the TBP- $H_2SO_4$  system, no extraction takes place because the sulfate complexes are not extracted. From  $HCl$ , though, both metals are extracted with a solvation mechanism, and, as expected, extraction of Sn species is stronger. In this study, no synergistic effects were observed for the mixture reagent, and the data followed approximately the sum of the effects of D2EHPA and TBP.

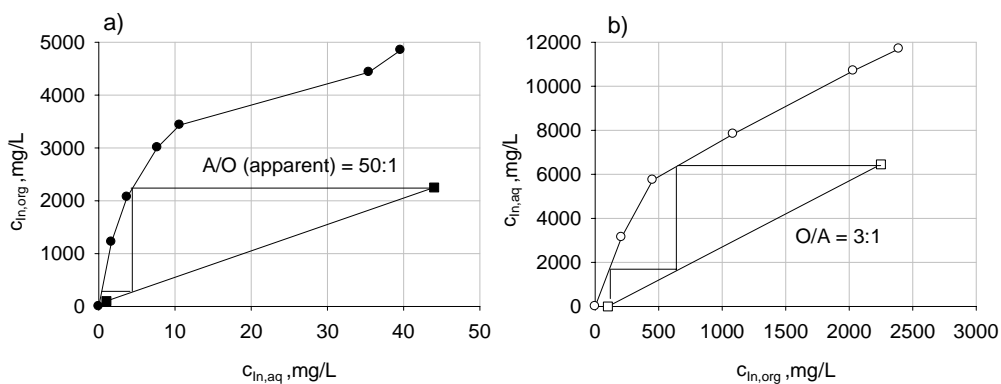


Figure 16. a) Loading isotherm for In – 1 M  $\text{H}_2\text{SO}_4$  – 20 wt.% D2EHPA –system, b) stripping isotherm for In – 1.5 M HCl – 20 wt.% D2EHPA –system, and corresponding McCabe-Thiele analyses.

In order to study more closely the suggested solvent extraction scheme, the loading isotherm for 20 wt.% D2EHPA from authentic 1 M  $\text{H}_2\text{SO}_4$  LCD glass leachate was constructed, as well as the stripping isotherm for 1.5 M HCl from loaded 20 wt.% D2EHPA (Fig. 16). For the isotherms McCabe-Thiele analysis was performed. As expected, the loading capacity of In to D2EHPA was very high, allowing a phase ratio  $A/O = 50:1$  to be used in two step counter-current extraction, where the In yield was 97.7% ( $44 \text{ mg/L} \rightarrow 1 \text{ mg/L}$ ). Such a high phase ratio is not technically feasible in a normal mixer-settler unit, but a so-called apparent phase ratio of 50:1 over the loading stage can be achieved by circulating the organic phase. In was stripped to 1.5 M HCl well, and with two step counter-current stripping, an  $O/A$  phase ratio of 3:1 can be used. With this flow sheet (Fig. 17), the In is concentrated 148 times from 44 mg/L to 6.5 g/L. Based on the Sn analysis of the stripping isotherm samples, the purity of the resulting In-HCl solution is at least 99.7%.

As a concluding remark, it is stated that solvent extraction is a high potential recovery method for In from LCD glass leachates. Although the leaching step was not optimized in this study, and was conducted with the simplest possible method, the simple 2+2 step solvent extraction unit operation would still be able to produce an HCl solution containing 6.5 g/L In. This solution could be followed by cementation to produce a In sponge, or by electrolysis to produce high purity In metal [243].

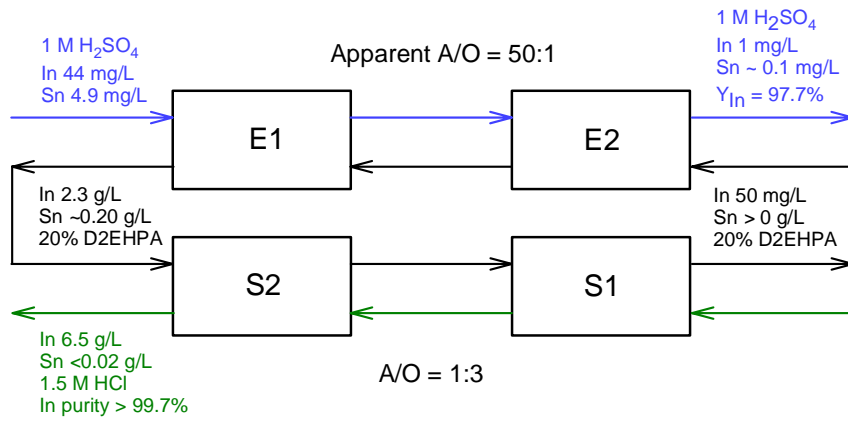


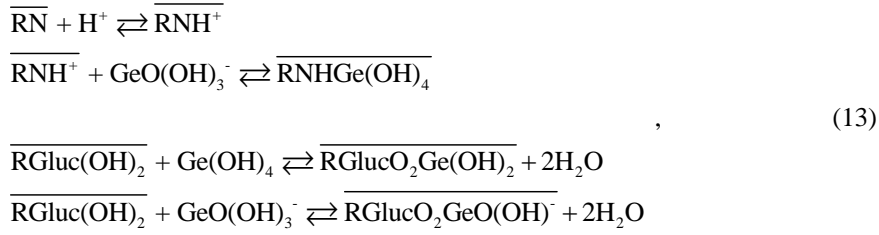
Figure 17. Suggested flowsheet for solvent extraction recovery of indium from 1 M H<sub>2</sub>SO<sub>4</sub> leachate of crushed LCD screens.



## 6.2 Ion exchange recovery of germanium as a by-product from sulfate process solutions (Publication II)

The aqueous chemistry of germanium is dominated by germanic acid,  $\text{Ge}(\text{OH})_4$ , and its dissociation products  $\text{GeO}(\text{OH})_3^-$  and  $\text{GeO}_2(\text{OH})_2^{2-}$  (Fig. 18). The first  $\text{p}K_a$  value is around 9, depending on the solution. This is an essential fact that has a bearing on the ion exchange behavior, since those resins that have a capability of adsorbing neutral  $\text{Ge}(\text{OH})_4$  may work in either a neutral or acidic range, and on the other hand an anion exchange mechanism may work in the alkaline range. It is verified in the literature (see a more detailed discussion in Publication II), that hydroxyl groups and N-donor groups enhance the adsorption. The resin used in this case study (IRA-743) has both of these functionalities: an N-methyl group and glucose group, and both groups have to be taken into account in theoretical treatment.

In the suggested mechanism the other metals and protons compete for the adsorption to the N-methyl group, and  $\text{Ge}(\text{OH})_4$  and  $\text{GeO}(\text{OH})_3^-$  compete for the glucose group. Subsequently, after protonation,  $\text{GeO}(\text{OH})_3^-$  is adsorbed through an anion exchange mechanism (Fig. 19). The second dissociation product of Ge was neglected, since pH was expected to stay below 12. Reaction equations involved in the mechanism are as follows:



where R is the PS-DVB matrix of the resin and Gluc is the glucose part of the functional group. A competitive adsorption isotherm by Koopal et al. [244] was used as a mathematical description of the competitions:

$$q_i = Q \frac{(K_i c_i)^{n_i}}{1 + \sum (K_i c_i)^{n_i}} \quad , \quad (14)$$

where  $Q$  is the amount of each functional group,  $K_i$  is an affinity constant for each component, and  $n_i$  is the respective non-ideality parameter. In order to simplify the calculation, lumped equilibrium parameters were given for the other metals in each solution. Fitted parameters are given in Publication II. The suggested equilibrium mechanism and model predicts the adsorption behavior of Ge from pure sulfate solutions well, with the effect of pH (Fig. 20). It can be clearly seen that the increasing initial pH, and thus also equilibrium pH, enhances the adsorption.

