THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Process Development for Extraction and Separation of In and Y from Discarded Flat Panel Displays

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Cover: Flow sheet of a countercurrent mixer-settler process for metal recovery

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Abstract

From the time of their invention in the 1970s, flat panel displays (FPDs) have slowly become the most used type of displays in televisions, computers, and cell phones. A major subgroup of FPDs is lLiquid crystal displays (LCDs). With the continuous growth of FPDs, the need and incentive to recycle the valuable components has also grown larger, as the displays will inevitably enter the waste stream.

Among the valuable components, indium from the transparent electrode coating on LCD glass and rare earth elements (REEs) from parts such as fluorescent lamp phosphors are of special interest for recycling from end-of-life products.

In this work, hydrometallurgical processes to recycle indium and REEs such as yttrium from different types of FPD waste were developed. The process comprised several steps such as leaching and solvent extraction. Result of the leaching studies showed that concentrations of metals such as iron and copper were much higher indium and yttrium. Furthermore, with respect to leaching efficiency and feasibility of subsequent solvent extraction process, 1 M H_2SO_4 was determined as the best leaching option for the recovery of indium from LCD glass and 1 M HCl for the recovery of both indium and yttrium from mixed FPD waste.

Several choices of aqueous and organic solutions were tested in a solvent extraction screening test to determine feasible choices of extractant and stripping agent. The results showed that extraction from H_2SO_4 using DEHPA in kerosene followed by back-extraction with HCl was a promising alternative for the recovery of indium. Indium and yttrium can be separated by selective extraction of indium from chloride media using Cyanex 923.

In order to further optimize the separation process, the effect of pH and temperature on the extraction of indium was investigated with H_2SO_4 or HCl as the aqueous phase and DEHPA in kerosene as the organic phase. From the temperature study it was concluded that the since the extraction of indium was an exothermic process, optimal extraction temperature was 20 ^{o}C. Furthermore, a process scheme was proposed for the recovery of indium and REEs from 1 M HCl leachate. This process was tested using laboratory mixer-settlers and was found to agree reasonably well with theoretical calculations based on the extraction isotherms of indium and yttrium.

Keyword: Recycling, LCD, Indium, Yttrium, Leaching, Solvent Extraction, DEHPA, Cyanex 923

LIST OF PUBLICATIONS

This Thesis is based on work contained in the following papers:

Paper I: **J.Yang**, T. Retegan and C. Ekberg, *Indium recovery from discarded LCD panel glass by solvent extraction*, Hydrometallurgy, 137, p. 68-77, 2013

Paper II: **J.Yang**, T. Retegan and C. Ekberg, *Optimization of Indium Recovery and Separation from LCD Waste by Solvent Extraction with Bis(2-ethylhexyl) Phosphate (D2EHPA)*, International Journal of Chemical Engineering, 2014

Paper III: **J.Yang**, T. Retegan and C. Ekberg, *Recovery of In, Y, Nd and Eu from WEEE by Solvent Extraction*, proceedings of ISEC 2014, Germany, 7-11 September, 2014, p. 53-60

Paper IV: **J.Yang**, T. Retegan and C. Ekberg, *Metal Separation by Solvent Extraction with Cyanex 471X,* proceedings of ISEC 2014, Germany, 7-11 September, 2014, p. 324-329

Paper V: **J.Yang**, T. Retegan,, B.M Steenari and C. Ekberg, *Recovery of Indium and Yttrium from Flat Panel Display waste using Solvent Extraction,* manuscript

Contribution Report

Paper I-IV: main author, all experimental work

Paper V: main author, majority of the experimental work

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1 Introduction

In many modern electronics, such as televisions, computer monitors and mobile telephones, flat panel displays (FPDs) have become the choice of display technology. FPDs can be further classified into several sub-categories based on the technology involved, including plasma display panels (PDPs), organic light-emitting diodes (OLED), and thin film transistor liquid crystal displays (TFT-LCDs), with TFT-LCDs forming the largest part. Taking into consideration the large quantity of products in use and the increasing rate at which old technology is being replaced, FPD waste has been acknowledged as the fastest-growing waste electronic and electrical equipment (WEEE) stream [1]. By 2015, it is expected that 25 million m^2 LCDs will enter the European waste stream [2]. In short, LCD waste and its recycling is a growing problem, and it is important with respect to economy, environment and sustainability to develop recycling processes to recover valuable materials from the waste, i.e. indium and rare earth elements (REEs).

The TFT material is a layer of Indium-Tin Oxide (ITO) with a thickness of approximately 150 nm, where the ratio between indium oxide and tin oxide is approximately 9:1 by weight. Oxides of REEs in LCDs can be found in parts such as loud speakers and backlights. In 2010 these metals were listed by the European Commission in a report as one of 14 critical raw materials, based on assessments of its supply and economic importance [3]. According to the most recent report, the price of indium metal averaged at 695 $/kg [4], which is slightly higher than silver, yttrium was priced at 16 $/kg for yttrium oxide and 60 $/kg for metal [5]. Yttrium and other rare earth elements are primarily recycled from the phosphor powder of fluorescent lamps in small quantities [5] and indium is recycled from scrap ITO in South Korea and Japan, but few to no recycling data are available for countries such as the USA [4].

Currently, there are a number of research projects on the topic of indium recycling from LCD waste, and many earlier studies on the recovery of REEs from sources such as discarded vehicle batteries and fluorescent lamps. However, not many earlier studies on indium recovery were based on real FPD waste, where other contaminants, both metallic and non-metallic are present. In addition, there are even fewer studies that investigated recovery of both indium and REEs from real mixed FPD waste.

The main goal of this project was to investigate and suggest a feasible laboratory process ready for scaling-up for the recycling of indium and REEs from real FPD waste. This process is intended to use mechanically crushed FPDs, most of which are LCDs as starting material, and the aim was to separate indium and yttrium into pure streams. It is also clear that the waste streams will be rather heterogeneous and thus the “total metal content” given in this work is only indicative and valid for this particular recycling facility. However, processes developed should be robust enough to be able to handle considerable variations in metal concentration. Due to the aforementioned criterion a hydrometallurgical route was suggested comprising leaching followed by solvent extraction to separate the different metals, mainly indium, yttrium, iron, tin and zinc, from each other. Since the process developed in this project is intended to be scaled up from laboratory scale mixer settlers were used for the final process testing.

2 Background

2.1 Indium and ITO

The element indium (Z=49) is a soft, silvery white metal that was discovered in 1863 by Ferdinand Reich and Theodor Ritcher and named after the indigo color of its spectrum [6]. While it is considered nonhazardous in commercial use, the metal and the metalloid is known to be severely toxic and carcinogenic to humans and animals. [7]

The major sources of primary indium production are found in South America, Canada, China, South Korea and Japan. While Canada has the potential to be the largest source of indium, China is currently the biggest indium producer, accounting for 50-60% of the world's indium production [6]. On the consumption side, Japan is by far the largest indium consumer, taking 60% of the world's supply of indium [8].

The most important application of indium at the moment is in the form of indium tin oxide (ITO), consisting of 90% wt. indium oxide and 10% wt. tin oxide. ITO accounts for 70% of the global indium consumption [9]. In FPDs, more specifically in LCDs, ITO is used coated onto LCD glass as thin conductive films of approximately 150 nm in thickness (can vary between different manufacturers). Other uses include photovoltaic cells, metal lubricants, alloys and jewelry etc. [10].

The amount of indium in LCD varies between different manufacturers. It is known from earlier literatures [2], [11] that indium content in an LCD panel is in the range of 200 – 300 mg/kg glass, or 0.65 – 0.95 g In/m^2 glass, with tin being 10% of indium in mass. It is also likely that other metals can be found on e.g. the edges of the LCD panel.

2.2 Rare earth elements

Rare earth elements (REEs), or rare earth metals, is the name given to a group of 17 metals in the periodic table of elements. This group consists of yttrium, scandium and the 15 lanthanides. REEs can be further divided into Heavy Rare Earth Elements (gadolinium-lutetium-yttrium) and Light Rare Earth Elements (cerium - europium) [12]. Despite the word "rare" in its name, REEs are relatively plentiful in Earth's crust. For example, the abundance of cerium is 68 ppm in the crust, which is similar to copper, and none of them are rarer than metals such as silver, mercury and indium [13]. Despite their abundance, rare earth elements are more dispersed than metals of similar rarity and thus the numbers of economically exploitable sources are few [14].

The discovery of the first mineral containing REE (gadolinite) can be dated back to the end of eighteenth century [12]. The chemical properties of the lanthanides are similar to each other due to similarities in ionic radii and configuration in the outermost electron shells. However, their physical properties are quite diversified and that give REEs wide range of applications. A brief account of industrial applications of different REEs can be seen in Table 1. Promethium was excluded from the table because it is produced from nuclear fission of uranium-235 and has no stable isotope. Therefore its application is mostly limited in the field of scientific research. From Table 1, it can be seen that REEs are vital components in various technological products. This combined with the fact that China makes up for close to 90% of current world production of REEs means that the recycling is an important issue with respect to sustainable development [15].

Table 1. Applications of different REEs [12] [13].

Element	Application
Sc	High performance alloys, ceramics
Y	Phosphors and neodymium-yttrium-aluminum (Nd-YAG) garnet laser
La	Nickel-metal hydride batteries
Ce	Glass polishing, UV protection, catalyst
Pr	Permanent magnets (substitute for Nd)
Nd	Permanent magnets (Nd-Fe-B type), infrared lasers, glassing tinting
Sm	Permanent magnets (SmCo type)
Eu	Red phosphor
Gd	MRI contrast agent, phosphor
Tb	Substitute for Dy in permanent magnet
Dy	Addition in Nd-Fe-B permanent magnet, high performance ceramics
Ho	Lasers
Er	Fiber optics
Tm	X-ray application
Yb	Optical lenses
Lu	Host for scintillation detectors, optical coating, tumor treatment research

2.3 Liquid crystal displays

TFT-LCDs can be further divided into two subcategories, depending on whether cold cathode fluorescent lamps (CCFLs, using Hg vapor for electron discharge) or light-emitting diodes are used as the lighting device. The typical components of a typical LCD and their respective weight are presented in Table 2 [11]. The general structure of an LCD is presented in Figure 1. Other than components common to all electronics, e.g. printed circuit boards, the central component in an LCD is referred to as the LCD module. Within the module, the LCD glass (panel), various optical films, and backlight are arranged in a laminar structure. There is a difference in the construction of the module between an LCD TV and a computer monitor. For TVs, especially a large LCD TV (more than 40 inches diagonal), the lamps are arranged in a row in the back of the module (backlights), with an optical diffuser between the lamps and the panel to make the lighting more homogenous. For monitors, one lamp is placed at each of the long edges of the module behind the panel, and a “light-guide” is used to redirect the lighting towards the panel.

Table 2: Typical components of an LCD and their respective weight in grams per weight [11]

	Density (g/cm^2)	Portables		PC Flat Screen		TV Flat Screen	
		Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Diagonal (inches)		12.1”	20.1”	15”	40”	15”	40”
Area (cm^2)		4.32E+02	1.17E+03	6.97E+02	4.96E+03	6.97E+02	4.96E+03
LC Assembly							
Glass	1.91E-01	8.27E+01	2.24E+02	1.33E+02	9.49E+02	1.33E+02	9.49E+03
Electrode	7.00E-05	3.02E-02	8.20E-02	4.88E-02	3.47E-01	4.88E-02	3.47E-01
Alignment layer	1.00E-05	4.32E-03	1.17E-02	6.97E-03	4.96E-02	6.97E-03	4.96E-02
Liquid crystals	6.00E-04	2.59E-01	7.03E-01	4.18E-01	2.97E+00	4.18E-01	2.97E+00
Spacers	5.00E-07	2.16E-04	5.86E-04	3.49E-04	2.48E-03	3.49E-04	2.48E-03
LC Assembly total		8.29E+01	2.25E+02	1.34E+02	9.52E+02	1.34E+02	9.52E+02
Film Set							
Brightness enhancement film	6.83E-02	3.22E+01	8.89E+01	4.95E+01	3.52E+02	4.95E+02	3.52E+02
Diffuser	6.83E-02	3.22E+01	8.89E+01	4.95E+01	3.52E+02	4.95E+02	3.52E+02
Prism foil	6.83E-02	3.22E+01	8.89E+01	4.95E+01	3.52E+02	4.95E+02	3.52E+02
Light guide	4.76E-01 to 9.52E-01	2.25E+02	1.24E+03	3.45E+02	4.91E+03	3.45E+02	4.91E+03
Reflection foil	6.83E+02	3.22E+01	8.89E+01	4.95E+01	3.52E+02	4.95E+02	3.52E+02
Film Set total		**3.54E+02**	**1.60E+03**	**5.44E+02**	**6.32E+03**	**5.44E+02**	**6.32E+03**
Backlight Assembly							
Mercury	0.00E+00	2.46E-03	6.67E-03	3.97E-03	2.82E-02	3.97E-03	2.82E-02

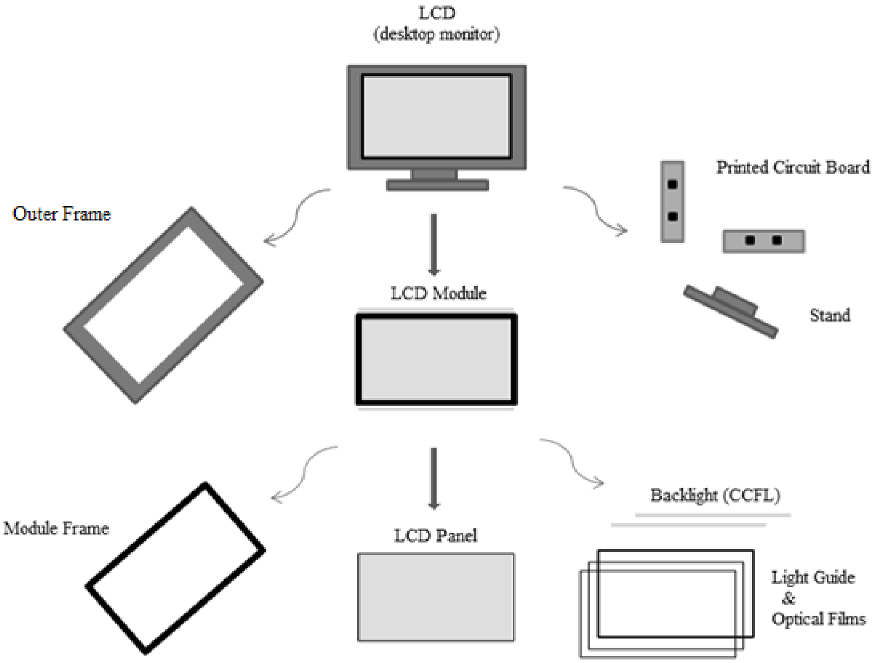
LCD
(desktop monitor)
Printed Circuit Board
Outer Frame
Stand
LCD Module
Backlight (CCFL)
Module Frame
LCD Panel
Light Guide
&
Optical Films

Figure 1: The main components within a LCD, and its general structure.

ITO is located in the LCD panel. Figure 2 illustrates the layered structure of the key components in a panel. It can be seen that the liquid crystal layer is situated between two glass panels. Other than the front panel having color filters they have identical structures. The majority of the weight is made up by the glass substrate layer, usually in the range of 1mm thickness, while the thickness of the liquid crystal, electrode (ITO) and color filter layers are 5 µm, 150 nm and 2 µm respectively [2].

It can be seen that on the outside of the glass substrates there are polymeric films called polarizing filters, or polarizers. The function of the polarizing filter is to allow only light waves of a certain orientation to pass through while absorbing or reflecting the rest. In the most common design of LCD, the orientation of the front and back polarizers is set to be perpendicular to each other. The general working principle of an LCD is shown in Figure 3. This is known as twisted nematic liquid crystal and was first presented in 1971 [16], allowing liquid crystals to be applied in the field of displays.

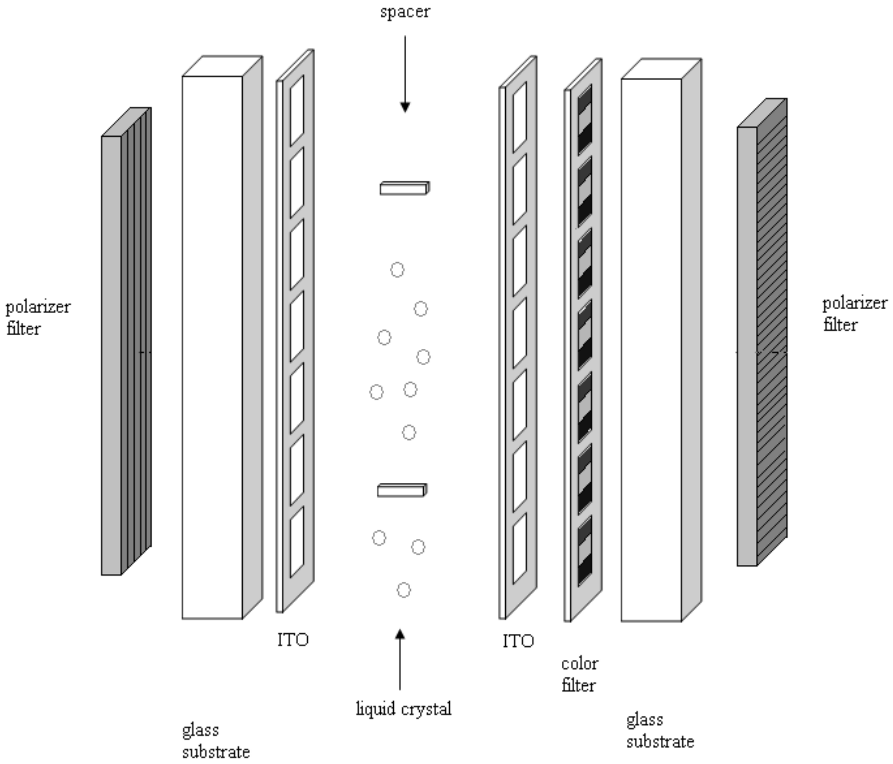

Figure 2: The internal structure and component of an LCD panel.

2.4 Recycling of LCDs

Previously there have been a number of studies on the recycling of indium from ITO scraps in the production waste of LCD manufacturing process. This is likely due to the fact that ITO is often coated onto LCD glass by sputtering, since one of the disadvantages of this process is that not all ITO particles ejected from the source material (ITO target) land on the glass substrate. However much research work has also been done regarding the recycling of indium and other valuable materials in LCDs and other types of FPDs. Some of these studies are outlined in this section.

A method for indium recovery through chloride volatilization, where HCl was produced by pyrolysis of poly-vinyl chloride (PVC) was presented in an earlier work [17]. At first a pure indium oxide sample was treated with HCl and studied in order to discern the effect of temperature and heating time on the volatilization of indium chloride. Afterwards, discarded cell phones were dismantled to collect the LCDs, which were then crushed and incinerated at 973 K to remove the plastic films and other organic materials. It was concluded that 84% of indium from LCD scrap could be vaporized with this method at 673 K. The main advantage of this method was that it uses one type of waste to recycle another type of waste. The drawback is the need to heat the samples to 973 K and the need of a specific atmosphere (nitrogen).

