Comprehensive Process for the Recovery of Value and Critical Materials from Electronic Waste

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Abstract

The development of technologies that contribute to the proper disposal and treatment of electronic waste is not just an environmental need, but an opportunity for the recovery and recycle of valuable metals and critical materials. Value elements in electronic waste include gold, palladium, silver, copper, nickel, and rare earth elements. This paper presents a technical assessment of the steps involved in a scheme that enables efficient recovery of value and critical materials from scrap mobile electronics. An electrochemical recovery process, based on the regeneration of ferric ion as a weak oxidizer, is studied for the selective recovery of base metals while leaving precious metals for separate extraction at reduced chemical demand. A separate process recovers rare earth oxides from magnets in electronics. Recovery and extraction efficiencies ca. 90 % were obtained for the extraction of base metals from the non-ferromagnetic fraction in the two different solution matrices tested (sulfuric and hydrochloric acid). The effect of the pre-extraction of base metals in the increase of precious metals extraction efficiency was verified. On the other hand, the extraction of rare earths from the ferromagnetic fraction, performed by means of anaerobic extraction in acid media, was assessed for the selective recovery of rare earths. A comprehensive flow sheet was developed to process electronic waste to value products.

Keywords: Electronic waste, Recycling, Precious Metals, Critical Materials, Electrowinning.

1. Introduction

Every year, billions of mobile electronic devices (e.g. cell phones, tablets, and laptops) are sold around the world. Because new technological developments emerge every day, the average time that a mobile electronic device is used before it is replaced by a newer model decreases. Most of these mobile devices can find a profitable market to a second life cycle, either as a refurbished or remanufactured product [1]. However, the exponential growth of the mobile electronics market, the increasing production of electronic waste (e-waste), and the reduced lifetime [2], vastly increase the need for the development of technologies for the recycling of end-of-life mobile electronic devices. Besides solving the environmental concerns associated with the landfill disposal and subsequent leaching of hazardous elements, such as brominated flame retardants, and heavy metals [2-4], the recycling of e-waste has an enormous potential as an alternative source of value metals and critical materials [5-7]. End-of-life mobile electronic devices possess a diverse composition of base and value metals, such as Cu, Ni, Pd, Au, and Ag, in concentrations that exceed those found in mineral ores [4, 8, 9]. This scenario has activated a significant growth of the e-waste recycling industry in the U.S., processing over 4.4 Mt of e-waste in 2011 to produce commodity products such as steel and copper [10]. Mobile electronic devices also contain small, but significant, quantities of rare earth elements (REE) in speakers, vibrators, and hard disks, which can also be recovered and recycled [11]. The U.S. Department of Energy (DOE) has classified REE as critical elements for national energy security. Therefore, the recycling and recovery of REE from e-waste can contribute to the stabilization of the REE market and reduce the dependence of REE mining [12, 13]. Nevertheless, the need of cost efficient technologies for the recovery of REE is slowing the development of the REE recycle industry [14].

The distribution of value and critical elements in cell phones is presented in Table 1 [1, 9, 11, 15]. An estimated percentual contribution of metals and rare earth elements (REE) to the total recoverable value of the e-waste, based on the average value of metals during 2014 (ca. USD 3.75 per cell phone unit and ca. USD 7.33 per laptop unit), is shown in Fig. 1 for cell phones (a) and laptops (b) . It is evident that the highest recovery value comes from metals with the lowest concentration. A small percentage of gold is found in mobile electronics, and yet it contributes to the highest portion of the total recoverable value of e-waste. Based on this fact, extensive research is currently being performed in the development and optimization of hydrometallurgical, non-cyanide, processes focusing on the recovery of value metals [16-21].

Hydrometallurgical treatment of e-waste has been found to be more efficient and environmentally friendly than other recovery processes, such as physical separation and pyrometallurgical processes [4]. With a hydrometallurgical approach, the low leaching selectivity and the low concentration of precious metals, relative to the total metal content, lead to a significant use of chemicals in the dissolution of the most abundant metals, such as Cu or Sn [4, 22, 23].