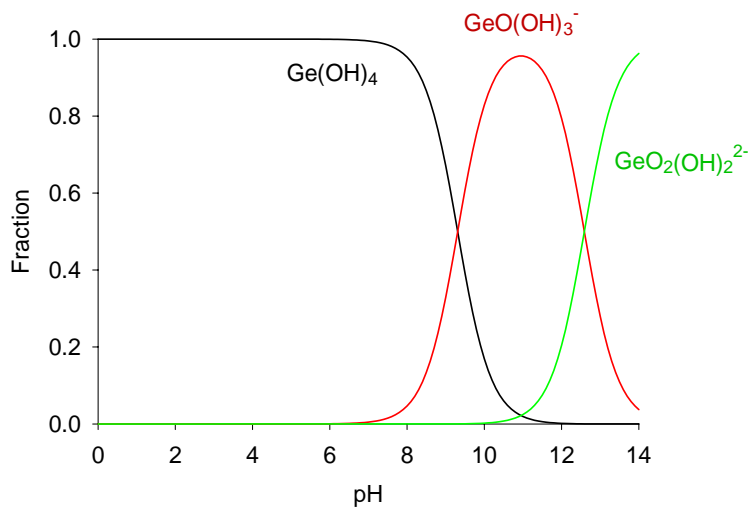


Figure 18. Dissociation of germanic acid  $\text{Ge(OH)}_4$ .

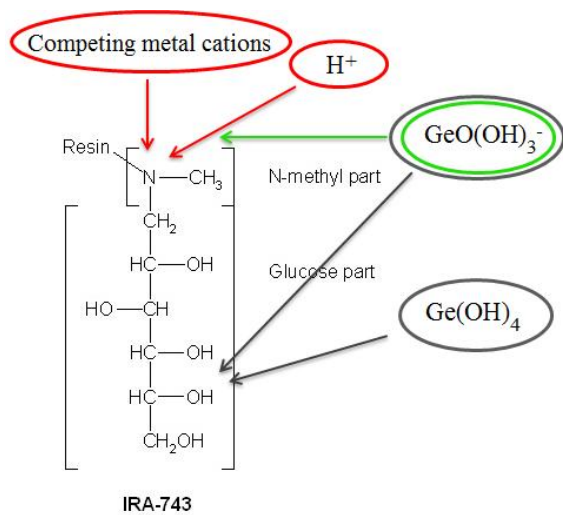


Figure 19. Suggested mechanism for germanium adsorption to N-methylglucamine functional resin.

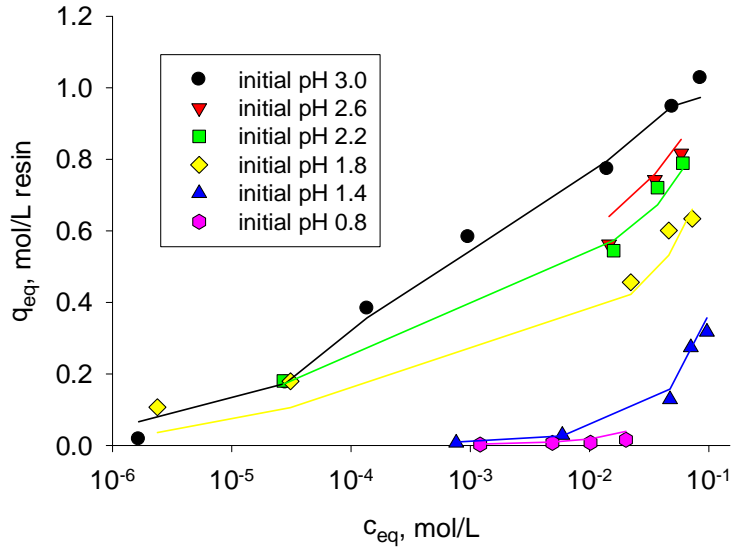


Figure 20. Adsorption of germanium from pure sulfate solutions with varying initial pH to N-methylglucamine functional resin (IRA-743).

In order to describe the dynamic column adsorption, a transport dispersive model with solid film linear driving force was used:

$$\begin{aligned} \frac{\partial c_i}{\partial t} + F \frac{\partial q_i}{\partial t} + u \frac{\partial c_i}{\partial z} &= D_{L,i} \frac{\partial^2 c_i}{\partial z^2} \\ \frac{\partial q_i}{\partial t} &= k_L (q_{eq,i} - q_i) \quad , \quad (15) \\ k_L &= \frac{15D_{s,i}}{R_p^2} \end{aligned}$$

where  $F$  is phase ratio between liquid and solid phases,  $u$  is velocity of liquid phase,  $z$  is the spatial coordinate,  $D_{L,i}$  is axial dispersion coefficient,  $k_L$  is mass transfer coefficient,  $q_{eq,i}$  is equilibrium concentration in solid phase,  $D_{s,i}$  is the diffusion coefficient in resin pores and  $R_p$  is the mean radius of the resin particles.

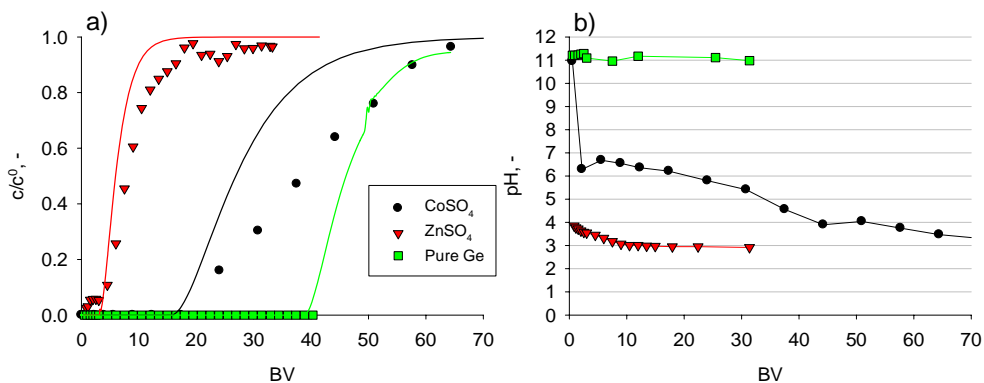


Figure 21. Dynamic adsorption of germanium into N-methylglucamine functional resin from sulfate solutions. a) Breakthrough curves of Ge and b) pH curves of respective experiments. The lines in the breakthrough plot are simulation results.

Dynamic adsorption of germanium to N-methylglucamine functional resin (IRA-743) was better from the CoSO<sub>4</sub> solution than from the ZnSO<sub>4</sub> solution. Breakthroughs were at ca. 5 and 19 BV, respectively, and the adsorbed amounts were 3.0 and 4.3 mg/g wet resin (Fig. 21 a)). However, the adsorption is much better from pure Ge solution, and the breakthrough was not achieved during the experiments (40 BV), though the simulated curve shows that the breakthrough would occur at ca. 40 BV. Explanation for the order can be found from pH curves of the corresponding experiments (Fig. 21 b)). With the pure Ge solution, the pH stays at ca. 11 for the whole experiment, while with the CoSO<sub>4</sub> solution it stays at ca. 6, until the breakthrough, and then slowly decreases towards the feed pH (3.0). With the ZnSO<sub>4</sub> solution, the pH decreases from ca. 4 to 3 within 10 BV. The model predicted the breakthrough points well, though the curve, especially for the CoSO<sub>4</sub> solution, is rather more abrupt than the one obtained experimentally. The fitted parameters are given in Publication II. The value of Ge in CoSO<sub>4</sub> and ZnSO<sub>4</sub> solutions is, respectively, 137 USD/m<sup>3</sup> and 564 USD/m<sup>3</sup>.