In Li J. et al [18], a set of treatment methods for the purpose of LCD recycling were investigated. The methods studied were: removal of polarizing filters by thermal shock in a furnace, removal of liquid crystal in an ultrasonic bath and acid leaching of indium. It was found that at 423 K the films became discolored and a temperature of 493 K was enough to allow the films to be easily separated by hand. For removing liquid crystals by ultrasonic cleaning, 40 kW power and a frequency of 40 kHz was found to be suitable. The acid dissolution of ITO was investigated by dissolving 1000 g of crushed glass in 500 ml solutions of various acid mixtures, at four different temperatures. The amount of indium dissolved over 60 minutes was then determined. The result graphs showed a positive proportionality between temperatures and amount of indium dissolved, up to 240 mg/l of indium could be obtained from the glass. However, in this work, no further study was done regarding the separation of dissolved indium from other metal species which might be present in the solution.

In a more recent publication [19, 19], the viability of an extraction system consisting of H_2SO_4 or HCl as the aqueous phase and tributyl phosphate (TBP) or DEHPA dissolved in kerosene as the solvent was investigated. The result for the extraction of indium from dissolved ITO showed that in sulfuric medium, DEHPA was found to be able to extract both indium and tin, and indium could then be selectively stripped (or back-extracted) by HCl. This work studied only the separation of two metals, while it is a good starting point, the material composition of the leachate of real FPD waste is much more complex. Therefore further work is needed to investigate the effect of other metal, e.g. iron, copper and zinc on the extraction and stripping of indium.

Between 2007 and 2009, a research project (Recovery of Flat LCDs using Advance Technological Processes, REFLATED) at the University of York investigated the recycling of liquid crystal from used LCD panels. Very high fractional extraction (>95%) of liquid crystal could be achieved by supercritical CO_2 extraction. However, as the liquid crystal layer is a mixture of various organic compounds, the separation of these components proved to be much more difficult. A spin-off study was also done to explore the possibility of recycling PVA in LCD polarizing films to produce materials with high specific surface area. [20]

2.5 Mercury

In older models of LCDs, mercury can be found in CCFLs. The design of these is dependent on the size of the display. A typical 37-inch TV contains 14 such CCFL tubes which in turn contain ~50 mg mercury per tube. Today the production of electronic equipment makes up for approximately 22% of the global mercury consumption **Error! Reference source not found.**. If the LCD glass waste is manually or mechanically sorted, the risk of mercury being found in the waste sample is low. However, if the discarded display is shredded without proper sorting, then it is possible that the shredded waste contains mercury.

One common method to remove mercury from the waste is thermal desorption [21], but for complete mercury removal temperatures of over 873 K are needed. Alternatively mercury can also be removed from solutions by solvent extraction. One example is extraction with triisobutyl phosphine sulfide (Cyanex 471X) from chloride or nitrate media. This extractant has been shown to have selectivity for mono- and divalent metal ions such as Ag(I) [22] and Hg(II) [23] [24].

3 Theory

3.1 Leaching

Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, usually permeable, solid phase with which it is associated. Leaching agents can include water, acid, bases and salt solutions. Oxidation-reduction reactions may also be involved [25].

In metal processing industries leaching has been extensively used to remove metals as soluble salts and is also referred to as a hydrometallurgical process [26]. Pre-treatment processes such as crushing and grinding are often used on the solid feed material prior to leaching, depending on the proportion of the soluble constituents, and their distribution in the bulk solid. This is often done in order to increase the rate of leaching.

When a material is being dissolved from the bulk solid to liquid, the rate of mass transfer from solid surface to the liquid is often the controlling factor. A simplified mass balance for the transport of solute from solid surface to liquid can be written as equation (1):

$$\frac{\bar{N}_A}{A} = k_L \cdot (c_{as} - c_a) \tag{1}$$

$\bar{N}_A$ is the rate of mass transfer, k_L is the mass transfer coefficient, c_{as} is the saturation concentration of the solute a and c_a is the concentration of solute a. A refers to the surface area of the solid. $\bar{N}_A$ can be further expressed as:

$$\bar{N}_A = \frac{Vdc_A}{dt} \tag{2}$$

V is the volume of the liquid. Substitute (2) into (1), and integrate with respect to time, with the boundary condition $c_a = c_{a0},\ at\ t = 0$ and$c_a = c_a,\ at\ t = t$, the analytical solution to the kinetics of leaching can be obtained:

$$\frac{c_{as}-c_a}{c_{as}-c_{a0}} = e^{\left(-\frac{k_L A}{V}\right)t} \tag{3}$$

When c_a is plotted against t, this result in the shape of a typical leaching kinetics curve, an example is shown in Figure 4.

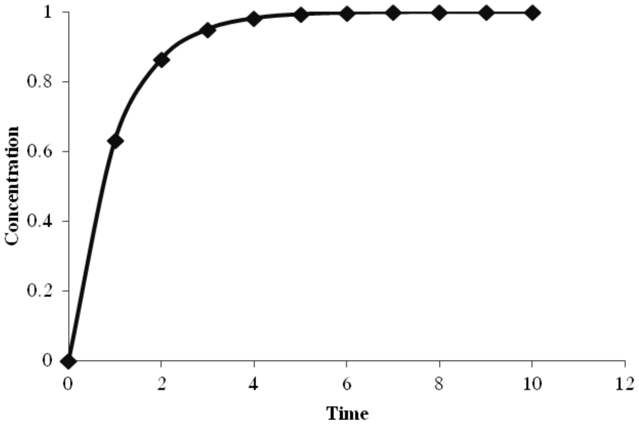

Figure 4: Theoretical plot of the amount of material leached as a function of time.

In general, leaching of a metal oxide can be represented by reaction (I). The choice of acid will not only affect the efficiency and kinetics of the leaching process, but also the subsequent solvent extraction process. In addition to the direct effect of the proton concentration, the leaching efficiency can also be affected by possible complexes between the metal and the anion of the acid. This complexation could either increase the solubility or cause another solid phase to precipitate depending on the different solubility products.

$$MO_v(s) + 2vH^+(aq) \leftrightarrow M^{2v+}(aq) + vH_2O(l) \qquad \text{(I)}$$

3.2 Solvent Extraction

Also named liquid−liquid extraction, this is a type of separation process has been applied in fields such as nuclear science, hydrometallurgy, as well as analytical and pharmaceutical chemistry.

A solvent extraction system comprises on several components, e.g. the elements to be separated, an aqueous medium, an organic phase made up of diluents and extractants [27]. All these parts will affect the performance of the extraction process such as distribution ratio and coalescence rate, and must be considered both separately and as a whole. The system is usually combined with other technologies, such as solidification/ stabilization, precipitation and electro-winning to produce the final product.

Some of the basic parameters in solvent extraction are defined in equations (4) – (7): the distribution ratio (D) is the ratio between the concentrations of a compound in the organic and aqueous phase. The separation factor (SF) is the ratio between D of two solutes A and B, and by convention the solutes A and B are chosen so that SF is greater than 1 [27]. The phase volume ratio θ is the ratio between the volume of the organic phase and that of the aqueous phase. The extraction factor P, is defined as the product of D and θ. In a continuous process, the aqueous stream leaving the extractor system is often referred as "raffinate" and the organic stream leaving the extractor system is referred as "extract"

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \tag{4}$$

$$SF_{A/B} = \frac{D_A}{D_B}, SF \geq 1 \tag{5}$$

$$\theta = \frac{V_{org}}{V_{aq}} \tag{6}$$

$$P = \theta D \tag{7}$$

D can be converted to extraction percentage (E) by equation (8)

$$E = \frac{\theta D_M}{1+\theta D_M} \times 100\% \tag{8}$$

Equation (14) is the linear form of Van't Hoff's equation. This equation was used to estimate the ΔH^o and ΔS^o of metal extraction as a function of 1/T.

$$Ln(K_{ex}) = -\frac{\Delta H^o}{R} \cdot \frac{1}{T} + \frac{\Delta S^o}{R} \tag{9}$$

For acidic extractants with extraction mechanism shown in reaction (II), the relation between D and K_{ex} can be derived according to equations (16) and (17). The mole fraction, m_{MLa} can be calculated from equilibrium calculations using appropriate stability constants, under the assumption that the concentration of solute is much smaller than the concentration of the inorganic ligand which forms chemical complexes with the solute. This assumption was for the most part true for the aqueous system studied.

$$(ML_a)^{\nu+} + \nu\overline{(HA)_2} \leftrightarrow \overline{(MA_\nu(HA)_\nu)} + \nu H^+ \tag{II}$$

$$D_M = \frac{\overline{[(MA_\nu(HA)_\nu)]}}{[M]_{tot}} \approx m_{ML_a} \cdot \frac{\overline{[(MA_\nu(HA)_\nu)]}}{[(ML_a)^{\nu+}]} \tag{10}$$

$$K_{ex} = \frac{(\overline{[MA_\nu(HA)_\nu]}[H^+]^\nu)}{([(ML_a)^{\nu+}]][(HA)_2]^\nu)} \approx \frac{D_M}{m_{ML_a}} \cdot \frac{[H^+]^\nu}{\overline{[(HA)_2]^\nu}} \tag{11}$$

3.2.1 Effect of extractants in solvent extraction

In general, charged or hydrated compounds such as dissolved metal ions are not soluble in most organic solutions. In order to extract metals to the organic phase, aqueous metal species must be modified to make them more hydrophobic. Organic molecules participating in such modifications are called extractants, and depending on the mechanism of extraction, they can be classified into three main groups [28]:

1) Acidic: the organic acid dissociates, and its conjugated base reacts with metal cation to form a neutral complex.
2) Basic/ion pair: forms an ion pair with a negatively charged metal complex in the aqueous phase
3) Solvating: replaces hydrated water molecules in the inner coordination sphere of the metal ion.

For industrial applications, the following criteria are used to assess the extractants [28]:

1) The ability to transfer the desired metals across the aqueous-organic interface
2) The ability of the extractant-diluent mixture to function efficiently with the proposed feed and strip solutions in terms of rates of operation and stability towards degradations

3) The ability of the extractant to perform with maximum safety to plant, personnel and environment at minimum cost

4) The ability of the process to interface with other unit operations both upstream (leaching) and downstream (winning) in the overall extraction flow sheet.

In the past, different types of organic molecules have been studied as extractant for indium separation in aqueous media. Many of these extractants are organophosphate compounds. A few of them will be briefly described:

Cyanex 923

This is a mixture of four different types of trialkyl phosphine oxides, with the general chemical formulae: $R_3P{=}O$, $R_2R'P{=}O$, $R(R')_2P{=}O$, $(R')_3P{=}O$, where R is an octyl- group and R’ is a hexyl-group. Compared to a similar extractant tri-octyl-phosphine oxide (TOPO), the advantages with Cyanex 923 are that it is completely miscible with most common organic diluents at low ambient temperature, and that it has low aqueous solubility [29]. In another work [30], an extensive study has been done on indium extraction with Cyanex 923 as extractant in toluene. Different aqueous phases consisting of indium and another metal dissolved in HNO_3, HCl or H_2SO_4 were tested. Results showed that with a few exceptions such iron, indium could be quantitatively extracted ($D \approx 10$) with good separation ($SF \approx 100$) from the impurity that was present.

Bis(2-ethylhexyl)phosphoric acid (DEHPA)

This molecule was first synthesized in the 1960s for nuclear technology-based applications, e.g. extraction of actinide ions in acidic solutions [31]. In an early study [32] regarding the extraction of indium from aqueous acidic media, D and extraction mechanism of indium from nitric, sulfuric and hydrochloric acid to DEHPA diluted in kerosene was investigated. The results showed that quantitative extraction of indium could be achieved at pH between 0 and 1 with H_2SO_4, HNO_3 or HCl being the aqueous phase.

Furthermore, other extractants such a as mixture of 5-dodecylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent (LIX984) [33], bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) [34] and tributyl phosphate (TBP) [35] have also been studied for the recovery of indium by solvent extraction. It can be seen that all of the aforementioned extractants are either acidic or solvating extractants. Extractants that extracts metals through forming ion pairs are rarely used in this case. This is because these types of extractants are anion exchanges (e.g. tertiary and quaternary amines), i.e. they form extractable complexes with anionic metal complexes in the aqueous phase. Since the concentration of these anionic metal species are often low, in e.g. 1 M inorganic acid solutions which are often used for leaching, this type of extractant is not as effective as acidic or solvating extractants.

3.2.2 Effect of organic diluents in solvent extraction

Other than the extractants, properties of the organic diluents can also influence the efficiency of the solvent extraction process. An important property of an organic diluent in solvent extraction is its mutual solubility with water. In solvent extraction, one of the classification methods for diluents in general divides them into five classes based on their abilities to form hydrogen bonds [36]. The classes can be summarized as:

Class 1: liquids capable of forming a three-dimensional hydrogen bond network.

Class 2: liquids having hydrogen bond donor atoms and active hydrogen atoms, but do not form a three-dimensional network themselves.

Class 3: liquids consisting of molecules with hydrogen bond donor atoms, but no active hydrogen atoms.

Class 4: liquids containing molecules with active hydrogen atoms, but no donor atom.

Class 5: liquids with no hydrogen bond forming capabilities and no donor atoms.

Since water belongs to class 1 according to this definition, organic diluents of the same class are likely to be miscible with water, and are thus a poor choice for the purpose of solvent extraction. Here it is of interest to note that diluents of class 3 can bind and extract metal ions in aqueous phase directly (e.g. cyclohexanone).

For a few common organic diluents, their water solubility (wt. %) are: toluene (0.03) [36]; cyclohexanone (8.0) [36]; octanol (0.06) [37]; kerosene (traces) [37]. Ideally, the organic diluent to be used in a solvent extraction process should be as water-immiscibility as possible.

Furthermore, the ability of an organic diluent to form hydrogen bonding can affect the solubility of extractants in the organic phase. For instance, octanol possesses both an active hydrogen atom and donor atoms for hydrogen bonding, but cannot form three dimensional networks. This factor could result in low solubility of extractants (large molecules), or aggregation of extractant molecules, which leads to reduced D [38].

Another important diluent property that can affect solvent extraction efficiency is the polarity of the solvent. Since extractants form neutral complex with metal ions, the solubility of the neutral complex in the organic phase is inversely proportional to the polarity of the organic diluent.

3.2.3 Screening test

Since the choice of aqueous media, extractant and diluent all affect the outcome of the extraction process, as a first step in process development, suitable aqueous and organic phases for both the extraction and stripping of the metal of interest are often investigated in a so-called screening test. In such tests a number of organic extractants, diluents and aqueous solutions by performing simple batch extraction using small volumes.

3.2.4 McCabe-Thiele Diagram

In the design of a continuous process on bench scale, the number of (countercurrent) stages needed is a vital parameter to determine. One useful method to estimate the number of ideal stages is to construct a McCabe-Thiele diagram.

There are two main components in a McCabe-Thiele diagram for modelling counter current extraction processes, as shown in Figure 5. Operating line represents overall material balance. It is constructed by plotting the solute concentration in aqueous phase and (desired) solute concentration of the solute in the extract as a point in a graph such as Figure 5, and then draws a line towards the origin with slope equal to the reciprocal of θ of the extraction stages until it intersects with x-axis. The value on x-axis at the intercept is the solute concentration in the raffinate. The curve in the diagram the extraction isotherm which contains data of extraction equilibrium of the solute studied. The isotherm is constructed from experimental data. There are two alternatives of experiments. One involves re-contacting of the organic phase with fresh aqueous phase and the other method involves varying θ. In the second method, a number of batches of the aqueous and organic phase are mixed at different phase volume ratios between e.g. 1:10 and 10:1 until equilibrium is reached. Equilibrium pH must be kept the same. [39] Metal concentrations in the aqueous and organic phase are then determined for each batch and are plotted in an organic concentration vs aqueous concentration graph as shown in Figure 5. The best-fitted curve between the points is the extraction isotherm.

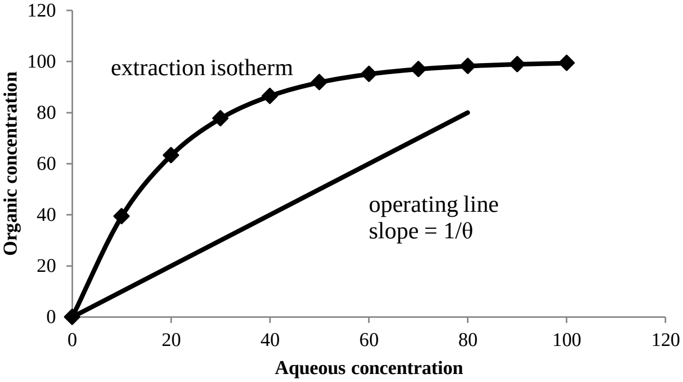

Figure 5. Example of a McCabe-Thiele diagram with extraction isotherm and operating line

An example of calculation for a multistage countercurrent process is shown in Figure 6. The calculation is made with the assumptions that θ is constant in all extraction stages and equilibrium is reached in each extraction stage. In order to calculate the number of theoretical stages, a horizontal line is drawn from point A towards the extraction isotherm until it intersects with the isotherm at point B. Then a vertical line is drawn until it intersects with the operating line. This procedure can be repeated until desired metal concentration in the raffinate is reached. The number of “steps” as shown in Figure 43 denotes the number of ideal stages. Values of coordinates (x,y) at point A are solute concentrations in aqueous feed (x) and organic extract (y). Coordinates at where the “steps” intersect with the extraction isotherm (e.g. points B and C) are the equilibrium concentrations of aqueous and organic phase at each extraction stage.

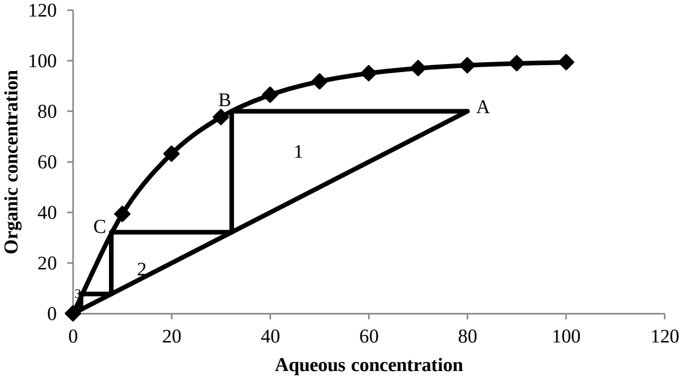

Figure 6. McCabe-Thiele Cascade for a 3 stages, countercurrent continuous extraction process.

3.2.5 Interfacial crud in solvent extraction

Crud, short for “Chalk river unidentified deposits”, is defined as the material resulting from the agitation of an organic phase, an aqueous phase and fine solid particles, that form a stable mixture. It often collects at the interface between the organic and aqueous phase [40]. In a continuous process the formation of crud can result in the loss of solvent, resulting in extra operation cost.

Many factors, including the composition and degradation of the organic phase can give rise to the formation of crud. Other factors such as the presence of humid material in the organic feed, presence of suspended solids, and hydrolysis of compounds in the solution can also contribute to the formation of crud. The presence of fine particles of silica in solutions is also a major cause of crud formation [41].

Since the problem with crud formation is often site-specific, methods to reduce and prevent it are also very different depending on the source of the crud material. For example, if suspended solid is the origin of crud, then its formation can be prevented by thorough filtration. But in other processes such as zirconium-TBP circuit, crud can be prevented by keeping the process below saturation loading [40].

4 Experimental

The processes proposed in this work focus on the recycling of indium and yttrium from genuine discarded FPDs by hydrometallurgical methods. Such processes are part of a complete recycling process, from collection and sorting of the waste, to the production of new products using recycled material.

In this project two waste fractions were studied; they are shown in Figure 7. Since the LCD glass was sorted from other wastes before being shredded, this fraction was used for the development of an indium recovery process since it contains almost no yttrium.