Electrochemical methods have been developed to reduce the use of reagents [4]. Electrochemically generated chlorine (Cl_2) is a strong oxidizer capable of dissolving most metals including gold. However, the leaching rate is limited by the solubility of Cl_2 [24, 25]. Moreover, the use of Cl_2 as an oxidizer presents issues regarding worker safety and corrosion of materials used in construction. An alternative electrochemical recovery (ER) process, already tested for the efficient recovery of metals from ores at low temperatures [26, 27], is based on the use of a weak oxidizer (Fe^{3+}), which selectively dissolves the less noble metals in the e-waste (Equation 1) [5, 28]. A thermodynamic analysis of the oxidation conditions required for the extraction of metals, such as Cu, Sn, and Ag, using Fe^{3+} as the oxidant was presented in a previous work [5].

In the ER process, the oxidizer is regenerated at the anode of an electrochemical cell (Equation 2), coupled with the electrowinning of metals in the cathode (Equation 3).

where M is the metal leached, n is the metal-ion charge, and E^0 is the standard reduction potential vs. standard hydrogen electrode (SHE).

Up to 50% energy reduction, compared to the current copper electrowinning processes [29], can be achieved just by the substitution of the oxygen evolution reaction ($E^0 = 1.229 \text{ V vs. SHE}$) with the oxidation of Fe^{2+} to Fe^{3+} in the anode during the electrowinning of base metals. The main advantage of this process is that it increases the concentration of gold and palladium in the waste material by the selective and complete removal of the base metals with minimal chemical input.

The ER process has shown promising results in terms of having a low environmental impact [30], low energy consumption [28], and high base metals recovery, while leaving Au and Pd intact for removal in separate stages [5]. Nevertheless, more research is required to improve the leaching kinetics, increase the solid to liquid ratio (S/L) in the leaching treatment, and assess the effect of the base metals extractions in the enrichment and recovery of precious metals.

Previous kinetic analysis of the dissolution of rotating copper disk alloys with Fe^{3+} in acidic media have demonstrated that the leaching process follows a mixed controlled

mechanism, which is independent of the solution pH [31]. It is then expected that mass transport control could be predominant in waste electronic material where the metal being leached is not readily available on the surface [18, 32]. According to previous work [4, 28], the current extraction processes require at least 8 liters of leaching solution per kilogram of e-waste. Although the volume of liquid can be reused to process new material in the ER process, the increase of the solid to liquid ratio will facilitate the processing of the leaching solution and will be reflected in lower capital and operational costs for the recycling process.

In this paper, a comprehensive process flow diagram, centered in the ER process, is proposed for the efficient recovery of different value streams from e-waste(Fig. 2). While previous work focused in the feasibility of the ER process [5, 28], this work develops an alternative for the integration of the ER process in a comprehensive scheme for the recovery of different value streams. A single packed leaching column in series with an electrochemical reactor, in the ER process for the recovery of base metals, was implemented as the core unit operation in the development of an efficient recovery process. The use of a packed bed column improved the contact between the leaching solution and the e-waste, allowing the potential to completely deplete the oxidant through a single pass, increasing the S/L ratio. Experimental results show that up to a 97% Cu removal efficiency could be accomplished in addition to completely removing the Sn and Zn. Two different solution matrices were tested, using H_2SO_4 and HCl as supporting electrolytes with $\text{Fe}_2(\text{SO}_4)$ and FeCl_3 as oxidants precursors, respectively. The effects of the leaching matrix on the leaching kinetics and on the recovery efficiency of the base and value metals were evaluated. Finally, the selective extraction of precious metals (Ag, Au, and Pd) was performed with acid thiourea leaching [16, 20], as an assessment of the effect of the ER process in the precious metals extraction. Extraction and recovery chemistry specific to

each precious metal is currently under development. The integration of the ER process in the comprehensive extraction and recovery of value materials significantly reduces the chemical consumption and waste generation in the overall process by: 1) the regeneration of the oxidants, which allows the re-use of the leaching solution in the processing of new material, and 2) the enrichment of precious metals in the e-waste, therefore, reducing the chemical requirements and waste generation. Parallel with the extraction of base and precious metals an anaerobic hydrometallurgical process is proposed for the selective recovery of REE from the ferromagnetic fraction of e-wastes. A process flow diagram is developed for the comprehensive recovery of value and critical materials from electronic waste.