When other metals are added to the solution, the situation cannot be described only by competition, since the other metals have also an effect on pH, by forming hydroxide complexes. Dependency of the pH on the total proton concentration – for the solutions used in dynamic adsorption experiments – was studied with theoretical calculations performed using the MEDUSA program (Fig. 22) [245]. It can be seen that there is a plateau in the curves after the total proton concentration falls below a certain level. This means that, although the N-donor resin adsorbs protons from the feed solution, the other metals in the solution form hydroxide complexes thus buffering the desired pH increment. Precipitation was neglected in the calculations. The level of the plateau is much higher in the case of CoSO<sub>4</sub> solution (pH 4.45) than with the ZnSO<sub>4</sub> solution (pH 2.91), thus explaining the higher pH values in the column and subsequent better Ge adsorption. The values of the plateaus were used in column simulations as constant equilibrium pH values, although the pH is slightly higher at the

beginning of the experiments, probably due to transient precipitation of some minor compounds, and near the pH of the feed solution (3.0) towards the end of the experiments (Fig. 21 b)). This simplification is justified by a much simpler, faster and easier calculation of the required solution equilibria in every grid point of the column, which are calculated for every temporal point.

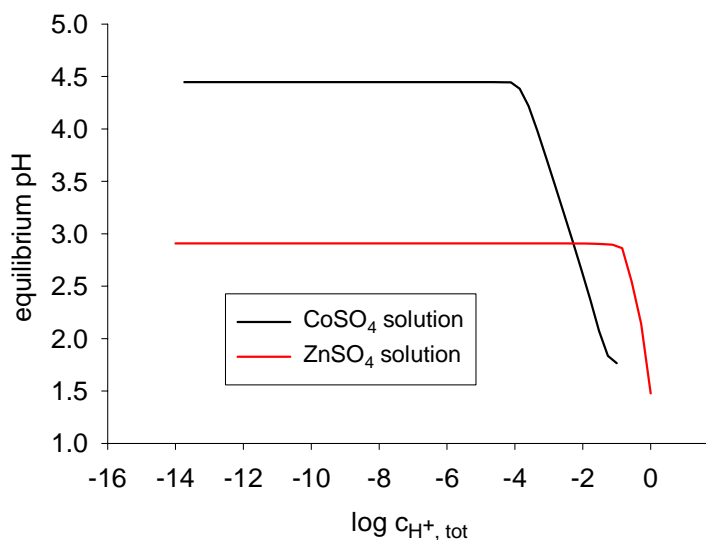


Figure 22. Effect of total liquid phase  $H^+$  concentration on equilibrium pH in the solutions used in the dynamic Ge adsorption experiments. Solutions:

CoSO<sub>4</sub>: Ge = 73 mg/L,  $I_c = 1.38$ , As = 8 mg/L, Cu = 202 mg/L, Co = 18.9 g/L,  $Fe^{3+} = 93$  mg/L, Ni = 117 mg/L, Zn = 1.12 g/L.

ZnSO<sub>4</sub>: Ge = 300 mg/L,  $I_c = 5.82$ , Al = 7.68 g/L, Cd = 14 g/L, Cu = 60 mg/L, Mg = 3.20 g/L, Mn = 4.10 g/L, Zn = 33.2 g/L.

More curves for various other solutions are presented in Publication II.

Ion exchange with N-methylglucamine functional resin can be seen as a potential recovery method for germanium as a side product from industrial sulfate solutions. However, the quantity and quality of impurity metals together with the pH of the feed solution have a very large effect on the adsorption behavior.

### 6.3 Characterization and leaching of fluorescent lamp waste

In a fluorescent lamp precipitate from a waste treatment plant (FLW2), the concentrations of all of the metals listed in Table 5, except for gallium and indium, were higher than in crushed fluorescent lamp glass (FLW1). The total REE content of FLW1 (15000 mg/kg) was slightly lower than for REE ores, and the REE content of FLW2 (75000 mg/kg) corresponds to that of high grade REE ores [135]. In the waste treatment process, part of the glass is removed, thus increasing the concentration of the luminescent powder within which the REEs are located. Gallium and indium are most probably located on the glass as semiconducting materials [246,247], and thus they are removed with the glass.

Based on the value analysis, done by multiplying the concentrations with market prices, europium and yttrium were the most interesting metals in original glass (Table 5). Terbium, gallium and indium had similar values, which are also meaningful in terms of potential recovery. In the enriched precipitate (FLW2) Eu, Tb and Y had very high values and also the value of gadolinium had increased to a meaningful level. Based on this characterization, the waste treatment plant precipitate was chosen as a raw material for leaching experiments, though it has to be mentioned that the original crushed glass could also be a good raw material for metals recovery, particularly because of the elevated amounts of Ga and In.

Table 5. Chemical and value analysis of some REEs and other significant elements in a crushed fluorescent lamp glass (FLW1), and a fluorescent lamp precipitate from a waste treatment plant (FLW2).

|                           | Ce   | Eu   | Gd    | La    | Tb   | Y     | Ga   | In   |
|---------------------------|------|------|-------|-------|------|-------|------|------|
| <b>Price USD/kg [143]</b> | 16   | 1400 | 133   | 14    | 1000 | 49    | 300  | 570  |
| <b>FLW1</b>               |      |      |       |       |      |       |      |      |
| Concentration mg/kg waste | 1400 | 700  | 10    | 59    | 270  | 9700  | 780  | 400  |
| Value USD/kg waste        | 0.02 | 0.98 | <0.01 | <0.01 | 0.27 | 0.48  | 0.23 | 0.23 |
| <b>FLW2</b>               |      |      |       |       |      |       |      |      |
| Concentration mg/kg waste | 4200 | 2300 | 2100  | 4800  | 3300 | 43200 | 220  | -    |
| Value USD/kg waste        | 0.07 | 3.22 | 0.28  | 0.07  | 3.30 | 2.12  | 0.07 | -    |

Eu and Y were leached well (74-91%) with all acids studied, while Gd was leached only slightly and Tb practically not at all (Fig. 23). Shimakage et al. [248] also obtained similar results by leaching fluorescent materials with HCl. The different behavior of the REEs is probably because Eu and Y are present as oxides, while Tb and Gd are present as phosphates. Takahashi et al. [242] stated that 36 N H<sub>2</sub>SO<sub>4</sub> would be needed to leach the phosphates. The leaching acids did not exhibit meaningful differences in leaching yields of REEs, and neither did increasing the concentration of any of the leaching acid from 1 M to 5 M. In the case of

H<sub>2</sub>SO<sub>4</sub>, the leaching yields decreased significantly between 2 M and 5 M. According to calculations made with the MEDUSA program, solubilities of REEs do not decrease with increasing H<sub>2</sub>SO<sub>4</sub> concentration. This could be explained by the other compounds in the luminescent powder forming precipitates, or not dissolving, thus also preventing the dissolution of the REEs. As stated in Section 4.3, leaching yields may be further increased if more aggressive conditions (temperature, pressure) were used.