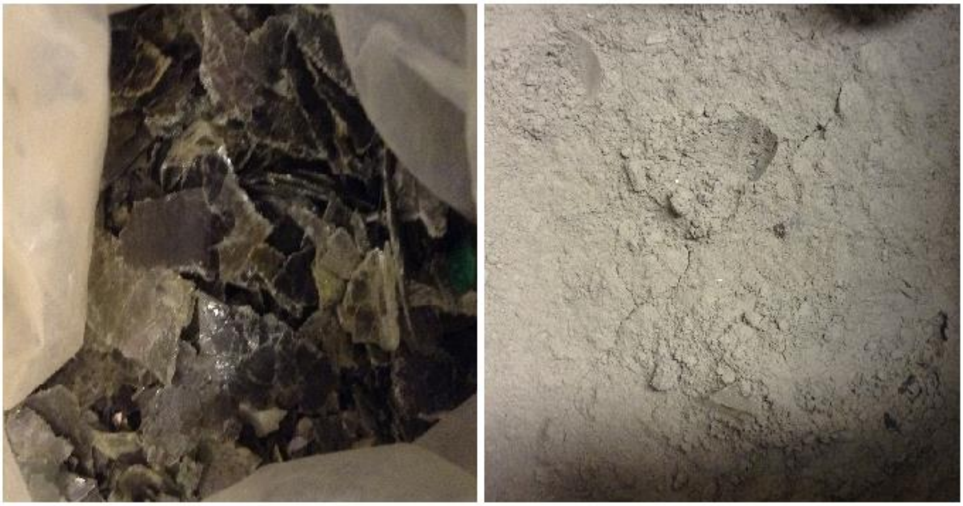

Figure 7. Images of LCD glass (left) waste and mixed FPD waste (right).

The other fraction is mixed FPD waste in form of a powder (<1 mm), and it was obtained from an automatic shredding line. As the result of no pre-sorting, it contains both indium and yttrium, along with higher concentration of other metals such as iron, this fraction was mainly used for the purpose of designing a process to recover yttrium.

Regardless of which type of waste was treated, the main steps are the same, as shown in Figure 8. The solid waste material is first leached with an acid to dissolve metal and metal oxides contained in the waste into the solution. The acid solution after leaching (leachate) is contacted with an organic solution composed of a diluent and an extractant (solvent or organic phase), where some of the metals were selectively extracted. Metals extracted to the organic solution were then stripped by a clean stream of aqueous solutions. Since the mixed FPD fraction is more complex, several pre-treatment procedures could be needed. For example since older models of LCDs used fluorescent lamps that contain mercury, it could be necessary to first remove mercury in the leachate by solvent extraction before other metals. Moreover, the more complex nature of mixed FPD waste also means that the solvent extraction part of the process would require, e.g. multiple types of different extractants and a larger number of extraction stages compared to the recovery of indium from LCD glass.

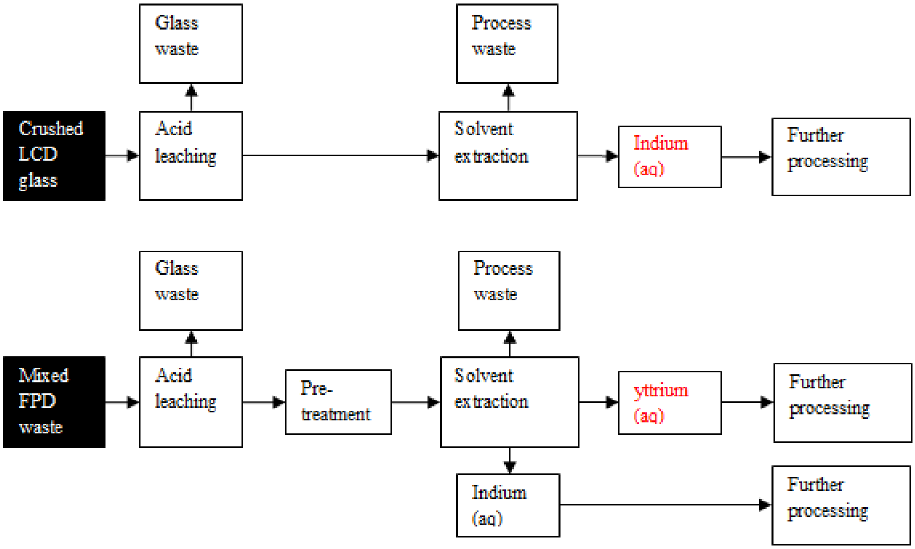
Glass waste
Process waste
Crushed LCD glass
Acid leaching
Solvent extraction
Indium (aq)
Further processing
Glass waste
Process waste
Mixed FPD waste
Acid leaching
Pre-treatment
Solvent extraction
yttrium (aq)
Further processing
Indium (aq)
Further processing

Figure 8: Flow sheet of the major steps in the recycling process for crushed LCD glass (recovery of indium) and Mixed FPD waste (recovery of yttrium).

4.1 Leaching

Metal concentrations in the leach liquor were determined using inductively coupled plasma with optical emission spectrometer (ICP-OES, Thermo iCAP-6000). The detection limit of the instrument for the metals of interest is in the range of parts per billion (<0.1µM), which is low enough for the quantification to be reliable. The samples were diluted by a volumetric factor of 10 in 0.1 M HNO_3. The metal contents were quantified using ICP-OES with standard solutions of known concentrations. All leaching experiments were performed in 120 ml polypropylene beakers. The rate of stirring was approximately 350 rpm with 6 x 20 mm stirring magnets.

4.1.1 Leaching of LCD glass

Leaching of crushed LCD glass by aqua regia over 2 days was done to characterize the types and approximate quantities of metals present in waste LCD glass. Scanning Electron Microscope (SEM, FEI Quanta 200 ESEM FEG) images were taken, and Energy Dispersive X-Ray analysis (EDX, Oxford Inca 300) was done of the glass before and after leaching with aqua regia to estimate the amount of ITO removed. Leaching kinetics for HNO_3 (65%, Sigma Aldrich), H_2SO_4 (>95%, Fisher Scientific) and HCl (>37% Sigma Aldrich) was studied at initial concentrations of 0.1 M, 1 M and 6 M. The solid-to-liquid (S/L) ratio of crushed glass and acid was 0.1 g/ml. The mixture of acid and sample was mechanically agitated for up to 4 days. Aliquots of 1 ml leachate were collected at multiple points between 20 minutes and 4 days after leaching started. Some of the glass samples were leached again in 6 M HCl to verify how much indium remained on the glass after leaching once. The effect of chloride concentration on leaching was investigated by preparing HCl solutions with different chloride concentrations. This was done by the addition of NaCl into 0.01 M HCl solutions.

4.1.2 Leaching of mixed FPD waste

As shown in the previous section, the mixed FPD waste is in the form of powder with unknown origin. Therefore it is even more important to characterize its content before additional studies are done. Leaching with aqua regia was first used to determine the total metal composition in the solid waste. Leaching behavior of the waste was studying by leaching with acid having concentration of 1 M. The leachate was sampled at multiple points between 1 h to 4 d, S/L=0.1 g/ml. The effect of temperature on leaching was studying by leaching at performed at 293 and 353 K. The acid solutions used for leaching were diluted from concentrated HNO_3 (65%, Sigma Aldrich) or HCl (>37%, Sigma Aldrich) with de-ionized water. Proton concentration after leaching was reduced by approximately 15% from 1 M. Due to this reduction there was no hindrance to the design of subsequent solvent extraction processes using this leachate as aqueous feed. Precise control of acid concentration using e.g. potentiometric titration equipment was not used.

4.2 Additional treatment for mixed FPD waste

Since the mixed FPD waste can be contaminated by small amounts of mercury, a hydrometallurgical method for mercury removal was tested, namely a pre-extraction step where Cyanex 471X (Cytec) dissolved in kerosene (Solvent-70, Statoil) was used to selectively extract mercury from leachate solutions. The concentration of Cyanex 471X was 0.1 M, unless otherwise stated. Equal volumes (1 ml) of both phases were mixed in 3.5 ml glass vials under mechanical shaking at 1500 rpm (IKA VIBRAX VXR). For kinetics study the mixing time varied between 5 min and 60 min while for the other studies a mixing time of 40 minutes was used. Extraction temperature was varied between 293 K and 333 K in the temperature study, in other experiments temperature was kept at 293±1 K.

In all the experiments performed, the aqueous phase was obtained by leaching of mixed FPD waste at a solid to liquid ratio of 0.1 g/ml in either 1 M HCl (37% puriss, Sigma-Aldrich).

4.3 Solvent extraction, batch experiments

Samples of the aqueous phase before and after extraction were analyzed by ICP-OES after dilution. D and separation factors were calculated by taking the mass balance in aqueous phase before and after the extraction. Due to several factors such as detection limit of the analytical instrument, phase entrainment and measurement error, there is a limit on the value of D that can be reliably determined. Therefore in this work if measured D is one standard deviation above 100, it is considered as “>100”, and “<0.1” for values more than one standard deviation lower than 0.1.

4.3.1 Extraction of indium from leachate of LCD glass

In batch experiments, equal volumes (1.5 ml) of organic and aqueous phase were shaken by machine (IKA VIBRAX VXR basic) at 1500 rpm and room temperature (293±2 K).By batch testing at different mixing times it was observed that the extraction of indium reached equilibrium in less than 10 min; therefore 10 min was selected as the contact time for the batch test. A screening test on various commercially available diluents and extractants was performed. The diluents chosen were kerosene (Solvent 70, Statoil), toluene (99.5%, Sigma Aldrich), n-octanol (96%, Acrōs Organics) and cyclohexanone (99.8% Lab-Scan Analytical Science), and the reagents were TBP (97%, Sigma Aldrich), Cyanex 272 (85%, Cytec) and 923 (93%, Cytec), and DEHPA (97%, Sigma Aldrich). All extractants were diluted to 0.1 M concentration. The extractant concentrations were selected based on several previous studied where the extraction of indium was studied [35] [30] [19]. The aqueous phase was prepared by dissolving salts of the most abundant metals found in total material analysis in sulfuric or hydrochloric acid. Metal concentrations in the prepared aqueous phase were as given from the dissolution experiments. In the extraction kinetics investigations, the shaking time varied between 5 and 150 min.

4.3.2 Extraction of indium and yttrium from leachate of mixed FPD waste

The aqueous phase used in the solvent extraction studies was obtained by leaching genuine solid FPD waste samples in H_2SO_4 (>95%, Sigma Aldrich), HCl (>37% Sigma Aldrich), and HNO_3 (65%, Sigma Aldrich) at 1 M and 6 M concentrations and 85±5^{o}C for 16 h. The solid-liquid (S/L) ratio was 0.1 g/ml and the acid solutions were mechanically stirred at 350 rpm. Solid samples were in the form of powders and were one of the fractions obtained from a FPD waste shredding line.

A screening test by batch extraction was performed in order to determine distribution ratios of metals between aqueous and organic phase. 1.5 ml of each organic and aqueous phase was added to a 3.5ml glass vial. The extractions were performed at room temperature (293±2 K). A simple kinetics study was performed and it was found that distribution ratios reached equilibrium after approximately 30 minutes of mechanical shaking (IKA VIBRAX VXR basic) at 1500 rpm. Therefore a contact time of 30 minutes was used.

The organic diluents studied were kerosene (Solvent 70, Statoil), MIBK (>99%, KEBO), n-octanol (96%, Acrōs Organics) and cyclohexanone (99.8% Lab-Scan Analytical Science), and the extractants were TBP (97%, Sigma Aldrich), Cyanex 923 (93%, Cytec), C2-BTBP and $CyMe_4$-BTBP was synthesized in-house. 2% volume n-decanol (99%, Sigma Aldrich) was added to organic phases containing TBP as third phase inhibitor.

4.4 Optimization of extraction temperature

Due to a few advantages such as low entrainment and the possibility of measuring a large number of points in a single experiment, AKUFVE (Swedish acronym “apparatus for continuous measurement of partition factors in solvent extraction”) was used for investigating the effect of temperature on the extraction of indium from LCD glass leachate. For more information about the AKUFVE system, see Appendix B. The aqueous phase used in the experiments was similar to that of the screening test. Based on the results in the screening test, two extraction systems were chosen for further study, namely H_2SO_4/0.1 M DEHPA in kerosene, and HCl/0.1 M DEHPA in kerosene. The effects of temperature on D were investigated between 283 K and 323 K. In each AKUFVE experiment, 100 ml aqueous and organic phase was used. At each sampling, 1 ml of both phases was taken for analysis. The sampled organic phase was contacted with 2 M HCl solution and shaken by machine for 20 min at 1500 rpm and 293±2 K to strip metals extracted for concentration determination. Metal concentrations were quantified with ICP-OES.

4.5 Mixer-settler experiments on mixed FPD waste

As a test for the practical feasibility of the metal recovery process proposed using data from batch extraction, experiments using continuous contactor were performed using laboratory scale mixer-settlers as described in an earlier report [42]. Up to three stages connected in a counter current flow setup were used. The mixer-settlers were made of PVDF, the volumes of the mixing and settling chambers were 100 ml and 500 ml, respectively. The pump rate was set to approximately 2 ml/min for both organic and aqueous flows. The rate of stirring was set to approximately 1000 rpm, and samples of both phases were taken after 600 ml (2 stages) or 900 ml (3 stages) of solution had been pumped through the system, in order to ensure that equilibrium had been reached. Leachate of the solid waste was used as aqueous feed (HCl with an initial concentration of 1 M). The organic feed was 0.25 M Cyanex 923 diluted in kerosene, with 1% toluene.

The separation and recovery process of indium and REEs such as yttrium from acidic leachate was divided into four major steps: (1) separation of indium and yttrium with Cyanex 923; (2) stripping of indium from loaded organic phase to another aqueous phase; (3) extraction of yttrium from the aqueous phase in step 1 with DEHPA; (4) back-extraction of yttrium from the loaded organic phase from step 3.

5 Results and Discussion

5.1 Acid Leaching

5.1.1 Characterization of the waste materials

As mentioned in section 2.1, the amount of indium in LCD glass can vary depending on manufacturers and manual or mechanical separation procedures. Therefore it is necessary to analyze the metal content of the waste received by e.g. leaching with aqua regia. The samples were then leached by more dilute mineral acids to study the leaching kinetics for indium, tin and the most abundant metal impurities.

The results of aqua regia leaching for LCD glass waste are given in Table 3. It shows that other than indium and tin from ITO, iron, copper, aluminum and zinc are also present as metal impurities. As can be seen, the content of metals other than indium and tin can vary greatly, especially aluminum, copper, iron and zinc. This is mainly due to factors such as the method used to dissemble the LCD, and how well the glass was separated from other parts of an LCD before the leaching stage. The leaching process reached equilibrium after 2 hours.

Table 3: Metal content of shredded LCD panel glass determined by leaching in aqua regia. The uncertainties are a calculated standard deviation from triplicates.

Element	Metal content (mg/kg glass)	Element	Metal content (mg/kg glass)
Ag	4±3	In	200±50
Al	65~825	Mg	6±1
Co	4±0.4	Mn	2±0.5
Cr	4±0.4	Ni	17±4
Cu	10~250	Sn	20±3
Fe	70~500	Zn	20~270

SEM image and EDX analysis on the LCD glass before and after leaching was performed in order to determine whether there was any indium remaining, as shown in Figure 9. The patterned ITO coating is clearly visible in Figure 9a. On the other hand, after leaching with aqua regia (Figure 12b), the ITO layer was no longer observed. Instead the rectangular-shaped color filter blocks positioned below the ITO coating were exposed. In addition, EDX analysis on the surfaces shown in Figure 9 was performed. The EDX results indicate that more than 95% of the ITO has been dissolved by aqua regia. Therefore 200±50 mg/kg glass can be taken as the average indium content in the LCD glass studied.

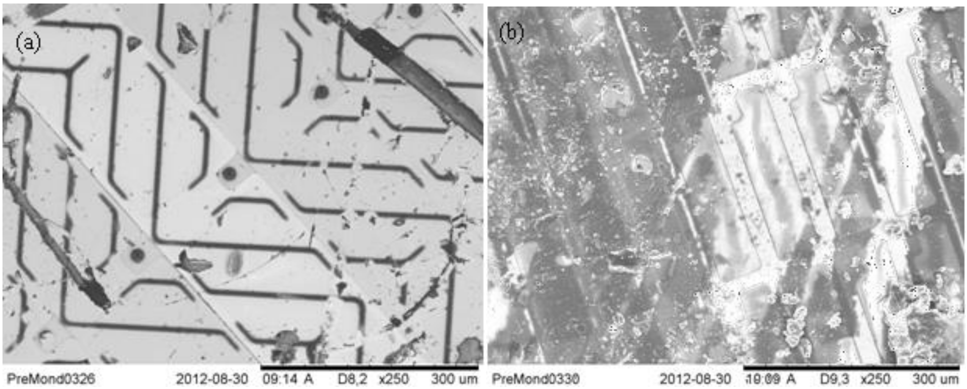
(a)
(b)
PreMond0326 2012-08-30 09:14 A D8,2 x250 300 um
PreMond0330 2012-08-30 10:09 A D9,3 x250 300 um

Figure 9: SEM image of crushed LCD glass: a) before leaching by aqua regia, where the ITO layer is visible, b) after the ITO has been dissolved by leaching with aqua regia

Similar to the leaching of LCD glass waste, aqua regia was used to leach samples of the mixed FPD waste to characterize the metal content. The result is shown in Table 4. The content of yttrium is an order of magnitude higher than that of indium. Moreover, other metals such as aluminum, iron, copper, and zinc were detected in much larger concentrations than that of indium and yttrium. The presence of these metals in such quantities is expected to be a challenge in the subsequent separation process.

Table 4. Metal content mixed FPD waste. The uncertainties were calculated as the standard deviation of triplicate samples.

Metal	Metal content (mg/kg waste)	Metal	Metal content (mg/kg waste)
Al	10300±500	Mo	110±5
Co	20±4	Nd	190±35
Cu	3700±220	Ni	410±85
Eu	310±200	Sn	720±40
Fe	22000±8000	Y	3190±350
In	300±50	Zn	3700±850

5.1.2 Leaching of indium from LCD glass waste

The results of the leaching test are presented in Figures 10-12. Measured values of metal concentration in the leachate were calculated back to mg metal/kg waste to facilitate comparison with material characterization data in Table 3. Regardless of the type of acid and concentrations of the acid used, the maximum amounts of indium leached are approximately 200 mg/kg glass, this corresponds to a concentration of 0.17 mM in solution. This is in good agreement with results from leaching in aqua regia is presented in Table 3. Some of the glass samples were leached for a second time with 6 M HCl, comparison of the results showed that roughly 90% of ITO was removed by leaching with acid once.