2. Materials and methods

2.1. Materials

Leaching solutions were prepared in DI water (18 M Ω -cm) using ACS grade or better chemicals. Samples of mechanically processed phones were provided by Advanced Recovery Inc. The device batteries were removed prior to mechanical processing. The phones were shredded followed by magnetic separation of the ferrous fractions including steel and magnets. The non-ferrous material was further size reduced using an in-house designed ball mill. Samples of shredded cell phones before magnetic separation (mean particle size of 0.59 mm), and after magnetic separation (magnetic fraction particle size > 1 mm, and milled non-ferrous fraction mean particle size of 0.31 mm) were obtained. The composition of REE and metals in the grinded cell phone material and in the non-ferrous fraction of the cell phone were determined after digestion in aqua regia and concentrated HNO₃. The results of the proximal composition of interest materials are presented in Table 1. Due to the heterogeneity of the ferromagnetic

fraction, the REE and metals composition in this fraction was determined after the selective dissolution of REE followed by the digestion of the undissolved material in aqua regia.

2.2. Packed bed extraction with Fe^{3+}

The oxidizer break through and metal elution curves were obtained using a vertical glass column (1.5 cm diameter and 5 cm long) packed with 5 g of milled, non-magnetic cell phone material (bulk density $\rho_b = 0.83 \text{ g cm}^{-3}$). The oxidizer solution was pumped at a rate of 1 ml min^{-1} using a Cole Parmer MasterFlex C/L peristaltic pump. Two tests were performed with 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ in 1 M H_2SO_4 , and 0.2 M FeCl_3 in 0.5 M HCl solutions. During the elution, 10 mL samples were collected in sequence to determine the oxidant concentration and dissolved metal ions in the effluent.

2.3. Electrochemical recovery (ER) of base metals

A diagram of the ER system is shown in Fig. 3. The electrochemical cell used a trough flow-cell configuration. Solution pulled from the anode was pumped through a leaching column and returned to the cathode section. The cathode, which consisted of a 6 cm by 30 cm piece of woven 304 Stainless steel (SS) (40 mesh), was folded to fit the electrochemical cell as shown in Fig. 3. The cathode was attached to a 304SS buss bar so that the mesh cathode was suspended in the bulk of the solution for easy removal/replacement as the deposit was formed. The submerged area was approximately 28 cm x 6 cm. At the other end of the cell, the anode was made out of a 6 cm x 6 cm piece of carbon felt in contact with a Pt wire, which was used as the current collector. The distance between the anode and the cathode was 3.5 cm. The packed bed column consisted of a 15 cm long Tygon tubing (1" ID) vertically oriented and packed with 70 g of grinded (non-ferrous) cell phone material.

To start the experiment, fresh leaching solution (either 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ in 1 M H_2SO_4 or 0.2 M FeCl_3 in 0.5 M HCl) was pumped through the packed bed column at a rate of 3 mL min^{-1} . This flow rate was established to perform the ER test at similar conditions, in terms of axial velocity through the column, to the packed bed extraction experiments in section 2.2. The solution leaving the column was then circulated to fill the electrochemical cell and $30 \mu\text{L}$ samples were taken every 30 minutes to measure the concentration of Fe^{3+} . A total of 310 mL of leaching solution was loaded to the system. Once the electrochemical cell was full, the feeding of fresh solution was stopped, and the recirculation of solution from the electrochemical cell was initiated. At the same time a current density of 138.9 A m^{-2} was applied to the electrochemical cell for the oxidant regeneration and metals deposition using a Princeton Applied Research Model 273 A galvanostat/potentiostat. Samples for Fe^{3+} measurement were taken every hour at the packed column inlet and outlet and in the electrochemical cell. Because the experiments lasted for more than a day, no samples were taken overnight. The experiments were stopped when the Fe^{3+} conversion through the column reached a value below 10%, suggesting that most of the target metals in the column were dissolved. Weight of the deposited metal at the cathode and final weight of the undissolved e-waste were recorded at the end of the experiment to calculate recovery and extraction efficiency. Samples of the deposit and undissolved e-waste material were digested in aqua regia for metal composition analysis.

2.4. Extraction of precious metals

Seven grams of the e-waste material after ER treatment in chloride matrix were packed in a 1.5 cm diameter glass column for the dissolution of precious metals Ag, Au, and Pd. Leaching of precious metals was performed with acidic thiourea using 0.2 M $\text{SC}(\text{NH}_2)_2$ in 0.5 M HCl solution. 0.1 M FeCl_3 was used as the oxidant. Precious metals extraction was also performed in

a sample of fresh non-magnetic e-waste fraction (no base metals extraction performed) to observe the precious metals extraction efficiency in untreated material.