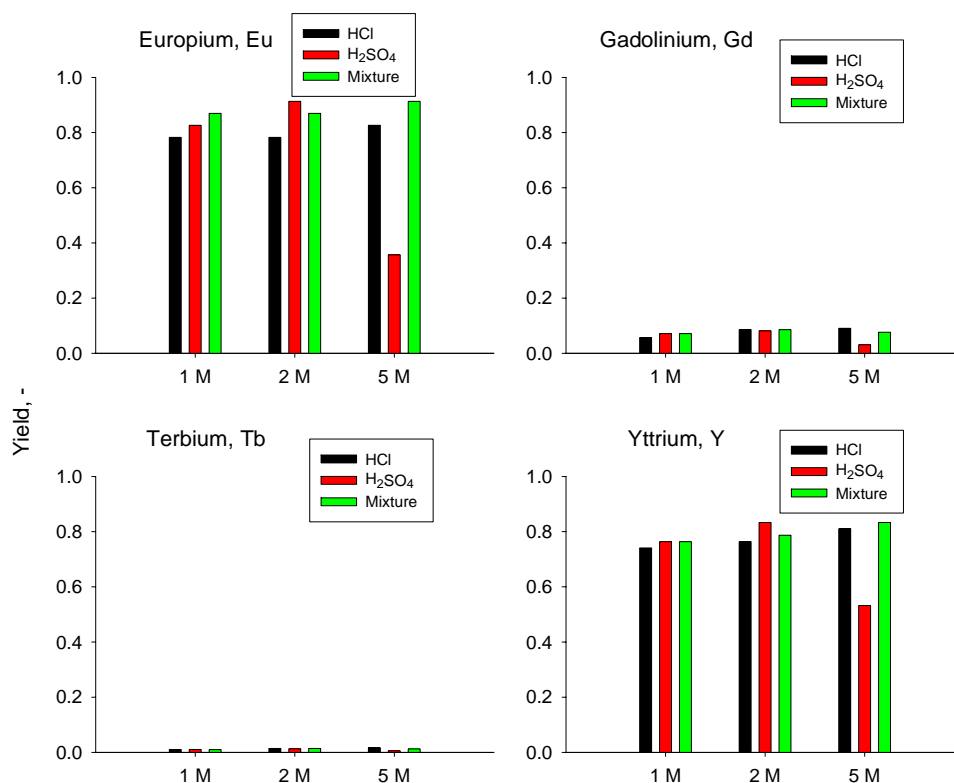


Figure 23. Leaching of Eu, Gd, Tb and Y from fluorescent lamp precipitate from a waste treatment plant (FLW2) with HCl, H<sub>2</sub>SO<sub>4</sub> and a 3:1 mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.

Since the leaching acids did not show any significant difference in the leaching yields, the economic values of the leachates are rather similar (Fig. 24). From Fig. 24, it can also be concluded that only Eu and Y had value in the leachates, with the value of Eu being a bit higher than the value of Y.

The matrix of the waste precipitate was also analyzed, and since, together with SiO<sub>2</sub> (39%), it contained CaO as a major compound (15%), the yields of Ca were also detected at 7 h of leaching (Fig. 25). With HCl, the leaching yields were much higher (57-63%) compared to H<sub>2</sub>SO<sub>4</sub> (2-7%) and the mixture (3-8%), due to the well-known low solubility of CaSO<sub>4</sub>.

Although the yield of Ca with the 5 M H<sub>2</sub>SO<sub>4</sub> was lower than with 1 and 2 M, one of the latter should be chosen as leachate given the higher yields of the Eu and Y. Using the more dilute acid would also have other technical, economic and environmental benefits.

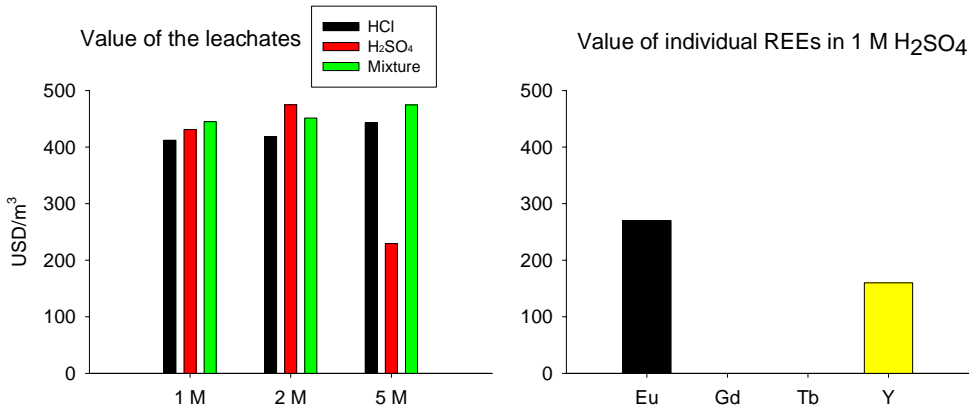


Figure 24. Total value of Eu, Gd, Tb and Y per unit volume of leachate from the leaching of fluorescent lamp precipitate from a waste treatment plant (FLW2) with HCl, H<sub>2</sub>SO<sub>4</sub> and 3:1 mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, and values of individual metals with 1 M H<sub>2</sub>SO<sub>4</sub> leachate.

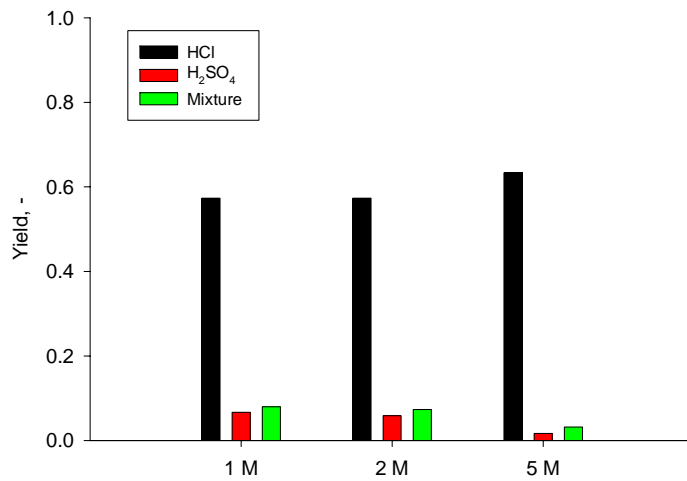


Figure 25. Leaching of Ca from fluorescent lamp precipitate from a waste treatment plant (FLW2) with HCl, H<sub>2</sub>SO<sub>4</sub> and 3:1 mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>.



#### 6.4 Recovery of zinc and molybdenum from steelmaking dusts (Publication IV)

The chemical composition of both argon oxygen decarburization dusts studied, AOD1 and AOD2, is typical for steelmaking dusts (Table 6). Iron is the main component with 38 and 26% shares respectively for AOD1 and AOD2. Other major components are Cr (9.7 and 9.8%), Zn (9.9 and 4.7%) and Ca (4.8 and 14.6%). A remarkable feature in AOD2 dust is the presence, and high concentration, of Mo (1.32%). Economic analysis, which was done by multiplying the concentration of each metal with its market price, reveals that, for AOD1 dust, the most interesting metal is Cr followed by Zn. Also in AOD2 dust Cr is the most valuable metal, while other metals having significant value include Ni and Mo.

Table 6. Chemical and economic analysis of the two argon oxygen decarburization (AOD) dusts in this study. Sources of metal prices: [www.metal-pages.com](http://www.metal-pages.com) and [www.lme.com](http://www.lme.com) [143,249].

| Metal | Price,<br>USD/kg       | AOD1<br>$c_i$ , g/kg dust | Value,<br>USD/kg dust | AOD2<br>$c_i$ , g/kg dust | Value,<br>USD/kg dust |
|-------|------------------------|---------------------------|-----------------------|---------------------------|-----------------------|
| Ca    | -                      | 47.8                      | -                     | 146                       | -                     |
| Cr    | 8.50                   | 97.4                      | 0.828                 | 97.9                      | 0.832                 |
| Fe    | 0.13<br>(steel billet) | 383                       | 0.050                 | 264                       | 0.034                 |
| K     | -                      | 9.26                      | -                     | 8.51                      | -                     |
| Mg    | 2.78                   | 12.5                      | 0.035                 | 24.6                      | 0.068                 |
| Mn    | 2.08                   | 27.6                      | 0.057                 | 33.8                      | 0.070                 |
| Mo    | 19.3                   | 0.32                      | 0.006                 | 13.2                      | 0.255                 |
| Ni    | 13.6                   | 7.15                      | 0.097                 | 29.2                      | 0.397                 |
| Pb    | 2.05                   | 0.99                      | 0.002                 | 5.21                      | 0.011                 |
| Zn    | 1.81                   | 99.3                      | 0.180                 | 47.0                      | 0.085                 |

With all leaching methods studied, and with both dusts, significant yields were achieved only for Zn and Mo (Fig. 26). From AOD1, Zn is leached with decent yields (67 and 55%) with both direct (0.5 M) and controlled (pH greater than, but close to, 3,) H<sub>2</sub>SO<sub>4</sub> methods. An important difference between the methods was that, with the direct method, some Fe was leached. Although the yield of Fe was low (2.0%) the concentration in leachate was significant (1.83 g/L), because the concentration in the raw material was high.