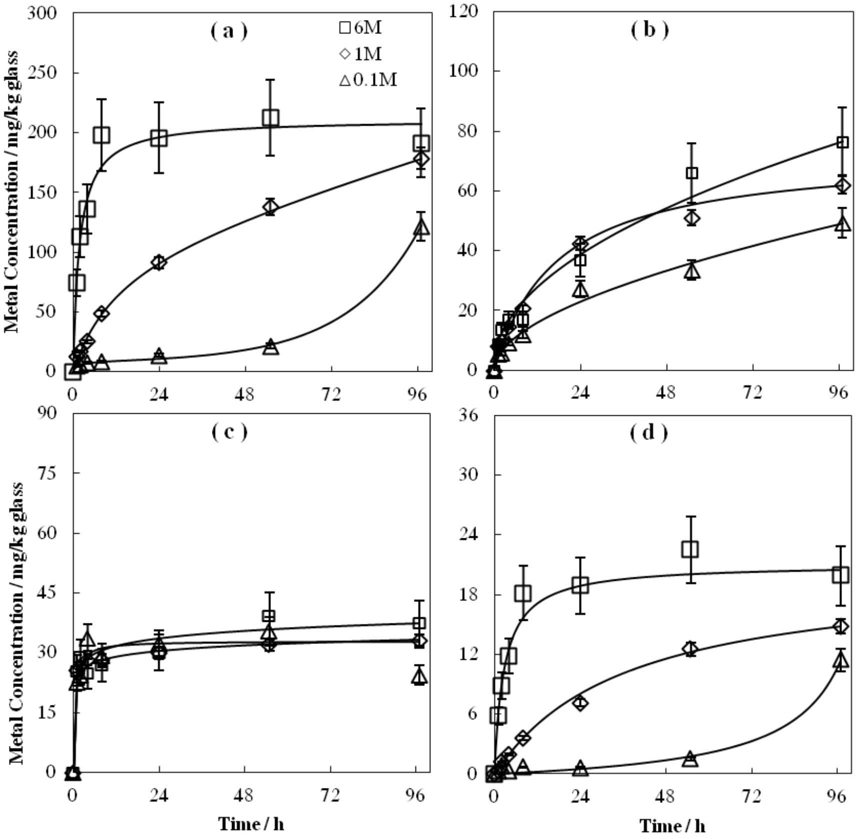

Figure 10: Leaching kinetics of (a) In (b) Al (c) Fe (d) Sn kinetics in HNO_3 between 1 hour and 4 days. Crushed glass of an LCD monitor was immersed in HNO_3 of different concentrations under mechanical stirring.

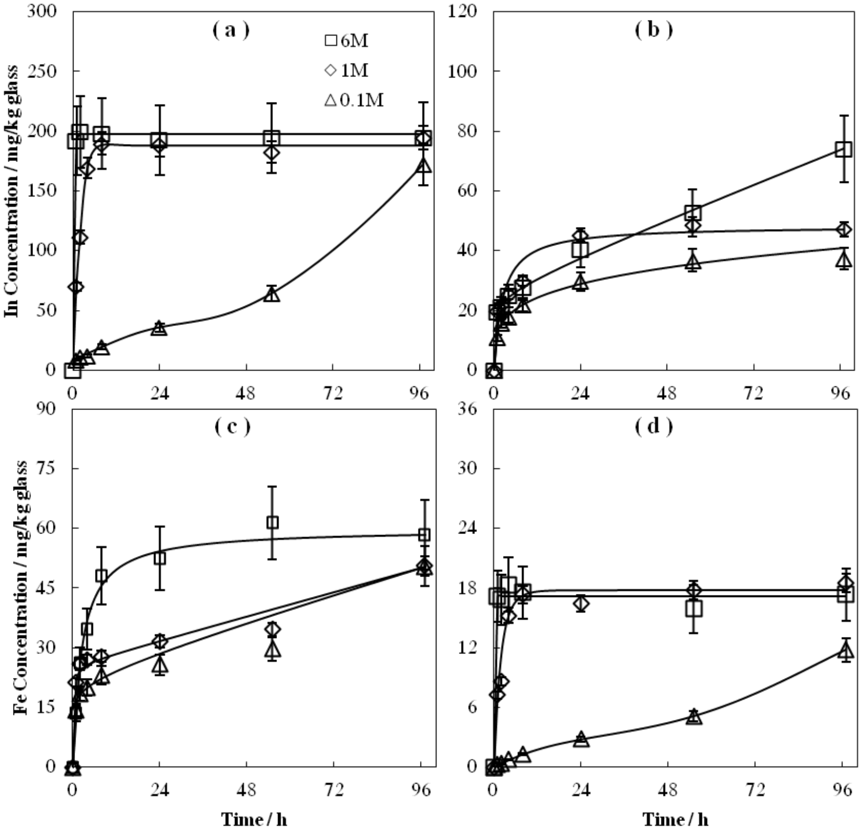

Figure 11: Leaching kinetics of (a) In (b) Al (c) Fe (d) Sn in HCl between 1 hour and 4 days. Crushed glass of an LCD monitor was immersed in HCl of different concentrations under mechanical stirring.

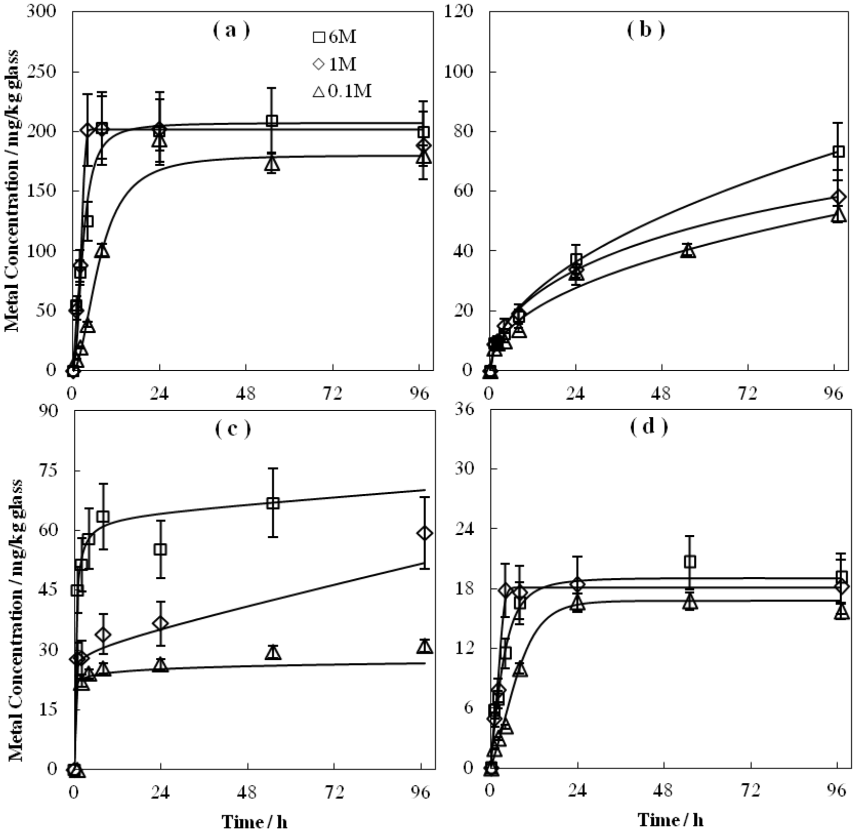

Figure 12: Leaching kinetics of (a) In (b) Al (c) Fe (d) Sn in H_2SO_4 between 1 hour and 4 days. Crushed glass of an LCD monitor was immersed in H_2SO_4 of different concentrations under mechanical stirring.

It can be seen by comparison that the dissolution kinetics of indium oxide is the fastest in chloride media at acid concentrations of 1 M or greater. At concentrations of 6 M, the maximum amount of indium was leached by HCl in 2 h, whereas at least 4 h were required for H_2SO_4 and HNO_3. In addition, it was visually observed that, for HNO_3 and HCl at 6 M, white flakes of partially dissolved plastic film appeared in the solution after a period of 1 to 2 days. However, this is a minor problem for 6 M HCl since almost all indium in the waste can be leached in much less than 24 h. A similar phenomenon was not observed for H_2SO_4 at any of the three concentrations. The dissolution of organic material is an undesirable effect since it can make the filtering of leach liquor more difficult, and may have a negative impact on the subsequent solvent extraction process. The kinetics of leaching for indium and tin were observed to similar, this could be due to that ITO is a solid solution [43] and congruent dissolution occurred when ITO came in contact with mineral acid. The leaching kinetics of aluminum and iron are shown in Figure 10b-c, 9b-c and 10b-c. For these two metals, which are most likely present in their metallic forms, the rate of leaching is much slower than for indium and tin. In most cases the leaching of aluminum and iron did not reach equilibrium after 4 days. Therefore it is possible that indium and tin can be partially separated from other metals during leaching stage.

By comparing with the leaching data for aqua regia, and the amount of indium in the solution after leaching the glass for a second time with 6 M HCl, it was seen that at 80-95% of indium on the glass can be dissolved into all of the acids tested by leaching once.

In order to investigate the effect of ligand ion concentration on leaching kinetics, the amount of indium leached by HCl solutions with various chloride concentrations was investigated. The results are presented in Figure 13. It can be seen that the increasing the chloride concentration did have a positive effect on the amount of indium leached. The increased rate of In_2O_3 dissolution in chloride solutions can be attributed to the high stability constant values of indium chloride complexes ($Log(K_1) \approx 2.4$, $Log(K_2) \approx 1.3$, $Log(K_1) \approx 0.3$) [44]. This means that at $[Cl^-] > 0.1$ M, less than 1% of dissolved In^{3+} will exist as free ions. According to reaction (I), a reduction of $[In^{3+}]$ will shifts the equilibrium of the reaction in the forward direction, thus the rate of leaching is higher in HCl than HNO_3 at the same concentration ($log(K_1) \approx 0.18$ for indium-nitrate complex). However, the increase in the amount of indium leached is small compared to the data obtained in Figure 10 with varying $[H^+]$; this indicates that $[H^+]$ has a larger impact on the leaching kinetics than the ligand concentration.

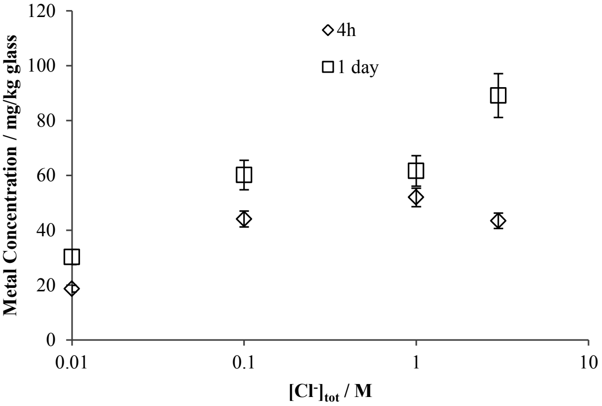

Figure 13: The effect of ligand concentration on indium leaching. Crushed glass of an LCD monitor was immersed in HCl, with initial $[H^+]=0.01$ M and $[Cl^-]$ varying between 0.01 M and 3 M under mechanical stirring, all sample were measured with ICP-OES, indium concentration was measured as ppm, and later converted to g In per g crushed glassed leached.

Due to having slower leaching kinetics and being able to dissolve plastic films on LCD glass, HNO_3 is deemed a poor choice for leaching indium from the panel glass. Both 1 M HCl and 1 M H_2SO_4 are feasible choices. If the concentration of HCl is higher than 3 M, some of the plastic materials on the LCD glass can also be dissolved.

5.1.3 Leaching of yttrium and indium from mixed FPD waste

The data presented in Figure 14 and Figure 15 shows the amount of yttrium and indium leached from mixed FPD waste between 1 h and 80 h with 1 M HCl. Furthermore, the leaching kinetics for indium in 1 M HCl is much faster than in 1 M HNO_3. In 1 M HCl indium concentration reached equilibrium after 24 h of leaching, while in 1 M HNO_3 indium concentration did not reach equilibrium after three days. This indicates that HCl is a more efficient medium than HNO_3 for leaching metal ions from the solid waste. Compared to the leaching results of LCD glass, the kinetics of metal leaching in this case was observed to be much slower. This could be the result of much higher content of metals and metal oxides in the FPD waste investigated in the present study compared to earlier studies.

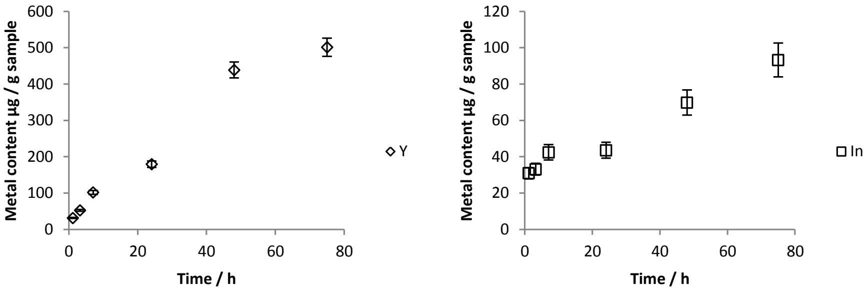

Figure 14: The effect of contact time on the leaching kinetics of In and Y when using 1 M hydrochloric acid at 293±2 K and S/L=0.1 g/ml. Uncertainties were determined by triplicate sampling.

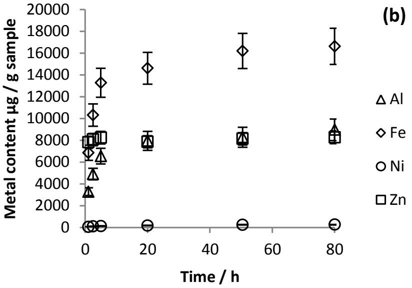

Figure 15: The effect of contact time on the leaching kinetics of Al, Fe, Ni, Zn in (a) 1 M nitric acid (b) 1 M hydrochloric acid at 293±2 K and S/L=0.1 g/ml. Uncertainties were determined by triplicate sampling.

Figure 14 show the leaching kinetics in 1 M HCl at room temperature (293±2 K) and 353 K plotted for the metals of interest. For neodymium an increase in temperature during leaching did not increase its leaching kinetics further, however the leaching kinetics of other metals increased significantly when the temperature increased from 293±2 K to 353±2 K. For example, the leaching of neodymium and yttrium in 1 M HCl reached equilibrium after 48 h at 293±2 K, while at 353 K equilibrium was reached in 10 h. In addition, leaching of indium required 4 days to reach equilibrium in 1 M HNO_3 at 293±2 K, while approximately 8 h were sufficient at 353±2 K. This could be explained by the difference between the standard enthalpy of formation for In_2O_3 (-925 kJ/mol) [45], Y_2O_3 (-1905 kJ/mol) [45] and H_2O (-241 kJ/mol) [45], taking reaction (I) into consideration, this indicates that the leaching of In_2O_3 and Y_2O_3 are endothermic process. Therefore the rate of leaching increases with increasing temperature. The main disadvantage with leaching at higher temperature, other than the extra energy requirement, was the increased solubility of other materials such as silica from e.g. LCD panel glass, which can give rise to the formation of crud in subsequent solvent extraction processes.

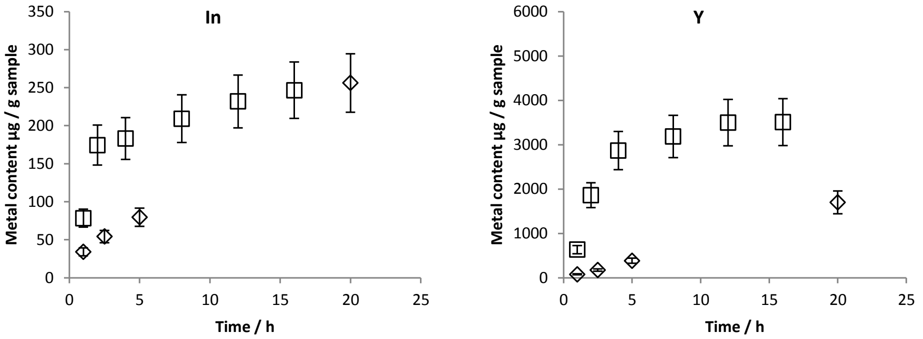

Figure 16. Leaching kinetics of In (left) and Y (right) at 293±2 K (◊) and 353±2 K (□) in 1 M HCl. S/L=0.1 g/ml. Uncertainties were determined by triplicate sampling.

5.2 Solvent extraction of indium and yttrium

5.2.1 Screening test for indium recovery from LCD glass waste

Results from the leaching study showed that both HCl and H_2SO_4 are feasible choice for leaching of indium from LCD glass waste and can be used as the aqueous phase for extraction of indium with Cyanex 272, Cyanex 923 and DEHPA. The initial acid concentrations of the aqueous phase were chosen based on results of previously published works on indium extraction with the extractants listed [30] [19] [35]. The initial metal concentrations in the aqueous phase are given in Table 6. Since the concentration of indium in the acidic leachate (0.2 µM) is considered too low for a solvent extraction process to be economically feasible, the concentrations of the simulated leachate were set to be approximately 10 times as much as in the leach liquor.

Table 5: Metal composition of the simulated aqueous phase

Name	Concentration / mM
Al	5.6
Cu	2.4
Fe	2.7
In	1.7
Sn	0.17
Zn	2.3

D calculated from the measured results of various extraction systems investigated are presented in Figures 17-19. Lines are drawn to aid the viewing of the results only. From the results, the effect of different organic extractants and diluents on metal extraction, and the extent of metal separation for each organic/aqueous system can be observed and analyzed.

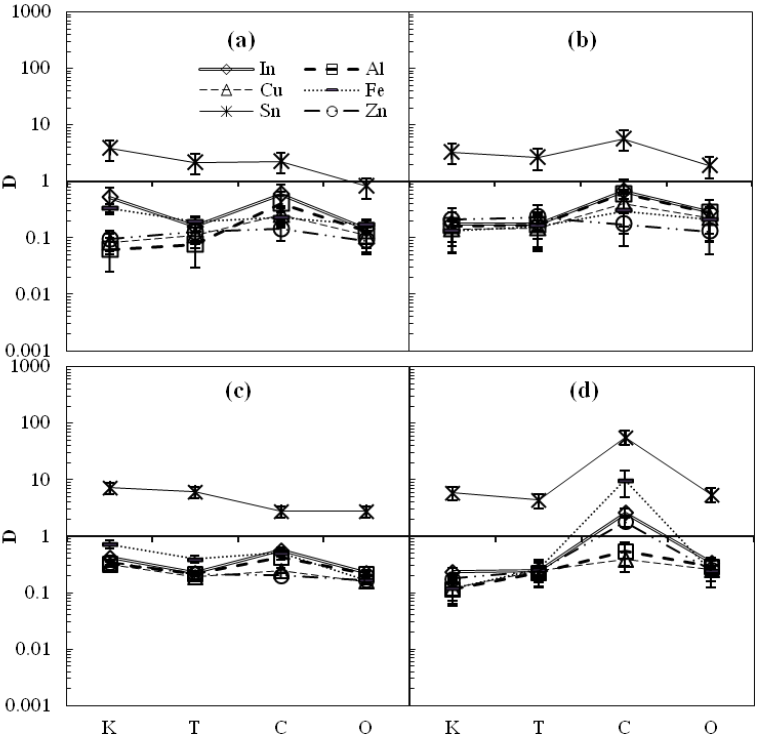

Figure 17: Distribution ratio between (a) 0.1 M H_2SO_4 (b) 1 M H_2SO_4 (c) 0.1 M HCl (d) 1 M HCl containing indium and five other metals and an organic phase of 0.1 M Cyanex 272 in kerosene (K), toluene (T), cyclohexanone (C) and n-octanol(O), respectively.