2.5. REE recovery

Selective extraction of REE from the ferromagnetic fraction of cell phone materials was performed in deaerated 1 M H_2SO_4 for 72 hours. The NdFeB magnet, found in vibrators and speakers, can be dissolved spontaneously in acid media [5, 14]. Water acts as the oxidizing agent, being reduced to H_2 gas [5]. In this approach, the leaching solution was deaerated with N_2 gas to suppress the steel corrosion with dissolved O_2 . After the extraction, REEs were precipitated from the leachate as sulfate double salts ($\text{NaRE}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$) by adding 5 M NaOH up to a pH ca. 2. Samples of the leachate, before and after REE precipitation, were taken for elemental analysis. The precipitated double salt was converted to the REE hydroxide ($\text{RE}(\text{OH})_3$) by addition of 10% excess 2 M NaOH, and reaction for two hours at 70 °C.

2.6 Analysis

A Barnstead Turner SP-830 spectrophotometer at 500 nm was used to measure the Fe^{3+} concentration in the leaching solutions after complexation with sulfosalicylic acid [33]. The concentrations of metals and REEs in the digested and leaching solutions were measured using a Thermo Scientific iCAP Q inductive coupled plasma mass spectrometer (ICP-MS). Calibration was performed using commercially prepared standards (VGH and Spex). X-ray diffraction (XRD) spectroscopy in a Bruker D8 Advance diffractometer operated at 40 kV and 40 mA, with a cobalt (Co) target ($K = 1.78897\text{\AA}$) was used for the characterization of precipitates obtained during the metal extraction process and for the REE deposits. The XRD spectra were obtained

with a step size of $0.02^\circ 2\theta$. A 2010 ICDD (International Center for Diffraction Data) data base in the EVA software was used for compounds and phases identification.

3. Results and discussion

3.1 Packed bed extraction with Fe^{3+}

A breakthrough curve for the extraction of base metals was built to observe the oxidant reaction and the metals elution profiles through the packed column. Relevant process information, such as apparent reaction kinetics, and length of the mass transfer zone (MTZ), can be obtained from the breakthrough curve. Fig. 4 shows the breakthrough curves for the leaching of base metals with Fe^{3+} in the packed bed for both sulfate and chloride matrices. It can be observed that the breakthrough point (BTP) in the sulfate matrix occurs earlier than the BTP in the chloride matrix. As the flow and bed dimensions are the same in both matrices, the early BTP in the sulfate matrix reflects a wider MTZ (length where the concentration profile is developed) within the packed column. The length of the mass transfer zones for the sulfate and chloride matrices were calculated as 2.8cm and 2.5cm, respectively. This indicates a wider reaction zone for the extraction in the sulfate matrix. The slopes of the breakthrough curves confirm slightly higher reaction rates for the metal extraction in the chloride matrix.

The metal elution plots for the sulfate and chloride matrix are presented on Figs. 5a and b, respectively. The concentration of total iron in effluent solutions remains stable at 0.2 M during the extraction experiment except for the first two points, in which ca. 30% of the Fe present in the cell phone material was extracted. A calculation of the Fe^{3+} concentration from the composition of eluted metals provides a profile that overlaps with the experimental Fe^{3+} profiles, which confirms that Fe^{3+} rather than the proton ions (H^+) is the main oxidant in the extraction

process. The concentration of metals extracted from the material is dominated by Cu with other metals being significantly lower as expected from composition.

In order to view the metal dissolution more clearly, the extracted percentage shown in Figs. 5c and d scales the amount of each specie dissolved in each sample to the total amount of that specie extracted during the experiment. In the sulfate matrix the Cu elution concentration reaches a plateau ca. 0.08 M between 50 and 100 minutes just after more than 50 % of the total Sn has been extracted; while in the chloride matrix the maximum possible Cu concentration (0.1 M) is reached ca. 100 minutes after 99% of the Sn have been extracted. These phenomena can be explained by galvanic reactions proceeding in the leaching bed, where the more noble metals are reduced over less noble metals contributing to the oxidation of those. The differences in the Cu elution profiles suggest that galvanic reactions could be facilitated in the chloride media allowing a better separation of the metals coming out of the columns. Silver elution profile in sulfate matrix serves as another example of the galvanic process occurring in the extraction column. Ag reaches its maximum concentration in the effluent after more than 70% of the Cu has been removed. The low solubility of AgCl did not allow the quantification of the Ag elution profile in the chloride matrix. Therefore, galvanic reactions define not just the order in which the metals are eluted, but also the order in which the metals will be recovered through electrowinning. The difference in solubility of the Ag species formed in each one of the matrix can be used as an advantage for the selective recovery of pure silver.