The best yield for Mo (37%) was achieved with pure water leaching of AOD2 dust (Fig. 26). Direct leaching gave a yield of 28%, but, with controlled leaching, the yield was significantly lower (11%). Some Zn was leached in both H<sub>2</sub>SO<sub>4</sub> leaching experiments, but not with water. The reason for worse Zn leaching from AOD2 than AOD1 is that the ZnFe<sub>2</sub>O<sub>4</sub> phase is not leached as easily as the ZnO phase.

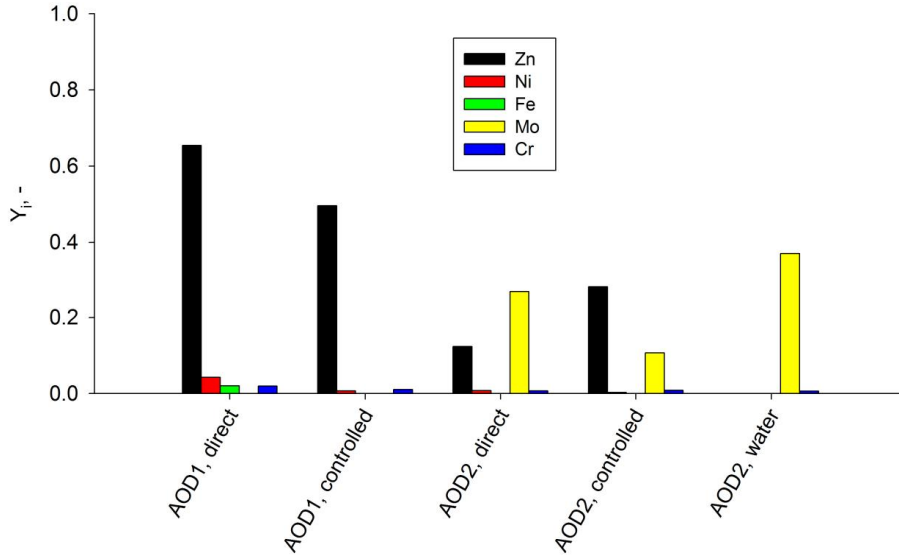


Figure 26. Yields of target metals and Fe with different leaching methods for two argon oxygen decarburization (AOD) dusts. For every  $H_2SO_4$  experiment, points from 2 h, and, for water leaching, a point from 1 h have been chosen. The points have been chosen so that the concentrations of the target metals were as high as possible. For controlled AOD2 leaching, the points at the beginning of the experiment, when the pH had not decreased enough, have been neglected.

The value of the Zn in AOD2 leachates was much lower compared to the AOD1 leachates, and also lower compared to value of Mo in direct  $H_2SO_4$  and water leachates. In AOD1 leachates, the Zn was by far the most valuable component (Table 7). Ni and Cr were leached in all the experiments with such a low yields that their value in the leachates was insignificant.

Detailed kinetic data of all leaching experiments, together with discussion, is given in Publication IV. In the same publication, the data is discussed in relation to theoretical solubilities of Zn, Fe and Mo. The discussion reveals that, although the data follows theoretical curves as a function of pH, a portion of the metals are blocked inside the physical structure of the dusts, so that the yields remain low for every metal in every experiment. It has been stated in the literature that leaching, for example, Zn with high yields from steelmaking dusts needs aggressive conditions (elevated temperature and pressure, high acid concentrations) [250].

Table 7. Chemical and economic analyses of target metals in leachates from two argon oxygen decarburization (AOD) dusts. For every H<sub>2</sub>SO<sub>4</sub> experiment, points from 2 h, and for water leaching a point from 1 h have been chosen. The points have been chosen so that the concentrations of the target metals were as high as possible. For controlled AOD2 leaching the points at the beginning of the experiment, when the pH had not decreased enough, have been neglected.

| Experiment      | Cr                    |                           | Mo                    |                           | Ni                    |                           | Zn                    |                           |
|-----------------|-----------------------|---------------------------|-----------------------|---------------------------|-----------------------|---------------------------|-----------------------|---------------------------|
|                 | c <sub>i</sub> , mg/L | Value, USD/m <sup>3</sup> | c <sub>i</sub> , mg/L | Value, USD/m <sup>3</sup> | c <sub>i</sub> , mg/L | Value, USD/m <sup>3</sup> | c <sub>i</sub> , mg/L | Value, USD/m <sup>3</sup> |
| AOD1 Direct     | 386                   | 3.28                      | -                     | -                         | 61.2                  | 0.80                      | 13000                 | 23.5                      |
| AOD1 Controlled | 209                   | 1.77                      | -                     | -                         | 10.5                  | 0.10                      | 9850                  | 17.8                      |
| AOD2 Direct     | 138                   | 1.17                      | 707                   | 13.6                      | 47.2                  | 0.60                      | 1160                  | 2.10                      |
| AOD2 Controlled | 168                   | 1.42                      | 282                   | 5.40                      | 19.7                  | 0.30                      | 2640                  | 4.80                      |
| AOD2 Water      | 133                   | 1.13                      | 979                   | 18.9                      | -                     | -                         | -                     | -                         |

Based on leaching results together with the economic analysis (Fig. 26 and Table 7), Zn (AOD1) and Mo (AOD2) were chosen as the target metals for solvent extraction studies. AOD1 leachate from direct H<sub>2</sub>SO<sub>4</sub> leaching was chosen for the solvent extraction experiment in order to study the recovery of Zn with D2EHPA. The reason for this choice was that whole process route was examined, and thus for each unit operation as comprehensive a set of data as possible was constructed.

From the pH isotherm of the D2EHPA-AOD1 leachate system (Fig. 27), it can be seen that good selectivity for Zn was obtained over all other metals, except Fe. For example, at pH 2.0, the yield for Zn was 89% and purity in the organic phase 98%, if Fe was neglected. With Fe included, the purity was 92.1%. Since Fe is also known to be hard to strip from the organic phase [251,252], the controlled leaching method where Zn is selectively leached over Fe, is preferred. The reagent did not appear to have enough capacity for the metals that were extracted at higher pH (Mg and Ni), which indicates that the extractant to metals ratio was close to optimal for achieving good selectivity for Zn. This was verified by comparing this pH isotherm to a similar one, but with lower metal concentrations (shown in Publication IV), in which the Zn selectivity was significantly worse. The data for all metals follows the cation exchange mechanism (Eq. 4), in which the extent of extraction depends on, and may be controlled with, the pH.

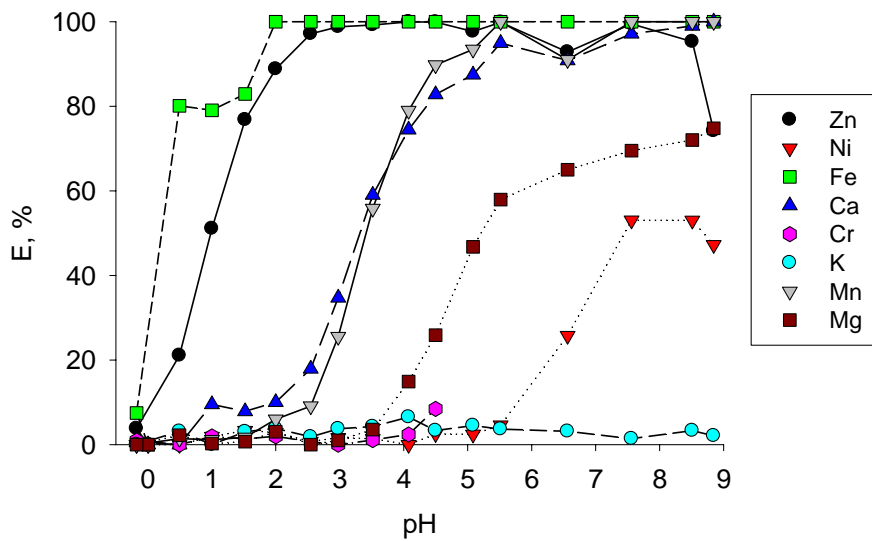


Figure 27. Solvent extraction of direct H<sub>2</sub>SO<sub>4</sub> method leachate from AOD1 dust with 20 wt.% D2EHPA.