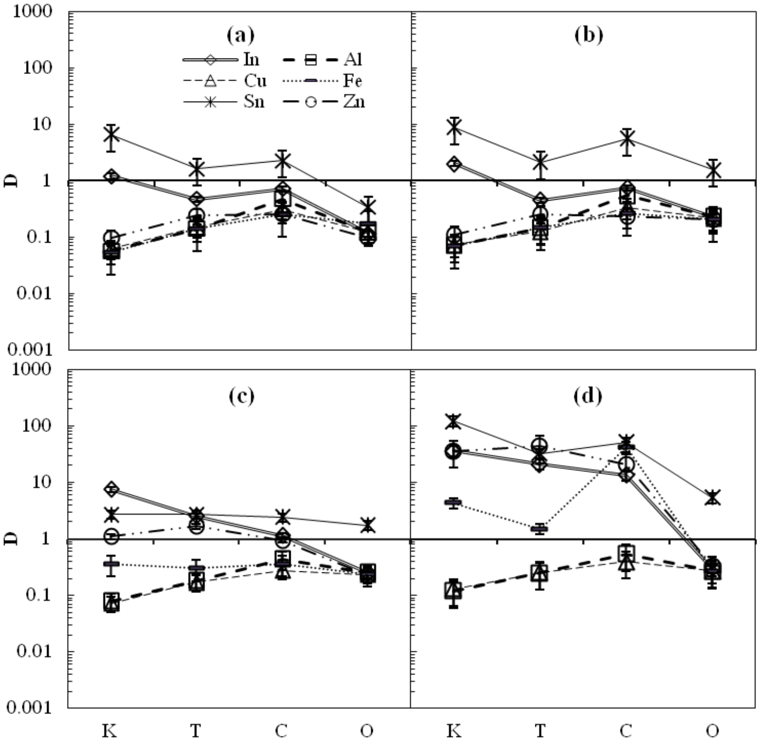

Figure 18: Distribution ratio between (a) 0.1 M H_2SO_4 (b) 1 M H_2SO_4 (c) 0.1 M HCl (d) 1 M HCl containing indium and five other metals and an organic phase of 0.1 M Cyanex 923 in kerosene (K), toluene (T), cyclohexanone (C) and n-octanol(O), respectively.

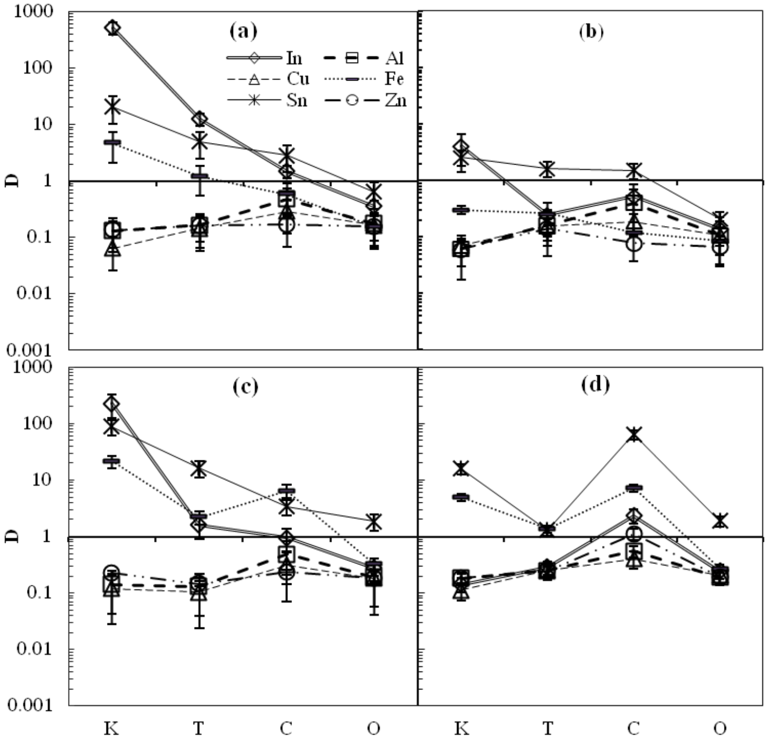

Figure 19: Distribution ratio between (a) 0.1 M H_2SO_4 (b) 1 M H_2SO_4 (c) 0.1 M HCl (d) 1 M HCl containing indium and five other metals and an organic phase of 0.1 M DEHPA in kerosene (K), toluene (T), cyclohexanone (C) and n-octanol(O), respectively.

The effect of diluents on metal extraction can be seen in e.g. Figure 18d). D_{In} between 1M HCl and Cyanex 923 in different diluents is summarized in Table 7, together with the dielectric constants (ε) of the diluents. In the table, an inverse proportionality between the dielectric constant and distribution ratio can be seen. However, it can also been seen that when n-octanol was used as diluents, the D_{In} of indium is more than one order of magnitude lower than with other diluents. A similar reduction of distribution ratio in octanol was observed in an earlier study [38], where a positive correlation between D and solubility of extractant in the diluent used was seen.

Table 7: Distribution ratio of indium between 1 M HCl and Cyanex 923 diluted in different organic solvent

Diluents	D_{In}	ε
kerosene	36±3	1.9
toluene	20±2	2.4
cyclohexanone	13±2	15.8
n-octanol	0.3±0.02	10.5

Furthermore, regardless of the organic extractant used, the overall metal extraction tends to be higher in cyclohexanone than toluene or n-octanol. This could be partially due to relatively high mutual miscibility of cyclohexanone and water. However, cyclohexanone is classified as a solvent with donor atoms for hydrogen bonding but no active hydrogen atoms. This causes such solvents to directly react with inorganic compounds [36]. Metal extraction by cyclohexanone as the organic extractant has been studied in previous papers, such as in the separation of titanium and niobium [46], ^{99}Tc [47] and light actinides (Th, Np, U) [48]. The results in e.g. Figure 17d also showed that the use of cyclohexanone diluents results in higher iron and tin extraction compared to other metals.

With respect to the separation of indium from other metals, it can be seen in Figure 18 and 17 that when 0.1 M or 1 M H_2SO_4 is used as aqueous phase, indium can be extracted with 0.1 M Cyanex 923 or 0.1 M DEHPA in kerosene. The main drawback with using Cyanex 923 compared to DEHPA is that for former has lower D_{In} in sulfate media and in chloride media Cyanex 923 will co-extract other metals such as zinc. However, in Figure 16, D_{In} is much smaller than 1, this indicates that indium can be selectively stripped from the organic phase. Therefore it can be concluded that within the conditions tested, extraction from 0.1 M or 1 M H_2SO_4 to 0.1 M DEHPA in kerosene, is the best alternative for the separation and recovery of indium. HCl could be a good choice of stripping agent.

After the extractant was chosen, different options for to strip indium from the organic phase was tested. Results for HCl and HNO_3 at different concentrations are shown in Table 8. The metal composition in the aqueous feed was similar to what was used in the previous screening test. Data of aluminum for the 1 M H_2SO_4 case, as well as the data for copper and zinc were omitted due to low D for extraction. In Table 8 it can be seen that there are deviations between e.g. D_{Fe} for stripping between the cases where 1 M H_2SO_4 and 0.1 H_2SO_4 were used as aqueous phase for extraction. This could be caused by measurement uncertainties since in all cases only small amounts of metal was stripped into the aqueous phase, which is difficult for the analytical instrument to reliably determine.

Table 8. Values of D for metal stripping of different aqueous media; uncertainties were calculated from duplicate samples.

Aqueous phase (extraction stage)	Aqueous phase (strip stage)	D_{In}	D_{Al}	D_{Fe}	D_{Sn}
1 M H_2SO_4	2 M HNO_3	>100		25±1	>100
	2 M HCl	<0.1		3.5±1.3	>100
	1 M HNO_3	>100		72±28	83±41
	1 M HCl	<0.1		30±1	>100
0.1 M H_2SO_4	2 M HNO_3	26±0.5	0.47±0.1	36±10	>100
	2 M HCl	<0.1	0.47±0.1	4.6±1.6	35±3
	1 M HNO_3	>100	0.31±0.1	>100	37±3
	1 M HCl	<0.1	0.43±0.1	55±16	51±4

Overall, it can be seen from the result that HCl is much more efficient at stripping indium than the other acids tested. It was suggested in an earlier work [19] that for an extraction system containing indium and tin, indium could be selectively stripped from 1 M DEHPA in kerosene with HCl at concentration of 2 M or greater. However, in the case of using real LCD recycling waste, additional metal impurities are present. Increased aqueous acidity will also reduce D_{Fe}, to the extent that both iron and indium will be stripped to the aqueous phase. Therefore even though the recovery of indium is higher when 2 M HCl is used for stripping, from the perspective of metal separation, it is more advantageous to use 1 M HCl. With respect to the purity of stripped indium, 1 M H_2SO_4 has a slight advantage over 0.1 M H_2SO_4. This is due to DEHPA is an acidic extractant, its dissociation in aqueous phase increases with decreasing acidity, leading to increased complexation with metal ions and increased D for all extractable metals, thus SF is decreased for indium.

5.2.2 Screening test for yttrium and indium recovery from mixed FPD waste

Several extractants were tested, such as Cyanex 923, DEHPA, and two types of bis-triazinyl bipyridines (C2-BTBP and CyMe4-BTBP) was tested in a screening test to determine if any of the extractants can be used to separate yttrium and indium from the leachate of mixed FPD waste. Cyanex 272 was not used in this case because the previous screening test showed that it has low D for metals when aqueous acidity is 1 M. Other less common extractants were chosen because they contain only carbon, hydrogen, oxygen and nitrogen atoms and is more environmentally friendly than commercial extractants, which often contain phosphates and sulfide groups. Both HCl and HNO_3 were tested as the aqueous phase. Although HNO_3 is a poor choice for leaching due to slow kinetics, it is still tested to determine if it could be used as e.g. a stripping agent for either yttrium or indium. The result of the screening test is shown in Figures 20-23. In chloride media none of the extractants studied was able to extract yttrium. However, this means that it is possible to use HCl to selectively strip yttrium from an organic solution containing Cyanex 923.

For most metal ions, their distribution ratios are higher in 6 M HCl than 1 M HCl. This could be the result of increased chloride concentration, as all of the extractants studied were solvating extractants. On the other hand silver has shown the reversed trend. The decrease in distribution ratio can be attributed to the formation of anionic silver chloride complex at high chloride concentration. The ability of BTBP molecules to extract silver was studied in a previous work [49], where it was found that both C2- and CyMe$_4$-BTBP was able to extract silver from nitrate media, with CyMe$_4$-BTBP having higher distribution ratio.

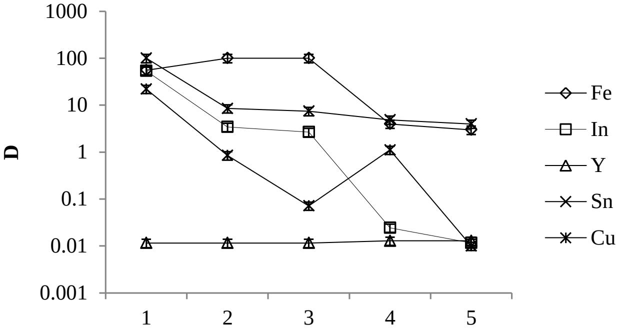

Figure 20. D for metals in different organic systems: 1= 1 M Cyanex 923 in kerosene; 2=0.005 M C2-BTBP in octanol; 3=0.005 M C2-BTBP in MIBK; 4=0.01 M CyMe4-BTBP in octanol; 5=0.01 M CyMe4-BTBP in MIBK. The aqueous phase was 6 M HCl.

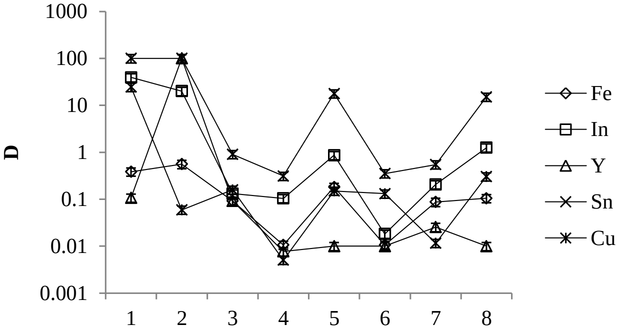

Figure 21. D for metals in different organic systems: 1=1 M Cyanex 923 in kerosene; 2= 1 M DEHPA in kerosene; 3= 0.005 M C2-BTBP in octanol; 4= 0.005 M C2-BTBP in MIBK; 5= 0.005 M C2-BTBP in cyclohexanone; 6= 0.01 M CyMe4-BTBP in octanol; 7= 0.01 M CyMe4-BTBP in MIBK; 8= 0.01 M CyMe4-BTBP in cyclohexanone. The aqueous phase was 1 M HCl.

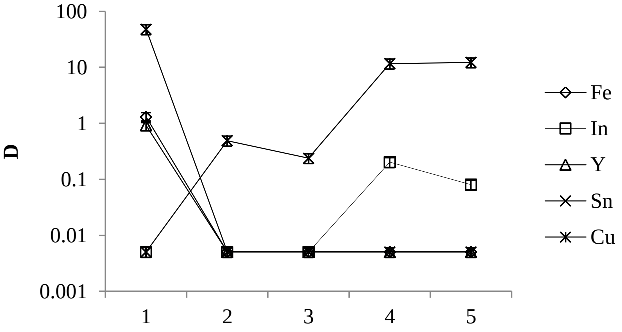

Figure 22. D for metals in different organic systems: 1= 1 M Cyanex 923 in kerosene; 2=0.005 M C2-BTBP in octanol; 3=0.005 M C2-BTBP in MIBK; 4=0.01 M CyMe4-BTBP in octanol; 5=0.01 M CyMe4-BTBP in MIBK.. The aqueous phase was 6 M HNO_3.

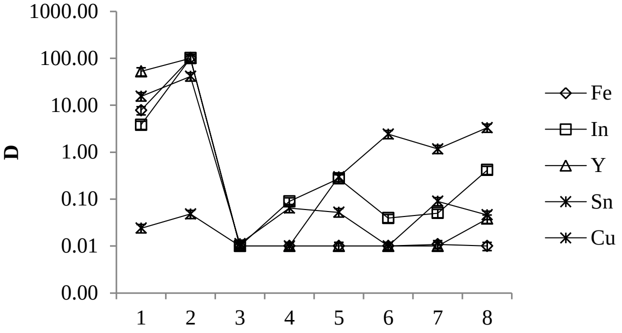

Figure 23. D for metals in different organic systems: 1=1 M Cyanex 923 in kerosene; 2= 1 M DEHPA in kerosene; 3= 0.005 M C2-BTBP in octanol; 4= 0.005 M C2-BTBP in MIBK; 5= 0.005 M C2-BTBP in cyclohexanone; 6= 0.01 M CyMe4-BTBP in octanol; 7= 0.01 M CyMe4-BTBP in MIBK; 8= 0.01 M CyMe4-BTBP in cyclohexanone. The aqueous phase was 1 M HNO_3.

When 6 M HNO_3 was used as the aqueous phase, it was observed that $CyMe_4$-BTBP selectively extracted certain divalent metal ions such as Cu(II) and Co(II). The same selectivity can also be observed at lower nitrate concentration. Furthermore, it was observed that compared to 1-octanol and MIBK, distribution ratios of e.g. Co(II) and Mn(II) are higher when cyclohexanone was used as diluent. This increase in D when cyclohexanone was used as diluent was also observed, again due to high miscibility this may not be the best choice as diluent.

With respect to recovery of indium and yttrium, Cyanex 923 diluted in kerosene can be used to selectively extract indium from 1 M HCl over yttrium, indium can then be stripped with 1 M HNO_3 and yttrium in the 1 M HCl raffinate can be extracted by DEHPA diluted in kerosene.

Since an extractant concentration of 1 M is likely too high relative to the concentration of indium and yttrium in the leachate of real waste, which lie in the range of mM, lower concentration of Cyanex 923 was tested. Table 9 shows a comparison of 1 M Cyanex 923 and 0.25 M Cyanex 923. It can be seen that at extractant concentration of 1 M, over 98% of indium was extracted to the organic phase in one stage by Cyanex 923,. However, in this case the co-extraction of other metals such as zinc and copper is significant (>95% extracted), and co-extraction of neodymium and yttrium is also slightly higher with 1 M Cyanex 923 compared to 0.25 M Cyanex 923. Another drawback of a higher extractant concentration is the need for more concentrated acid when metals are to be back-extracted or stripped into another aqueous phase. At extractant concentration of 0.25 M, Cyanex 923 diluted in kerosene was still able to quantitatively extract indium from 1 M HCl. However, co-extraction of other metals, most notably copper was reduced. Stripping of indium from the organic phase was tested with HNO_3 and H_2SO_4 at different concentrations, as shown in Table 10. Less than 15% of indium extracted into the organic phase was stripped into 1 M H_2SO_4, whereas 1 M HNO_3 and 6 M HNO_3 were able to strip 70% and 99% of extracted indium in one stage, respectively. This difference is likely due to $[SO_4^{2-}]$ (K_{a2}=0.01) being much lower than $[NO_3^-]$ (K_a≈20) at 1 M acid concentration, leading to the reduced formation of soluble indium complexes. Despite the fact that 6 M HNO_3 was more efficient for stripping indium than 1 M HNO_3, the separation of indium from co-stripped iron and copper in the subsequent extraction step would become more difficult with e.g. DEHPA. Therefore 1 M HNO_3 was considered to be the more suitable aqueous phase for stripping.

Table 9. Distribution ratio of metals in the extraction step. The aqueous phase was 1 M HCl; kerosene was used as the diluent.

	D_{Cu}	D_{Eu}	D_{Fe}	D_{In}
1M Cyanex 923	32.0±3	0.07±0.04	0.91±0.06	43.7±5
0.25M Cyanex	<0.1	<0.1	0.43±0.03	10.2±0.9
	D_{Mo}	D_{Sn}	D_Y	D_{Zn}
1M Cyanex 923	59.4±0.6	>100	<0.1	82.8±35
0.25M Cyanex	31.2±0.3	>100	<0.1	6.76 ±0.1

Table 10. Distribution ratio of metals in the stripping step using different aqueous phase. The organic phase was 0.25 M Cyanex 923 diluted in kerosene.

	D_{Cu}	D_{Fe}	D_{In}	D_{Mo}	D_{Sn}	D_{Zn}
6M HNO3	0.34±0.24	<0.1	<0.1	7.03±0.7	91.1±1	<0.1
1M HNO3	2.99±1.5	<0.1	0.29±0.03	5.37±0.5	>100	<0.1
1M H2SO4	0.93±0.63	<0.1	6.51±0.07	64.6±0.6	>100	0.5±0.05

The results for yttrium extraction can be seen in Table 11. The aqueous phase used in this part of the study is the raffinate solution after extraction with 1 M Cyanex 923 in kerosene. Therefore D_{In}, D_{Mo} and D_{Sn} were not shown because their concentrations in the raffinate are too low. With 1 M DEHPA diluted in kerosene the extraction of yttrium was nearly complete (>99%) in one stage. However, at such high extractant concentrations the co-extraction of zinc and europium became significant. Therefore an extractant concentration of 0.2 M was chosen, since at this concentration yttrium extraction was still high, while very little europium and zinc were co-extracted. Distribution ratios of the stripping stage after extraction with 0.2 M DEHPA in kerosene is shown in Table 12. It can be seen that both 2 M and 3 M HCl could quantitatively strip yttrium from the organic phase. However, due to the stripping of iron being less in 2 M HCl than 3 M HCl, the former was considered to be the better stripping agent. 1 M H2SO4 and 1 M HNO3 were also tested, but their results were not shown because the percentage stripping of yttrium was low (D_Y>1 for stripping).

Table 11. Metal distribution ratios between 1 M HCl raffinate after extraction with1 M HCl leachate and DEHPA of different concentration in kerosene.

	D_{Cu}	D_{Eu}	D_{Fe}	D_{Nd}	D_Y	D_{Zn}
1M DEHPA	<0.1	0.77±0.08	0.15±0.02	<0.1	155±45	1.11±0.1
0.2M DEHPA	<0.1	<0.1	0.35±0.04	<0.1	19.8±6	<0.1
0.1M DEHPA	<0.1	<0.1	0.40±0.05	<0.1	0.86±0.3	<0.1

Table 12. Metal distribution ratio in the yttrium stripping step, the organic phase is 0.2 M DEHPA diluted in kerosene after extraction from 1 M HCl leachate.

	D_{Cu}	D_{Eu}	D_{Fe}	D_{Nd}	D_Y	D_{Zn}
2 M HCl	0.10±0.08	<0.1	4.74±0.95	46.49±5	<0.1	<0.1
3 M HCl	0.09±0.07	0.08±0.02	1.03±0.2	40.87±4	<0.1	<0.1

5.2.3 Additional treatment of mixed FPD waste

Before the extraction process for mixed FPD waste can proceed further onto testing on continuous extractors, a few inherent issues with this highly mixed waste fraction needs to be solved. Examples of these issues are the possible presence of mercury in the sample, since the waste came from discarded FPDs which were shredded with minimal mechanical separation. Another issue is the powdered nature of the waste, which can give rise to high concentration of suspended solids in the acidic leachate, which in turn will promote the formation of crud. Experimental work in this section was mainly focused on studying and possibly solving these two issues.

5.2.2.1 Pre-extraction of mercury

In this section, an organic phase consisting of Cyanex 471X diluted in kerosene was studied for the purpose of selectively removing Hg from the leachate of mixed FPD waste before other metals are separated in further solvent extraction processes. Several parameters were studied, such as contact time, temperature and extractant concentration. Extraction kinetics for Hg are shown in Figure 24. The extraction of other metals except Ag were negligible. From Figure 24, it can be seen that short contact times such as 5 minutes was still enough to achieve distribution ratios which were approximately the same as the equilibrium values. However, to ensure that equilibrium is reached, 40 min was used as contact time for other experiments using Cyanex 471X as the extractant.

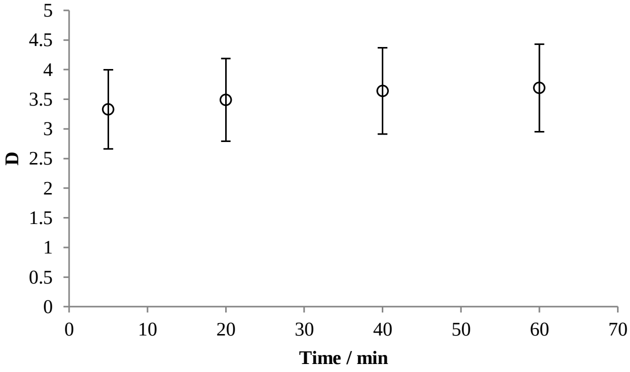

Figure 24. The effect of mixing time on the distribution ratios of Hg(II) in 1 M HCl. Organic phase is 0.1 M Cyanex 471X in kerosene, T=293±2 K and θ=1.

The effect of extractant concentration on the extraction of Hg is shown in Figure 25. It was also noticed that at small amount (D≈0.2) of other metal ions such as copper and tin were also extracted when the extractant concentration exceeded 0.5 M. Quantitative extraction of Hg can be achieved at extractant concentration of 0.2 M. By linear regression, the slope of Hg(II) extraction in chloride media was approximately 2. The result obtained from this work for chloride media was lower than it was previously reported [24]. This could be due to the presence of large amounts of other metal ions in the aqueous phase, which forms soluble chloride complex.

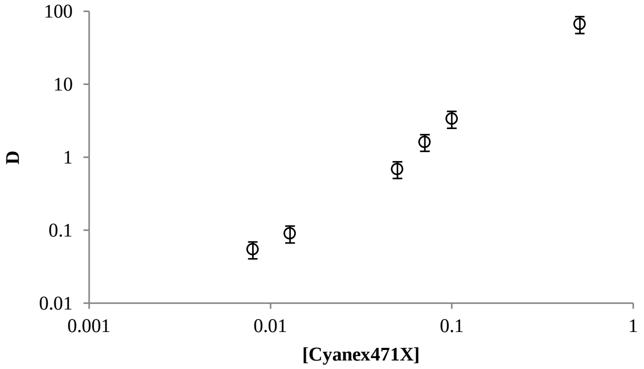

Figure 25: The effect of Cyanex 471X concentration on D_{Hg} in 1 M HCl. Organic phase is 0.1 M Cyanex 471X in kerosene, T=293±2 K and θ=1.

A possible extraction mechanism based on the stoichiometric ratio obtained from Figure 25 is shown in reaction (III).

$$HgCl_2 + \overline{2[TIBPS]} \leftrightarrow \overline{HgCl_2TIBP_2} \qquad \text{(III)}$$

Based on reaction (III), $Ln(K_{ex})$ was calculated for the extraction of mercury between 293 K and 333 K. The result is shown in Figure 26. ΔH^o of extraction were calculated from the slope of the fitted line.

For 1 M HCl ΔH^o=-45±9 kJ/mol. The extraction of Hg(II) from 1 M HCl is an exothermic processes, since the distribution ratio of Hg(II) is inversely proportional to temperature. ΔS^o=-106.3 J/mol/K is also negative , the extraction reaction of Hg(II) is enthalpy-driven reactions within the temperature range studied.

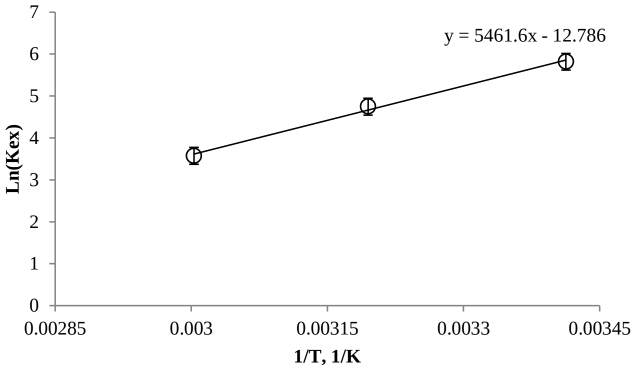

Figure 26. The effect of extraction temperature on the distribution ratios of Hg(II) in 1 M HCl. Organic phase is 0.1 M Cyanex 471X in kerosene, θ=1.

In order to strip Hg from the organic phase, it has been shown that several aqueous media such as 0.01 M NaS_2O_3, 0.01 M NaCl at pH = 12.3 and 0.01 M NH_4Cl at pH = 10.8 can be used to strip Hg from the organic phase [23] [24].

5.2.2.2 Third phase and crud formation

For mixed FPD waste, it was noticed that during the extraction of indium from 1 M HCl leachate with 0.25 M Cyanex 923 in kerosene, third phase and crud could form and accumulate at the phase interface. This is detrimental to the solvent extraction process as it can result in the loss of solvent, and can make phase separation more difficult [50].

Several previous works [50] [51] have studied the formation of third phase in extraction systems using organophosphate compounds similar to Cyanex 923 and concluded that the formation of third phase was proportional to the concentration of inorganic ligands (e.g. NO_3^-, Cl^-) and extractable metal ions. In a comprehensive review on cruds in solvent extraction processes [40], the formation cruds were attributed to several factors, such as the presence of suspended solids, organic materials, silica, aluminum and molybdenum etc.

From batch extraction experiments it was seen that the formation of third phase could be prevented by the addition of 5 vol% of TBP, cyclohexanone, or 1-decanol. However, after the addition of any of these phase modifiers a small amount of crud (<10mg per 1ml aqueous phase) remained at the aqueous/organic interface. Since the waste material studied was FPD waste in the form of powders, substances such as suspended solid, organic material and silica could exist in the acidic leachate and contribute to the formation of cruds, even after filtration with a filter pore size of 0.45 µm.

Samples of crud formed during extraction were collected and characterized EDX. The results are shown in Figure 27 and in Table 13. It was seen that the crud material mainly consisted of oxygen and silicon in an approximate ratio of 2:1, indicating that the crud is mostly silica, with minor amounts of other elements such as calcium and iron.

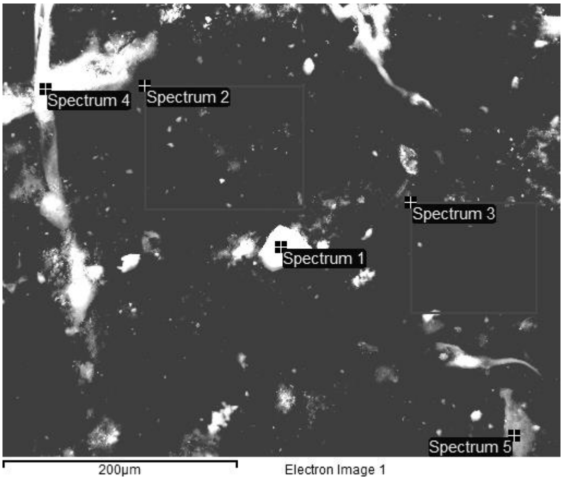

Figure 27. SEM image of the crud material collected.

Table 13. Material composition of the crud material determined by EDX. Positions of the scanned locations labelled as "Spectrum 1-5" are shown in Figure 14.

Position scanned	O	Al	Si	Ca	Fe	Y	Sn
Spectrum 1	59%	5%	30%	2%	0%	0%	1%
Spectrum 2	52%	1%	32%	1%	1%	1%	1%
Spectrum 3	56%	1%	31%	1%	1%	1%	1%
Spectrum 4	59%	1%	26%	2%	1%	1%	0%
Spectrum 5	58%	1%	31%	1%	1%	0%	1%

Washing of the FPD waste with 1 M NaOH, ethanol or acetone before leaching with 1 M HCl could reduce the amount of crud formed to some extent. Filtration of the leachate with filter pore size <45 µm can prevent the formation of cruds, indicating that the presence of fine suspended solids could be a major cause of crud in this case, as was suggested by Ritcey [40]. However, it could be costly to perform such filtration at industrial scale.

5.2.4 Optimizations of indium extraction from leachate of LCD glass

In addition to the choice of aqueous and organic phase, other parameters such as contact time, extractant concentration and extraction temperature can also affect the distribution ratio of metal ions and the purity of indium recovered. The following section will focus on studying the effect of these parameters on indium extraction and find the optimal values of these parameters maximize the amount and purity of recovered indium. Since results from previous section showed that 0.1 M DEHPA in kerosene could quantitatively extract indium from both 0.1 M and 1 M H_2SO_4, and HCl was the best choice of stripping agent, optimization of different parameters will be done using H_2SO_4 or HCl as the aqueous phase.

5.2.4.1 Metal extraction and stripping kinetics

From screening test in section 5.2.2.1, it was concluded that 0.1 M or 1 M H_2SO_4 were suitable aqueous phases for indium extraction and 1 M HCl for stripping of indium. The effect of mixing time was investigated for the extraction of metals from 0.1 M H_2SO_4 or 1 M H_2SO_4 as well as the kinetics of metal stripping from loaded organic phase to 1 M HCl. The organic phase was 0.1 M D2EHPA in kerosene. Results are shown in Figures 28-30. Data for aluminum, copper and zinc were omitted since their distribution ratios were lower than 0.1 and stayed relatively constant during experiments.

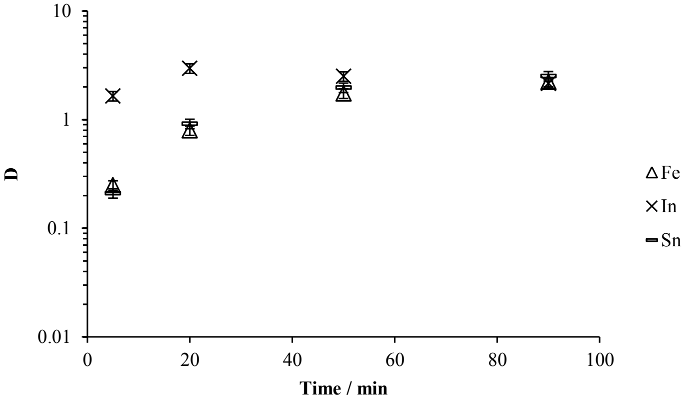

Figure 28. Kinetics of metal extraction using 1 M H_2SO_4 and 0.1 M D2EHPA in kerosene, θ=1. Mixing time of the mixtures was between 5 minutes and 2.5 hours under mechanical shaking at 1500 rpm and 293±2 K.

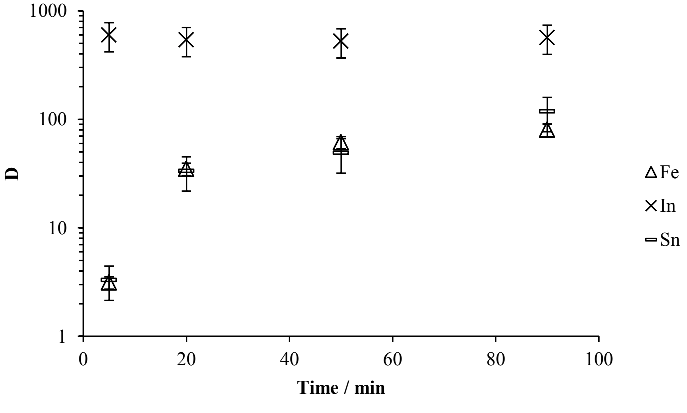

Figure 29. Kinetics of metal extraction using 0.1 M H_2SO_4 and 0.1 M D2EHPA in kerosene, θ=1. Mixing time of the mixtures was between 5 minutes and 2.5 hours under mechanical shaking at 1500 rpm and 293±2 K.

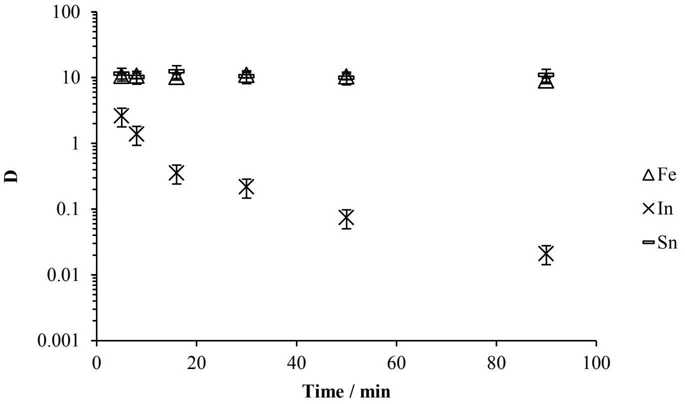

Figure 30. Kinetics of metal back-extraction from loaded 0.1 M D2EHPA in kerosene into 1 M HCl at θ=1. Mixing time of the mixtures was between 5 minutes and 2.5 hours at 1500 rpm and 293±2 K.

From Figures 28-30 it could be seen that time required for D_{In} to reach equilibrium was less than 5 min in the 0.1 M H_2SO_4 system, while for 1 M H_2SO_4 and 1 M HCl 20 min was needed. It could also be seen that time required for iron and tin extraction to reach equilibrium was slightly longer than for indium in all three cases. Therefore, shorter mixing time has the advantage of improving separation between indium and the co-extracted metals (iron and tin). This is especially true for the 0.1 M H_2SO_4 system shown in Figure 29, where the separation factor between indium and iron was greater than 100 when mixing time was less than 5 min. For stripping, Figure 20 indicates that a mixing time of 20 min or longer was preferred. Due to the amount of time required for extraction and stripping to reach equilibrium, in a continuous process it will likely require multiple extraction and strip stages and low flow rate in order to quantitatively extract indium. Since short contact time is not a requirement, centrifugal contactors would not be necessary, while mixer-settlers can be a more appropriate choice since it is easy to assemble a large number of mixer-settler stages and it allows relatively long residence time.

5.1.3.2 The effect of initial extractant concentration on metal extraction

Metal distribution ratios at different extractant concentrations are shown in Figures 31 and 32. Linear regression analysis was performed for indium extraction with results shown in Figure 31 for 1 M H_2SO_4 and 30 for 1 M HCl.

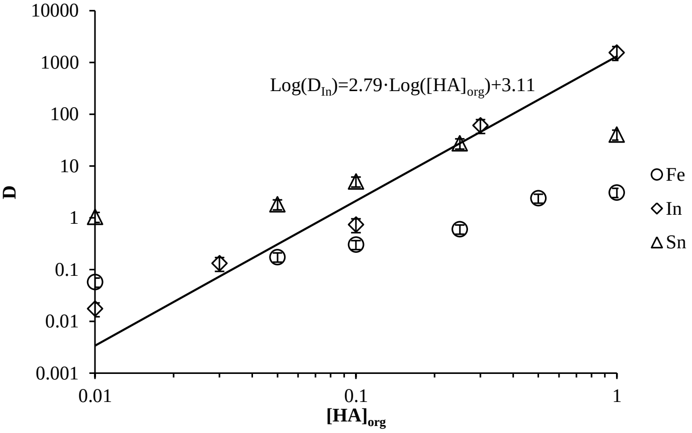

Figure 31. Effect of free D2EHPA concentration on the extraction of metals from 1 M H_2SO_4.

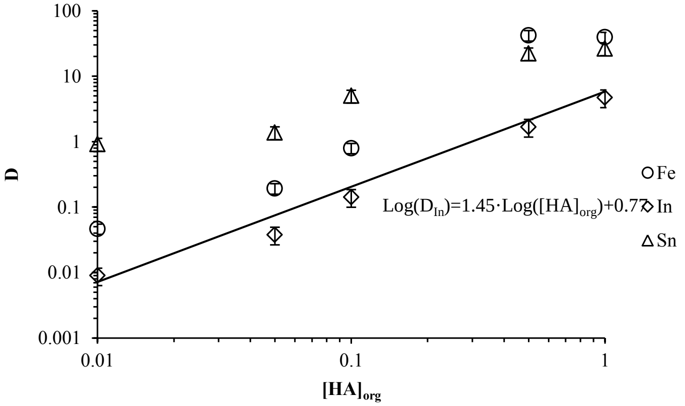

Figure 32. Effect of free D2EHPA concentration on the extraction of metals from 1 M HCl.

The stoichiometric ratio between indium and the extractant in 1 M H_2SO_4 was calculated to be close to 3, while for indium extraction in 1 M HCl it was close to 1.5. Distribution ratios of aluminum, copper and zinc were not included due to small changes in D. The results obtained in this work agreed well with the proposed extraction mechanisms in an earlier work [32]. By inserting the value of stoichiometric coefficients obtained, the extraction of indium from chloride and sulfate media can be seen in reaction (IV) and (V).

$$\text{HCl:}\quad 2InCl^{2+} + \overline{3(HA)_2} \leftrightarrow \overline{In_2Cl_2H_2A_6} + 4H^+ \qquad \text{(IV)}$$

$$\text{H}_2\text{SO}_4\text{:}\quad In^{3+} + \overline{3(HA)_2} \leftrightarrow \overline{InH_3A_6} + 3H^+ \qquad \text{(V)}$$

The effect of anionic ligand on indium extraction is shown in Figure 33. An increase in total chloride concentration at 1 M or above led to a decrease in distribution ratio. This was due to large stability constant for indium chloride species; this means that as chloride concentration increases the mole fraction of non-extractable indium chloride species also increase. A reversed trend was observed for H_2SO_4, where D_{In} increased with total sulfate concentration in the aqueous phase. The increase of D_{In} with sulfate concentration indicates the extraction of an indium sulfate complex into the organic phase. However, the increase diminishes when sulfate concentration became higher than 1.5 M. Therefore the effect of total sulfate concentration on indium extraction was not as significant as extractant concentration.