Figs. 28 and 29 are pH isotherms for controlled pH leachate and water leachate of AOD2 dust, respectively. The reagents used were LIX 84-I (active component 2-hydroxy-5-

nonylacetoophenone oxime), Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid), TOA (trioctylamine) and Aliquat 336 (quaternary ammonium salt, made by methylation of mixture of trioctyl- and decyl amines). Though there is doubt that Mo might precipitate below pH 2 and Cr between pH 4.5-8, the data in those ranges has been left in the figures since there was no precipitates observed during the experiments.

From the acid leachate of AOD2, Cyanex 301 was the only extractant by which Mo and Cr could not be selectively extracted at any pH (Fig. 28). Though Fe was co-extracted in most cases, it should not be present in the leachates, but was included in the H<sub>2</sub>SO<sub>4</sub> aqueous phase, due to contamination. However, the poor selectivity of Cr and Mo over Fe reveals that the dissolution of Fe should be avoided if the raw material for Mo was a dust, from which Fe could be leached with significant yields. Selectivity over Fe was only achieved with LIX 84-I, in the pH range 0-1.5. A satisfactory selectivity for Mo, over Cr, was not achieved at any data point, but it should be noted that pure Mo/Cr mixture could also be a viable (intermediate) product. With LIX 84-I, at pH 2.7, the purity of Mo/Cr mixture was 69%, with TOA at pH 3.8 of 70%, and with Aliquat 336, at pH 2.0, 99% (Fe excluded from the calculations). The yield of Mo was over 98% in all of these points.

The solvent extraction mechanism with LIX 84-I and Cyanex 301 is cation exchange (Eq. 4). Though in the predominance plot in Publication IV there are no cationic Mo species, there are references (given and discussed in Publication IV) that claim the presence of such species. With the amine reagents, the mechanism is ion association, i.e. anion exchange (Eq. 5), and it was expected that Mo would be extracted as oxoanions. The aqueous chemistry of Cr is complicated, and both cationic and anionic species may be present in solution. Thus, the observed extraction with all four extractants is possible.

In the TOA-AOD2 water leachate system, the pH had to be decreased down to 4 for Mo and Cr to be extracted with over 80% yields (Fig. 29 a)). This is because the tertiary amine needs to be protonated before it can function as an anion exchanger. The purity of the Mo/Cr mixture at pH 3.0 was 63%. With the quaternary ammonium salt, Aliquat 336, the yields were > 80% over the whole pH range studied, and some Mo/Cr selectivity was even achieved at pH < 3 (Fig. 29 b)). At the initial point (pH = 13.7) the purity of Mo/Cr mixture in the organic phase was 100%. At pH 1.4, the Mo yield was 100% and purity in the organic phase 80%. With AOD2 leachates, the selectivities did not improve by decreasing the reagent to metals ratio with any of the studied reagents (data shown in Publication IV).

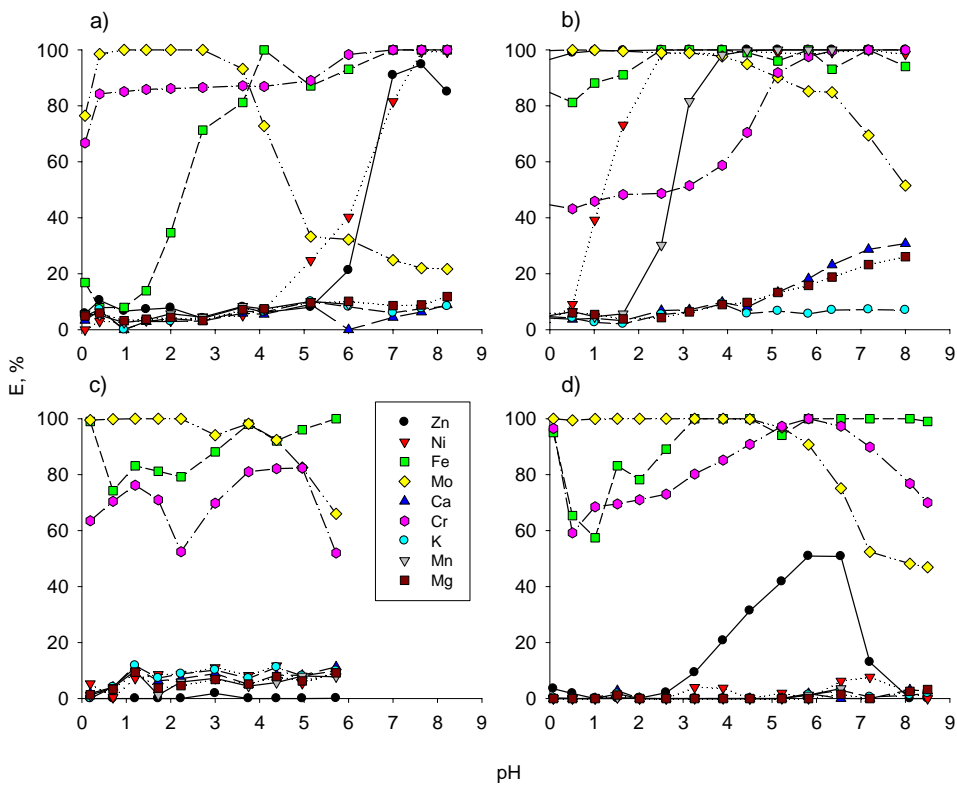


Figure 28. Solvent extraction of controlled  $H_2SO_4$  leachate from AOD2 dust with 0.5 M a) LIX 84-I, b) Cyanex 301, c) TOA and d) Aliquat 336.

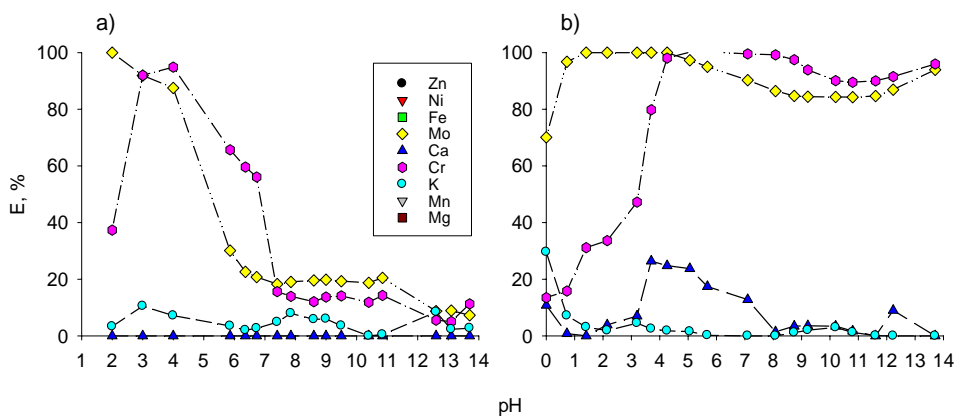


Figure 29. Solvent extraction of water leachate from AOD2 dust with 0.5 M a) TOA and b) Aliquat 336.