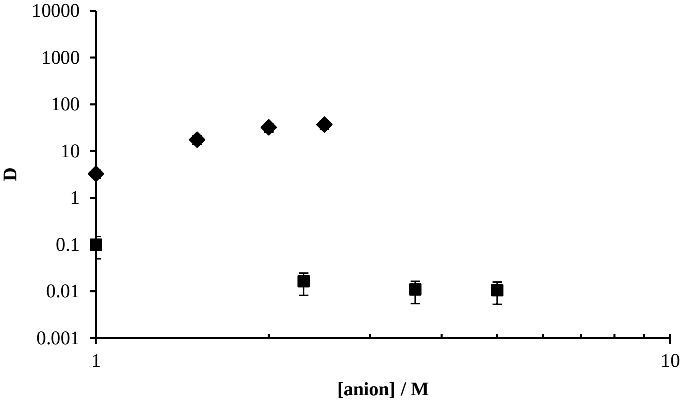

Figure 33: effect of inorganic anion concentration on the distribution ratio of indium, (♦) $[SO_4^{2-}]_{tot}$, (■)$[Cl^-]_{tot}$. Organic phase was 0.1 M D2EHPA/kerosene, $[H^+]$ = 1 M.

With respect to indium recovery, increasing D2EHPA concentration can result in higher D_{In} without significantly affecting the separation of indium from iron and tin during stripping. 1 M H_2SO_4 could be a better choice of aqueous phase than 0.1 M H_2SO_4, since the latter will co-extract zinc and aluminum at higher extractant concentrations. However, higher extractant concentrations will also hinder stripping with 1 M HCl. Therefore, extraction of indium from 1 M H_2SO_4 and stripping using 1 M HCl, the recommended D2EHPA concentration is 0.25 M.

5.1.3.4 Temperature effect on extraction equilibrium

In Figures 34 and 35, the effect of temperature on extraction constant, K_{ex} was calculated for indium, iron and tin according to equation (11). Molar fractions of metal complexes needed for equation (11) were calculated from stability constants given in Table 14, and the results are shown in Table 15. Sulfate and chloride concentrations were assumed to be constant, since these were much greater than the concentrations of the metal ions. Soluble tin complexes in sulfate and chloride media were assumed to be $Sn(SO_4)_2$ and $SnCl_6^{2-}$, respectively [52]. K_{ex} for indium was calculated from reaction (IV) and (V). Based on results shown in Figures 31 and 32, reaction (VI) to (IX) were proposed for the extraction reactions for iron and tin, and these equations were used to calculate K_{ex} values for these two metals.

Table 14. Stability constants of Fe(III) and In(III) in sulfate and chloride media [44].

Sulfate complex	$\log(k_1)$	$\log(k_2)$	Chloride complex	$\log(k_1)$	$\log(k_2)$	$\log(k_3)$
In(III)	1.78	0.75	In(III)	2.36	1.27	0.32
Fe(III)	1.88	0.97	Fe(III)	1.48	0.65	-1.1

Table 15. Calculated molar fractions of sulfate and chloride species.

$[SO_4^{2-}]_{tot}$=1 M				$[Cl^-]_{tot}$=0.1 M			
In^{3+}	0.611	Fe^{3+}	0.547	In^{3+}	0.013	Fe^{3+}	0.186
$InSO_4^+$	0.368	$FeSO_4^+$	0.415	$InCl^{2+}$	0.304	$FeCl^{2+}$	0.561
$In(SO_4)_2^-$	0.021	$Fe(SO_4)_2^-$	0.039	$InCl_2^+$	0.565	$FeCl_2^+$	0.251
				$InCl_3$	0.118	$FeCl_3$	0.002

$$FeCl^{2+} + \overline{2(HA)_2} \leftrightarrow \overline{FeClA_4} + 2H^+ \quad \text{(VI)}$$

$$SnCl_6{}^{2-} + \overline{(HA)_2} \leftrightarrow \overline{SnCl_4H_2A_2} + 2Cl^- \quad \text{(VII)}$$

$$Fe(SO_4)^+ + \overline{(HA)_2} \leftrightarrow \overline{Fe(SO_4)HA_2} + H^+ \quad \text{(VIII)}$$

$$Sn(SO_4)_2 + \overline{(HA)_2} \leftrightarrow \overline{Sn(SO_4)_2H_2A_2} \quad \text{(IX)}$$

Acid concentrations of the aqueous phases were chosen where the D_{In} were greater than 1 at 293 K. Since $Ln(K_{ex})$ of indium is inversely proportional to temperature and since the distribution ratio is proportional to K_{ex} according to equation (11), extraction of indium decreases with increasing temperature in the temperature range studied. This agreed well with the results from Sato et al [32], where an inverse proportionality between D_{In} and temperature was also observed. In this part of the experiment the organic phase was stripped with 2 M HCl to determine the concentration of metals in the organic phase. However the results showed that 2 M HCl was not able to quantitatively strip iron and tin from 0.1M DEHPA in kerosene. Therefore D_{Sn} and D_{Fe} were still determined by mass balance in the aqueous phase of before and after extraction.

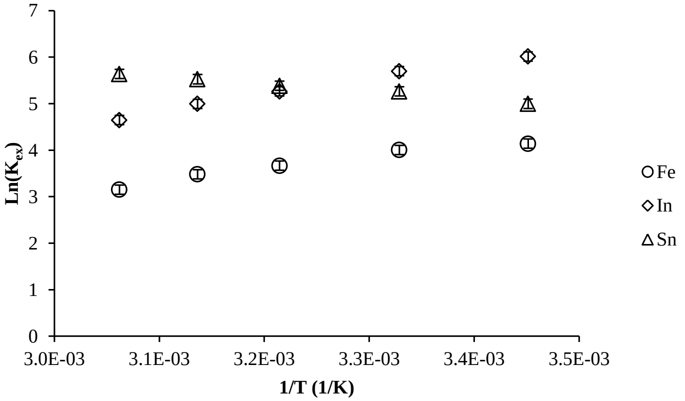

Figure 34. The effect of temperature on the extraction equilibrium of Fe(III), In(III) and Sn(IV). The aqueous phase was 1 M H_2SO_4 and the organic phase was 0.1 M D2EHPA/kerosene.

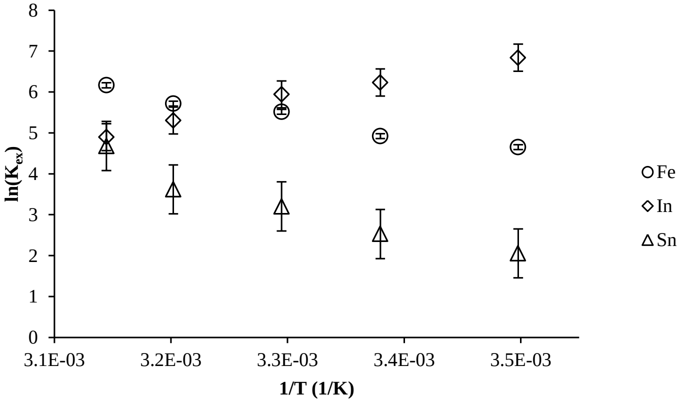

Figure 35. The effect of temperature on the extraction equilibrium of Fe(III), In(III) and Sn(IV). The aqueous phase was 0.1 M HCl and the organic phase was 0.1 M D2EHPA/kerosene.

Unlike indium, the extraction of tin was an endothermic process. The extraction of iron from sulfate media was exothermic, although in chloride media it was shown to be endothermic. In a previous work, a similar change in the extraction enthalpy of bismuth extraction from $HClO_4$ was observed [53]. When dinonyl naphthalene sulfonic acid (HDNNS) was used as the extractant, the extraction process was slightly endothermic, but when 2-ethylhexyl phenylphosphonic acid (HEHΦP) was used, extraction of bismuth was exothermic. It could be concluded that due to different metal complex being formed and broken, the enthalpy change of an extraction process was affected by factors such as the choice of aqueous media and organic extractant. Changes in enthalpy and entropy during the extraction of indium, iron and tin were obtained by linear regression, and listed in Tables 16 for 1 M H_2SO_4 and Table 17 for 1 M HCl. Values for aluminum, zinc and copper were not calculated due to low D. Between 293 K and 333 K, extraction of iron and extraction of indium in the sulfate system was driven by changes in enthalpy, since both ΔH^o and ΔS^o are negative, and $\Delta H > T\Delta S$ in the temperature interval studied. On the other hand, extraction of iron and extraction of tin in the chloride system was driven by changes in entropy, due to both Δ°H and Δ°S being positive in these cases and $\Delta H < T\Delta S$.

Table 16. ΔH^o and ΔS^o for extraction from 1 M H_2SO_4, based on proposed reaction mechanism for Fe, In and Sn shown in reaction (VIII), (V) and (IX), respectively. Values are obtained by linear fitting of equation (14).

Metal	Fe	In	Sn
ΔH^o / kJ/mol	-20.9±1.2	-29.1±3.8	13.3±0.6
ΔS^o/ J/mol/K	-36.1±1.0	-48.6±6.6	123±5.4

Table 17. ΔH^o and ΔS^o for extraction from 0.1 M HCl, based on proposed reaction mechanism for Fe, In and Sn shown in reaction (VI), (IV) and (VII), respectively. Values are obtained by linear fitting of equation (14).

Metal	Fe	In	Sn
ΔH^o / kJ/mol	35.3±11	-44.9±1.3	57.9±6.1
ΔS^o / J/mol/K	161±45	-99.7±3.1	218±25

It can be seen from the data in Table 16 and 17 that both Δ°H and Δ°S are lower in the chloride system compared to the sulfate system. The difference can be explained by reaction (IV) and (V). In sulfate media, for each extracted In^{3+} ion, three times as many H^+ ions were released, while for chloride media the ratio was 1:2. Therefore there was a greater increase in configurational entropy when indium was extracted from H_2SO_4. The differences for iron and tin could be attributed to the difference in extraction stoichiometry. Figures 31 and 32 showed the ratio between D_{Fe} and extractant concentration was 1:1 in 1 M H_2SO_4, but in chloride systems it was 1:2. This trend is the same for tin. Thus compared to sulphate media, in chloride media a greater number of hydrated water molecules were replaced by extractant molecules for each extracted metal ion. The dehydration process often causes both an increase in the randomness of the system and an increase in enthalpy, due to the disruption of bonds in hydrated species [54]. Moreover, since the aqueous phase is acidic and $[Cl^-]$ is much higher than $[Fe^{3+}]$, different iron chloride complexes exist in the aqueous phase [55]. Therefore iron could be partially extracted through a mechanism similar to reaction (X). It can be seen that this reaction also results in positive entropy change; this could contribute to the much higher Δ°H and Δ°S values observed for iron extraction in chloride media compared to sulfate media.

$$FeCl_2^+ + \overline{2(HA)_2} \leftrightarrow \overline{FeClH_2A_4} + Cl^- + 2H^+ \qquad \text{(X)}$$

Experimental results showed that low temperatures favor the extraction of indium from sulfate media, and that stripping with HCl at greater than 293 K will increase both the amount of indium recovered and its separation from iron and tin. However, with factors such as the need and cost to install cooling and heating systems taken under consideration, 293 K to 298 K is still likely to be the optimal extraction temperature.

5.2.4 Mixer-settler tests yttrium and indium extraction from mixed FPD waste

5.2.4.1 Ideal stages calculation

McCabe-Thiele diagrams for indium and yttrium extractions were constructed in order to determine the number of minimum counter-current mixer-settler stages required for each step of the process. The results are shown in Figure 36 for indium and in Figure 37 for yttrium. It can be seen in Figure 36 that when indium concentrations in the aqueous feed are between 0.2 and 0.4 mM, 1 ideal stage was nearly sufficient to obtain quantitative extraction of indium. However 2 stages would ensure the quantitative extraction of indium. In Figure 37 the results show that if yttrium concentration in the feed solution is less than 3.4 mM, quantitative extraction of yttrium can be obtained with 2 ideal stages. Based on these results, two counter-current stages were used for the extraction and stripping of indium, and three stages were used for the extraction and stripping of yttrium.

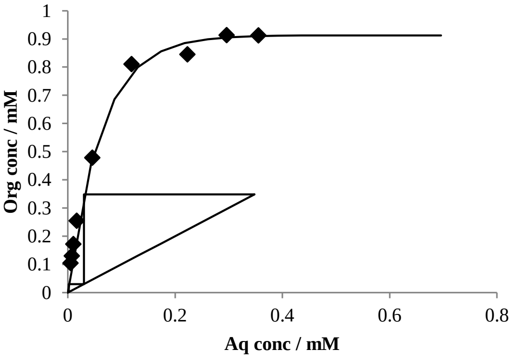

Figure 36. McCabe-Thiele diagram for the extraction of indium in a countercurrent continuous process. Aqueous phase is 1 M HCl, organic phase is 0.25 M Cyanex 923 diluted in kerosene. The diagonal line is an operating line with θ=1

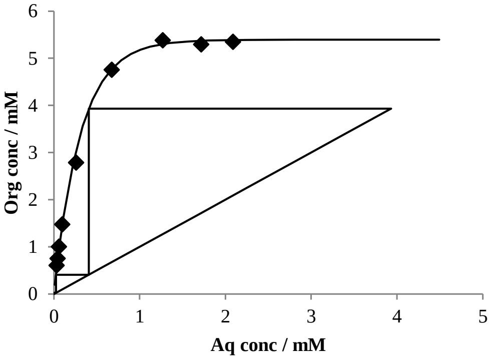

Figure 37. McCabe-Thiele diagram for the extraction of yttrium in a countercurrent continuous process. Aqueous phase is 1 M HCl, organic phase is 0.2 M DEHPA diluted in kerosene, The diagonal line is an operating line with θ=1.

5.3.4.2 *Extraction and stripping of indium*

The results presented in Figure 38 show that due to rapid extraction kinetics, more than 90% of indium and tin in the feed solution was extracted to the organic phase after the first stage. Changes in concentrations of REEs were small over the mixer-settler stages. However, it was observed that by adding a second extraction stage, larger amounts of iron, zinc and copper were extracted into the organic phase, e.g. the concentration of iron decreased from 38 mM in the feed to 30 mM after the first stage and 23 mM after the second stage. This was expected, since according to the results shown in Table 9, D_{Fe} in this extraction system is approximately 0.4, which corresponds to 30% extraction in one stage.

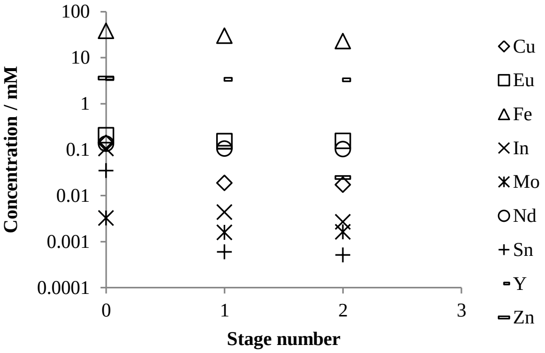

Figure 38. Aqueous metal concentrations of mixer-settler stages in the indium extraction step. Aqueous phase is 1 M HCl leachate on solid FPD waste, organic phase is 0.25 M Cyanex 923 diluted in kerosene, stage 0 is the aqueous feed.

The extract from the extraction system shown in Figure 38 was stripped using 1 M HNO_3. It can be seen that more than 90% of extracted indium was recovered into the 1 M HNO_3. The data in Figure 39 also shows that small amounts of REEs were found in the strip acid; however their concentrations were much lower than in the aqueous feed in the extraction stages shown in Figure 38. Other quantitatively stripped metals were iron and zinc, and their concentrations in the raffinate of the strip stages are more than one order of magnitude higher than indium. Further separation of indium from the strip raffinate can be achieved by e.g. extraction with 0.2 M DEHPA diluted in kerosene, followed by stripping with 1 M HCl. Comparisons between the results shown in Figure 36 and Figure 37 showed that the theoretical prediction based on the McCabe-Thiele diagrams agreed well with the experimental results; indium was quantitatively extracted in 2 mixer-settler stages, and most of the indium extraction occurred in the first stage.

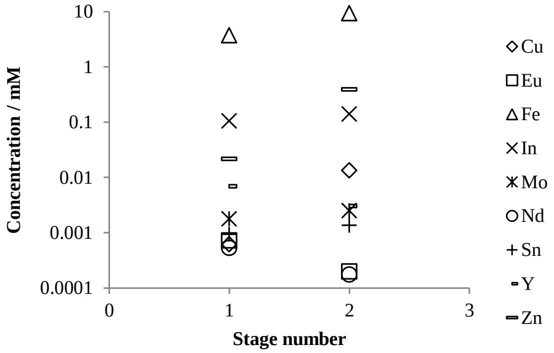

Figure 39. Aqueous metal concentrations of mixer-settler stages in the indium stripping step. Aqueous phase is 1 M HNO_3, organic phase is 0.25 M Cyanex 923 diluted in kerosene.

5.2.4.3 *Extraction and stripping of yttrium*

Mixer-settler results of the extraction and stripping of yttrium are shown in Figures 40 and 41. Data for neodymium, neodymium, molybdenum and zinc were omitted in Figure 40 as their concentrations in the aqueous phase did not change in any noticeable way. It can be seen from the figures that although most of the yttrium in the aqueous feed can be extracted and stripped in three stages, which was more than was predicted from Figure 37. It can also be seen from Figure 41 that there was a large increase in the concentrations of several metals such as neodymium and tin in the third strip stage. Therefore, with respect to yttrium purity, it could be more beneficial to reduce the number of strip stages from three to two.

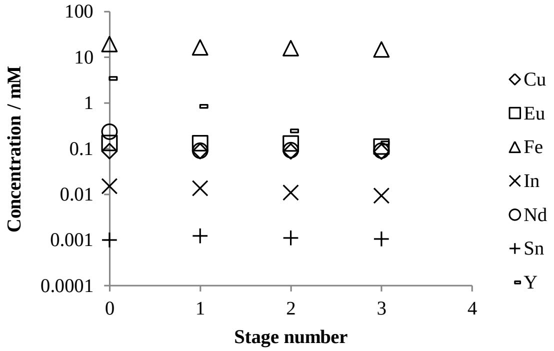

Figure 40. Aqueous metal concentrations of mixer-settler stages in the yttrium extraction step. Aqueous phase is 1 M HCl, organic phase is 0.2 M DEHPA in kerosene, and stage 0 is the aqueous feed, which is the aqueous HCl raffinate after extraction with 0.25 M Cyanex 923 in kerosene.

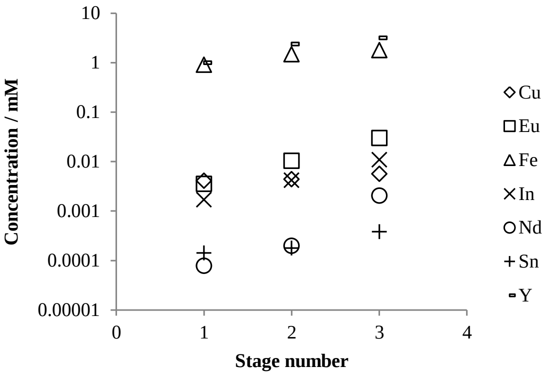

Figure 41. Aqueous metal concentrations of mixer-settler stages in the yttrium stripping step. Aqueous phase is 2 M HCl, organic phase is 0.2 M DEHPA diluted in kerosene.

Furthermore, it is clear from the data in Figure 41 that iron is the most significant impurity in the strip raffinate. Several options were therefore explored to reduce the concentration of iron in the raffinate solution containing yttrium. One of the options was to use Cyanex 923 diluted in kerosene to extract iron from the 2 M HCl raffinate containing iron and yttrium. The other option was to use 3 M HNO_3 instead of 2 M HCl in the yttrium stripping step of the process. The results are shown in Table 18. Both options effectively increased the purity of yttrium with respect to iron. Due to the much higher separation factor between iron and yttrium, the first option was concluded to be the better choice.

Table 18. Values of D for different options to further purify the aqueous raffinate solution containing yttrium. Option 1: extraction of the 2 M HCl after yttrium stripping with 0.25 M Cyanex 923 diluted in kerosene. Option 2: using 3 M HNO_3 instead of 2 M HCl for yttrium stripping.

	D_{Cu}	D_{Eu}	D_{Fe}	D_{In}	D_{Nd}	D_{Sn}	D_{Y}
Option 1	0.32	<0.1	295.95	36.27	<0.1	2.97	<0.1
Option 2	5.60	<0.1	18.30	23.23	0.55	13.92	<0.1

5.3 Metal recovery process

5.3.1 Indium recovery from LCD glass waste

Batch experiments using an extraction system consisting of single extraction, and strip stage were performed. H_2SO_4 Leachate of LCD glass waste with an initial acid concentration of 1 M was used as the feed. The results obtained are presented in Table 19. It can be observed that the extraction of indium was quantitative using 0.25 M D2EHPA diluted in kerosene. Stripping by 1 M HCl could selectively recover indium into the aqueous phase while leaving co-extracted iron and tin in the organic phase. Since iron and tin would accumulate in the organic phase when 1 M HCl is used to selectively strip indium, higher concentration of HCl (> 3 M) is needed to strip iron and tin. Iron can be removed from the organic phase with 3 M HCl. With more concentrated HCl solutions (>8 M), it is possible to strip tin from the organic phase but the stripping efficiency was only 25% in a single stage at 1:1 A/O ratio.

Table 19. Single stage batch test of extraction, washing and stripping. Aqueous phases were 1 M H_2SO_4 (extraction and scrubbing) and 1 M HCl (stripping). The organic phase was 0.25 M D2EHPA diluted in kerosene with 2% 1-decanol.

Metal	Indium extration (1 M H_2SO_4)	Indium stripping (1 M HCl)
Al	<0.1	0.5±0.3
Cu	<0.1	9±8
Fe	4.13±0.65	77.3±8
In	98±30	0.03±0.01
Sn	42±19	>100
Zn	<0.1	3±2

Based on the results obtained in this work, a possible process for the recovery of indium from waste LCD glass was outlined, and was further optimized in another research project [56]. The resulting process flow sheet can be seen in Figure 42. S/L in that process is twice as much compared to the experimental work in this project, meaning that indium concentration in the aqueous feed should be approximately 0.35 mM (40 mg/ml). The inclusion of a scrubbing stage removed some of co-extracted zinc and aluminum from the organic phase, however small amounts of indium can be lost in this stage. Furthermore it was shown that an aqueous stream containing indium with a purity >90 wt% can be obtained after the stripping stages.

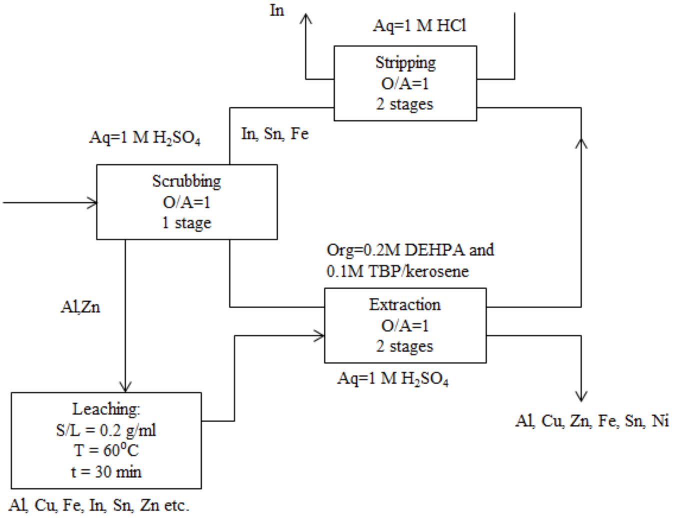
In
Aq=1 M HCl
Stripping
O/A=1
2 stages
Aq=1 M H_2SO_4
In, Sn, Fe
Scrubbing
O/A=1
1 stage
Org=0.2M DEHPA and
0.1M TBP/kerosene
Al,Zn
Extraction
O/A=1
2 stages
Aq=1 M H_2SO_4
Al, Cu, Zn, Fe, Sn, Ni
Leaching:
S/L = 0.2 g/ml
T = 60°C
t = 30 min
Al, Cu, Fe, In, Sn, Zn etc.

Figure 42. Schematic diagram of a recycling of indium from LCD glass, showing an extraction, scrubbing and stripping step. The aqueous phase was 1 M H_2SO_4 (extraction and scrubbing) and 1 M HCl (stripping), organic phase is 0.2 M D2EHPA diluted in kerosene with 0.1 M TBP as phase modifier.

5.3.2 Yttrium and indium recovery from mixed FPD waste

A preliminary solvent extraction process for the recovery of yttrium is shown in Figure 43. In the step labeled “indium extraction”, indium, iron, copper, tin and molybdenum were extracted into an organic phase consisting of 0.25 M Cyanex 923 in kerosene. REEs such as yttrium, neodymium, and europium remained in the aqueous phase. In the step “indium stripping”, indium, copper, iron and zinc are stripped with 1 M HNO_3. Yttrium could be extracted by 0.2 M DEHPA diluted in kerosene followed by stripping with 2 M HCl. After indium was stripped from 0.25 M Cyanex 923 in kerosene with 1 M HNO_3, it was possible to use this organic phase to separate iron and yttrium, as shown in the “yttrium purification” step in Figure 42.

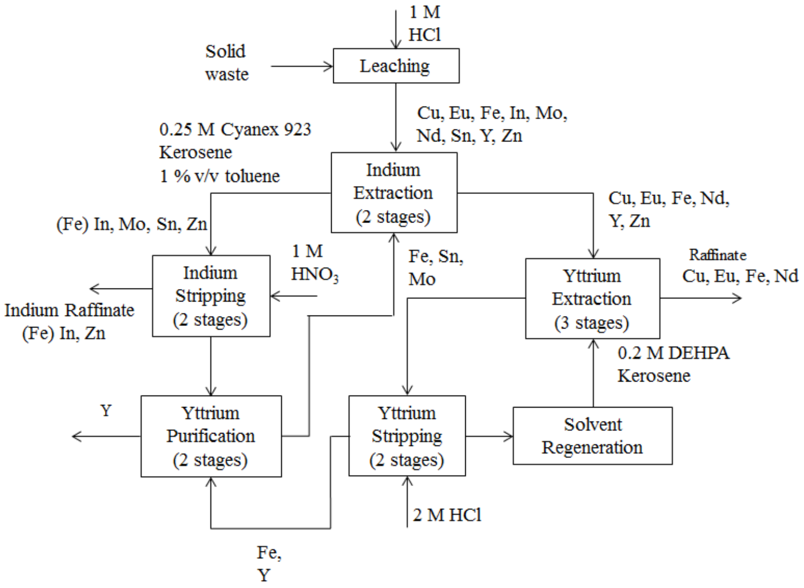
1 M
HCl
Solid
waste
Leaching
Cu, Eu, Fe, In, Mo,
Nd, Sn, Y, Zn
0.25 M Cyanex 923
Kerosene
1 % v/v toluene
Indium
Extraction
(2 stages)
Cu, Eu, Fe, Nd,
Y, Zn
(Fe) In, Mo, Sn, Zn
1 M
HNO_3
Fe, Sn,
Mo
Raffinate
Cu, Eu, Fe, Nd
Indium
Stripping
(2 stages)
Yttrium
Extraction
(3 stages)
Indium Raffinate
(Fe) In, Zn
0.2 M DEHPA
Kerosene
Y
Yttrium
Purification
(2 stages)
Yttrium
Stripping
(2 stages)
Solvent
Regeneration
2 M HCl
Fe,
Y

Figure 43. Flowchart for the indium and yttrium recovery process using Cyanex 923 and DEHPA as extractants.

Concentrations of indium, yttrium and major impurity species such as iron and zinc at aqueous feed and each extraction step outlined in Figure 43 are shown in Table 20. It can be observed that the yttrium stream obtained in the end is relatively pure, but the proposed process still has large room for improvement with respect to the amount and purity of yttrium and indium recovered. The raffinate from the indium stripping stage as shown in Figure 43 can be used as the feed solution in the indium recovery process shown in Figure 42, where indium can be further separated from other metals in the solution.

Table 20. Concentrations of metals in the aqueous raffinate at process steps outlined in Figure 42, converted as % of feed concentration. Data was obtained from laboratory scale mixer-settler tests.

Concentration	Indium	Indium	Yttrium	Yttrium	Yttrium
(mM)	extraction	stripping	extraction	stripping	purification
Y	94.49%	0.32%	3.65%	91.30%	87.83%
In	5.00%	54.38%	5.63%	5.63%	5.63%
Zn	0.70%	10.89%	0.42%	0.42%	0.42%
Fe	59.52%	24.55%	38.36%	4.26%	0.05%

6 Conclusion

The current work investigated a potential hydrometallurgical method to recycle indium from the panel glass of used LCD monitors and TVs. This method involves leaching of indium-tin oxide from the surface of crushed LCD glass, followed by separation of indium from other metals in the leaching acid through solvent extraction.

HNO_3, HCl, and H_2SO_4 of different concentrations were tested for the leaching of indium from crushed LCD glass. 1 M H_2SO_4 most feasible alternative based on kinetics studies. HNO_3 had both slower leaching kinetics and a more noticeable effect of partially digesting the polymeric material adhered on the LCD glass during leaching. Since the dissolution of plastic material occurs at a similar time as equilibrium in indium leaching is reached, this makes the filtration of leach liquor more difficult. It could also negatively impact the subsequent solvent extraction process. For mixed FPD waste, leaching kinetics of metals in 1 M HNO_3 and 1 M HCl was studied at both 20 ± 2^oC and 80 ± 2^oC. Results showed that the latter could be more time-efficient for leaching. In addition, improving mechanical separation and pretreatment processes could be extremely beneficial for the subsequent solvent extraction process by separating the solid waste into different fractions containing less mixed materials.

In the solvent extraction screening experiments, different extraction systems were prepared from different aqueous and organic phases. The results showed that out of the systems studied, extraction from 1 M H_2SO_4 to 0.1 M DEHPA in kerosene followed by stripping with 1 M HCl was a promising alternative for the recovery of indium. Further studies on extraction kinetics were performed. It was concluded that the extraction in the aforementioned system reached equilibrium with respect to indium in 5-10 minutes, also that longer extraction time had a negative impact on the separation of indium.

The pH and temperature dependence of metal extraction was investigated for the two extraction systems chosen in the screening test. The results reinforced the conclusion from the screening test, that indium could be separated into a relatively pure fraction with DEHPA. Furthermore, the pH study also showed that good indium separation could also be achieved by extraction at lower acid concentrations. It was concluded from the temperature dependency that the optimal condition for indium extraction was 293 K or lower.

Studies using laboratory scale mixer-settler methods showed that a combination of DEHPA in kerosene and Cyanex 923 in kerosene was able to separate indium into 1 M HNO_3 and yttrium could be recovered in 2 M HCl. The indium stream can be further purified by extraction with 0.2 M DEHPA in kerosene followed by back extraction with 1 M HCl. Contacting the yttrium stream with 0.25 M Cyanex 923 in kerosene can selectively extract the majority of the iron impurities into the organic phase.

It was observed that cruds could form during the extraction process. Several methods, such as washing the solid waste with 1 M NaOH before leaching with 1 M HCl, can drastically reduce the formation of crud. Further study could be performed in this area, however, to gain a better understanding of both the formation and prevention of crud.

The results of the experiments have shown through solvent extraction, yttrium and indium can be separated from other impurities to a purity of 95%. Higher purity could be achieved by optimization of the solvent extraction, or by additional processes such as electrolysis.

7 Future Work

One of the interesting continuations of the work is electrochemical study on the final strip raffinate of the processes which contains relatively pure yttrium or indium to test the feasibility of recovery these two elements as metals, or to test whether this treatment can increase the purity of recovered material. Additional ways to prevent the formation of crud during the extraction of indium from mixed FPD waste leachate can be explored by e.g. looking for better filtration methods or other ways to remove suspended solid. The mixer-settler process for indium and yttrium recovery from mixed FPD waste can also be further optimized to reduce the amount of iron impurity. This could be done by adjusting parameters such as organic phase composition and phase volume ratio of different extraction stages. Different ways to selectively extract or otherwise remove tin from the leachate solution before other metals are extracted can be explored, since it is difficult to strip it from organic phase once extracted.

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10 Abbreviations and terms

θ	Phase volume ratio
AKUFVE	Apparatus for Continuous Measurement of Partition Factor in Solvent Extraction (“Anordning för Kontinuerlig Undersökning av Fördelningsjämvikter vid Vätske-vätske Extraktion”)
Cyanex 272	Bis(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 923	A mixture of four different trihexyl/octyl phosphine oxides
DEHPA	Bis(2-ethylhexyl) phosphoric acid
D	Distribution Ratio
D_{In}	Distribution Ratio of indium, subscript can be replaced with the symbol of another element
Diluent	A liquid phase (often organic) in which extractants and modifiers are dissolved
Extract (noun)	A liquid phase (often organic) that contains materials extracted from another immiscible liquid phase
Extractant	The compound that is primarily responsible for the transfer of solute from one liquid phase to another in solvent extraction
Extraction	The initial transfer of solutes from e.g. the aqueous feed to the organic phase in a solvent extraction process or a step in a solvent extraction process
Feed	The liquid phase (often aqueous) containing solutes to be extracted along with impurities that enters a solvent extraction process or a step in a solvent extraction process
FPD	Flat Panel Displays
ICP-OES	Inductively-Coupled Plasma with Optical Emission Spectrometer
ITO	Indium Tin Oxide
LCD	Liquid Crystal Display
Leachate	An aqueous solution (often acid) after contact with a solid that contains materials dissolved from the solid
Modifier	Additives to the liquid phase containing extractants, improving properties of the liquid phase by e.g. increasing extractant solubility, and reducing surface tension which allows for faster phase separation

Raffinate	A liquid phase (often aqueous) from which materials have been extracted by another immiscible liquid phase
S/L	Solid-Liquid ratio
Scrubbing	Removal of impurities or unwanted materials from an extract by contacting it with a clean immiscible phase
SEM-EDX	Scanning Electron Microscope and Energy Dispersive X-ray
$SF_{A/B}$	Separation Factor of metal A and B defined to be >=1
Solvent extraction	The process of transferring a substance from one liquid phase to another immiscible liquid phase, Also named liquid−liquid extraction
Solvent regeneration	Treatment of an organic phase before reuse to remove substances such as impurities which are difficult to strip and degradation products
Stage	A basic compartment in a solvent extraction process where processes such as mixing of phases, material transfer from one phase to another, and phase separation occurs
Step	A part of the overall solvent extraction process where solutes are transferred from one liquid phase to another, e.g. extraction of the solute of interest along with impurities
Stripping	Removal of the main solute or materials of interest from an extract by contacting it with a (clean) immiscible phase
TBP	Tributyl Phosphate

11 Appendices

Appendix A

ICP-OES

This was the method used for all the metal concentration measurements. The instrument is a Thermo iCAP-6000 ICP-OES. This technique is used to measure liquid or gas sample, which is introduced into the instrument along with a carrying gas (argon) as an aerosol mist. The sample is then ionized and excited by heating with the plasma to a temperature of 6000-7000K. The wavelength of the photon release upon de-excitation is used to identify the type of elements present in the sample. Most elements with exceptions such as hydrogen, fluorine and inert gas can be detected by this method, at a concentration level of 1mg/L.

For more information on ICP-OES, see [57]

SEM-EDX

In SEM, focused beams of high energy electrons are utilized to scan across the surface of a sample. When the incident electrons are decelerated by the sample, different types of emissions are generated, such as secondary electrons, backscattered electrons, and X-rays. Secondary electrons are used to produce images of the external morphology on a sample. With energy dispersive x-ray (EDX) technique, the X-ray emitted can be used to identify the elements present on the surface of the sample. The images shown in this work were taken by a FEI Quanta 200 ESEM FEG. It is equipped with a Everhardt Thornley Secondary Electron Detector and a solid state detector for backscattered electrons. the images were taken between operating voltages of 12 and 20 kV and pressure of 1 Torr.

More information on SEM-EDX can be found in e.g. [58]

Appendix B

AKUFVE

The acronym AKUFVE means Apparatus for Continuous Measurement of Partition Factor in Solvent Extraction ("Anordning för Kontinuerlig Undersökning av Fördelningsjämvikter vid Vätske-vätske Extraktion"). A simple sketch of its construction is shown in Figure B1.

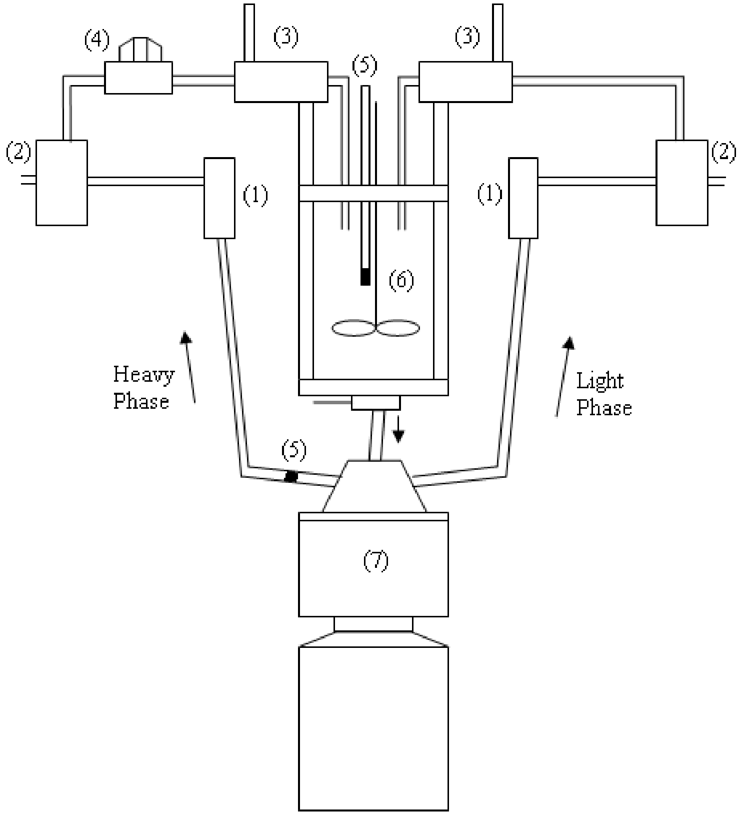

Figure B1: Basic construction of a lab-scale AKUFVE unit: (1) flow meter (2) sampling and mixing pumps (3) heat exchanger (4) pH electrode (5) thermo-element (6) mixing chamber (7) centrifuge

This apparatus was developed in the 1960s [59], and later improved by adding the pumps (2) [60]as well as including a redox control [61]. The mixture is introduced into the centrifuge through the middle tube, where the two phases are quickly separated at rotational speed of 5000-50000 rpm. The main advantage of the technique is that the pure phases (less than 0.01% entrainment from the other phase) can be achieved by the centrifuge. This allows determination of distribution ratios of over 10^3 or under 10^{-3}. With AKUFVE, it is also possible to determine a large number of data points (50-100) over one day of experiments. However, as a centrifugal separator, the construction of AKUFVE is mechanically complicated, meaning that it has a large need for maintenance and is sensitive to solid contaminants.