Based on the leaching and solvent extraction experiments, together with the economic analysis of the raw materials and leachates, the following routes are suggested for recovering valuable metals from the studied argon oxygen decarburization (AOD) dusts:

1. High purity Zn is obtained from AOD1 dust by controlled  $\text{H}_2\text{SO}_4$  leaching and solvent extraction with D2EHPA. The dust is leached with  $\text{H}_2\text{SO}_4$  so that the pH does not drop below, but is kept as close as possible to, 3. Solvent extraction is performed with 20 wt.% D2EHPA, at pH 2.0.
2. A pure mixture of Mo and Cr is obtained from alkaline AOD2 dust by water leaching and solvent extraction with quaternary ammonium salt Aliquat 336 at pH 13.7 (no need for pH adjustment).

### **6.5 Purification of Ag-NaCl solution by normal column operation and simulated moving beds (Publications III and V)**

For experimental reasons (easier ICP analysis) the concentration of Ag in the synthetic solutions used for the experiments shown in this section and in Publications III and V was about ten times higher than typical for Ag in process solutions (~500 mg/L vs. ~50 mg/L), from which it might be recovered as a side product. The monetary value of 50 mg/L Ag is 35.8 USD/m<sup>3</sup>.

The results for batch wise column operation for the purification of Ag-NaCl solution from divalent impurity metals with aminomethylphosphonium functional Lewatit TP-260 ion exchangers are given in Fig. 30. When controlled partial neutralization was utilized, breakthroughs occurred in the following order: Pb 6.0 BV, Mg 6.5 BV, Ca 8.0 BV, and Zn 15.2 BV (Fig. 30 a)). The feed flow rate in this experiment was 0.14 BV/min (4 mL/min). When controlled partial neutralization was not utilized, the corresponding breakthroughs were at 0.8, 2.6, 3.8 and 3.6 BV (Fig. 30 c)), meaning that practically none of purified solution is obtained. The curves of Ag are not shown, since it broke through immediately. From the elution curves (Fig. 30 b) and d)), it is seen that the eluted (and thus also adsorbed) amount of Zn is much higher than the other metals. Zn is more strongly adsorbed to the resin and drives some of the other metals out from the resin in the loading step. The collected extract is thus enriched towards Zn, meaning that it could also be separated if desired.

The difference in metal loading capacities, with and without controlled partial neutralization is, explained easily by the pH curves for loading steps, since protons were known to compete with divalent metals (Fig. 30). With the controlled partial neutralization, the pH stayed almost at 6 until the breakthrough of Pb, and then gradually decreased below 4, until 100% breakthrough for Zn had occurred. On the contrary, without the controlled partial neutralization the pH stayed at around 1 until almost all of the breakthroughs had been completed, and then slowly increased towards 2. The previous observations mean that the controlled partial neutralization had removed protons from the resin, and thus better adsorption capacity was achieved. Also, since the pH of the feed solution was 6.3 and, if base

form resin was used, protonation of the resin would have increased the pH substantially and thus precipitations could have occurred.

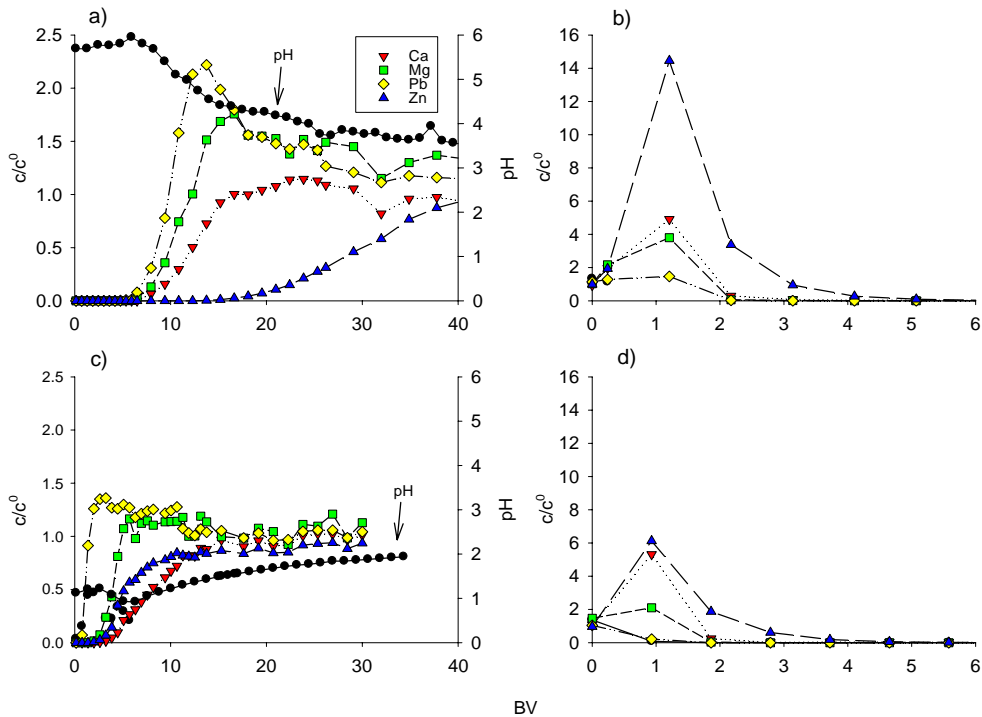


Figure 30. Purification of Ag-NaCl solution from divalent impurity metals by aminomethylphosphonium functional resin Lewatit TP-260 in batchwise column operation. a) Loading and b) elution curves with controlled partial neutralization. c) Loading and d) elution curves without controlled partial neutralization.

In cross-current operation (Fig. 31), 2.5 BV/switch of feed was introduced to each column in the purification zone. Pure product was only collected from the last column, and if all the three raffinates were joined, the purity was only 79% (Fig. 31). Since the switch time was 10 min, 0.25 BV/min of pure product was obtained during the whole run. The pure raffinate in the last feed column is diluted, in relation to, Ag to almost 60% of the feed concentration. This is because the column comes from the washing stage and has washing solution inside. The extract profiles (Fig. 31 b)) verify that no Ag traveled to the extract, but, since the washing stage was not connected to the feed, some Ag was lost to the washing solution. The cross-current run was at steady-state after six switches, that is, before one full cycle was operated.



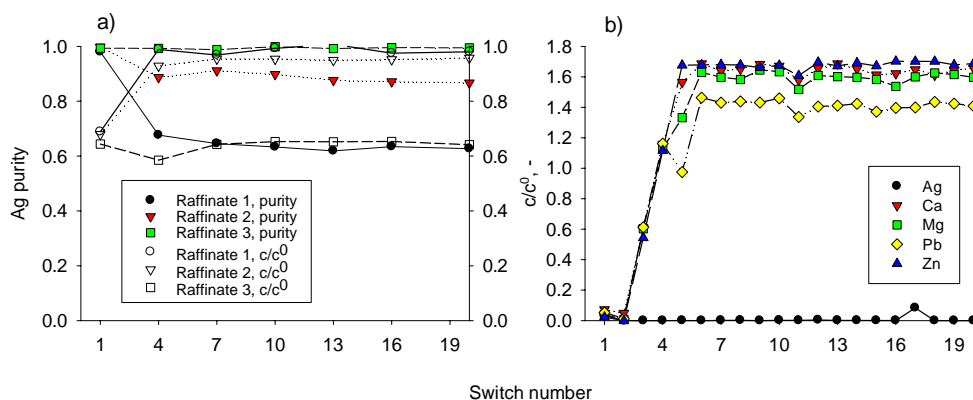


Figure 31. Purification of Ag-NaCl solution from divalent impurity metals by aminomethylphosphonium functional resin Lewatit TP-260 in cross-current SMB operation. a) Purities and dilutions of Ag in the three raffinates and b) concentration profiles in the extract.

In counter-current SMB operation, one column washing zone was added after the loading zone. These were connected so that the washing solution was recycled back to the feed (Fig. 32) in order not to lose the Ag in the void fraction of the bed. The drawback of the recycling is that the raffinate is diluted in relation to the ratio of the wash and feed flow rates. 8.0 BV/switch was the highest ratio of liquid and solid flows in loading step, by which the raffinate was pure during the whole SMB run (Fig. 32). The run lasted for 24 switches, meaning that 192 BV (0.32 BV/min) of Ag-NaCl was purified by that time. With 11.0 BV/switch feed rate, the raffinate was contaminated with Pb after 18 switches, though 198 BV (0.44 BV/min) of purified Ag-NaCl was collected by that time without the need to regenerate. It is also possible that the steady-state would be achieved with a slightly lower feed rate, but this was not studied in within this work.

The controlled partial neutralization worked as expected in both cross-current and counter-current SMB. The data with and without controlled partial neutralization in counter-current operation is shown in Publication V. More data from counter-current SMB runs is presented in Publication V, in which the effect and functioning of the controlled partial neutralization in counter-current SMB is also discussed.

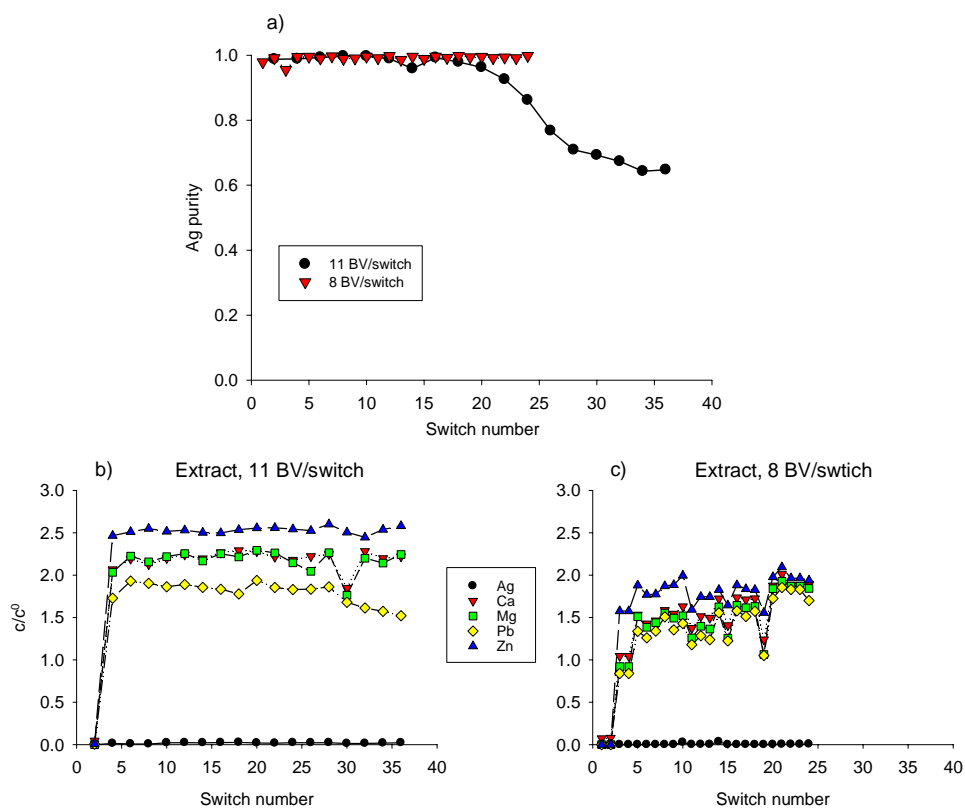


Figure 32. Purification of Ag-NaCl solution from divalent impurity metals by aminomethylphosphonium functional resin Lewatit TP-260 in counter-current SMB operation. a): Ag purities, and b), c): concentration histories of extracts in two runs with different feed rates.

The results indicate that counter-current SMB would be the more efficient process option for this particular purification task compared to cross-current operation, which is usually used in hydrometallurgical ion exchange processes. Thus, it is expected to be useful for complex and/or unconventional hydrometallurgical purifications, which the use of secondary raw materials often demand.

## 7 CONCLUSIONS

In this thesis, five different raw materials, both liquid and solid, were studied for the recovery of valuable metals. 99.7% Pure indium solution was obtained from LCD screens by leaching In and Sn to  $\text{H}_2\text{SO}_4$ , extracting both to D2EPHA, and selectively stripping In to HCl. In was also concentrated in solvent extraction stage by 148 fold from 44 mg/L to 6.5 g/L.

Ion exchange was concluded to be viable option for the recovery of Ge as a side product from different base metal process liquors. In this task, a chelating ion exchange resin with N-methylglucamine functionality was successfully used, and the mechanism for this moderately complex adsorption process was suggested based on equilibrium and dynamic modeling. Also, the crucial effect of pH to the adsorption was explained through theoretical examination of the feed solutions' aqueous chemistry. Germanic acid,  $\text{Ge}(\text{OH})_4$ , and its dissociation products ( $1^{\text{st}} \text{p}K_a \sim 9$ ) dominate the aqueous chemistry, and the dissociation products have better affinity to the resin by an anion exchange mechanism. Base metals in the feed solutions do not only compete on the adsorption to N-methyl site with proton, but also act as pH buffers, thus preventing the desired increment of pH via proton adsorption to the N-methyl sites.

Two different fluorescent lamp wastes were studied as possible raw materials for REEs. Each of these had significant amounts of Eu, Tb and Y. One waste was obtained from waste treatment plants process, and it was enriched in relation to REEs. Thus it also contained significant amounts of Gd and was chosen as a raw material for leaching experiments.  $\text{H}_2\text{SO}_4$ , HCl, and a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  were used as leachates at ambient conditions. Eu and Y were leached with all acid solutions with almost equally good yields, while the yields for Gd and Tb remained low. However, the selectivity over Ca was much better with  $\text{H}_2\text{SO}_4$  and the mixture leachates than with HCl, because of the low solubility of  $\text{CaSO}_4$ .

In steelmaking dusts, Zn is the most common target metal for recovery processes. In this case study, two argon oxygen decarburization (AOD) dusts were examined, and alongside Zn, Mo, Cr and Ni were defined as viable targets based on dust characterization and economic analysis. Leaching was done in ambient conditions, and only Zn and Mo were leached with high enough yields to be considered as targets for further purification. Three different leaching methods were used. Direct acid leaching gave the best yields, but Fe was also leached as an impurity. By controlling the pH during the leaching – so that it did not decrease below 3, but was as close as possible to 3 – gave good selectivity for Zn over Fe with only a small decrease in yield. Leaching with pure water gave the best yield and selectivity for Mo. Though ambient conditions were used in all of the leaching experiments, yields for the target metals were only, at most, 67%, and therefore more aggressive conditions should be considered. Zn was extracted with good yield and selectivity by D2EHPA, but not over Fe, meaning that the controlled leaching method should be used. High selectivity for Mo over Cr was not achieved with any of the solvent extraction reagents, but a Mo/Cr mixture was obtained with hydroxyoxime LIX 84-I, trioctylamine (TOA) and quaternary ammonium salt

(Aliquat 336). Extracting the water leachate without pH adjustment at pH 13.7 gave the best purity (100%) for the Mo/Cr mixture.

An Ag-NaCl solution was purified from divalent impurity metals with an aminomethylphosphonium functional ion exchange resin, Lewatit TP-260. However, it was also shown that controlled partial neutralization, so that the protons in the phosphonium groups were removed with conjugate bases of weak organic acids, was needed to achieve reasonable capacity. Counter-current SMB operation was shown to enhance the performance of the separation task, and almost 100% purity, without any loss of Ag, was achieved.

From the studied raw materials, a precipitate from waste fluorescent lamp treatment process was economically clearly the most promising.

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