Total base metals extraction efficiencies for the leaching experiment were Cu (97.5%, and 99.6%), Sn (43%, and 100%), Zn(97.1%, and 94.4%), Pb(6.41%, and 100 %) for the sulfate and chloride matrix, respectively. Extraction efficiencies below 60% were observed for Ni and Fe while the extraction efficiency of Ag in the sulfate media reached 78%.The low extraction

efficiency measured for Sn and Pb in sulfate media is due to the precipitation in the collected samples of SnO_2 [5] and PbSO_4 , respectively. XRD analysis of the precipitates (Fig. 6) confirmed the formation of SnO_2 and PbSO_4 . SnO_2 was detected in the precipitate formed in the leaching solutions after extraction, while PbSO_4 precipitated in the washing water used to clean the undissolved material after extraction. In the case of Ni, some of the Ni on the cellphone material may be coated with gold, preventing the Ni-oxidant contact.

3.2 Electrochemical recovery (ER) of base metals

After studying the behavior of the metal extraction process in the packed bed column, the metal extraction was integrated with the metals recovery and oxidant regeneration in the ER process shown in Fig. 3. Table 2 presents the results obtained with the ER process in both sulfate and chloride media. The use of a packed extraction column in series with the electrochemical reactor enhanced the mass transfer and extraction kinetic processes, allowing an increase of the S/L ratio from 0.17 g mL^{-1} to 0.23 g mL^{-1} when compared with a similar process reported in other work [28]. It was observed that the metal extraction in the HCl matrix proceeded almost twice as fast as that in H_2SO_4 matrix. Part of the processes' time difference could be explained by the extraction kinetics (corrosion rate) observed in the breakthrough curves (Fig. 4). Other operational factors that could contribute to the difference in processing time could be associated to the performance of the electrochemical cell as explained below.

Figs. 7 a and b show the Fe^{3+} concentration profiles obtained from the sulfate and chloride matrix ER experiments, respectively, for the column inlet (electrochemical reactor outlet), column outlet (electrochemical reactor inlet), and inside the electrochemical reactor (between anode and cathode). As can be observed in Fig. 7, under the same flow and applied current conditions, the ER process in chloride matrix provides a slightly higher Fe^{3+}

concentration leaving the electrochemical reactor than in the sulfate matrix (average 0.086 M vs. 0.075). This is likely explained by the effect of the oxidation of Sn^{2+} to Sn^{4+} in the sulfate media. While Sn^{4+} forms soluble complexes in the chloride matrix, it precipitates as SnO_2 in sulfate matrix[5]. Preliminary ER experiments performed on pure elements, showed a significant decrease in the amount of Fe^{3+} formed at the anode of the electrochemical cell after Sn leaching in the H_2SO_4 matrix. Additionally, an increase in the electrochemical cell voltage confirms that deposition of SnO_2 , on the anode, inhibits the oxidation of Fe^{2+} to Fe^{3+} . No effect was observed in the HCl matrix. This parallel anodic reaction in the sulfate matrix also explains the lower dissolution efficiency (Table 2) defined as the ratio between the total amount of metal extracted and the theoretical amount of metal that should have been leached by the Fe^{3+} fed to the column at the beginning of the process and the Fe^{3+} produced during the ER process assuming a 100% efficiency for the anodic reaction. Due to the facility to follow the extent of base metals extraction, by means of the conversion of Fe^{3+} through the column, the ER process can be used with different e-waste materials of diverse compositions.

It can also be observed, in Fig. 7, that the Fe^{3+} conversion through the column decreases due to the extinction of metals in the packed e-waste material. At the same time, some fraction of the current in the cathode is used for the reduction of Fe^{3+} to Fe^{2+} , affecting the Faraday efficiency of the deposition process and the specific power consumption. The effect of the reduction of unreacted oxidizer in the cathodic current efficiency (Faraday efficiency in Table 2) is more pronounced at longer processing times. Optimization of parameters and the use of process alternatives, such as using columns placed in a serial fashion are currently being studied to increase the process efficiency.

Figs. 8a and b show the composition of the metal deposits recovered during the ER processes and the extraction and recovery efficiencies of the processes, respectively. The recovery and extraction efficiencies were obtained based on the elemental composition of the deposits and undissolved cell phone material. Overall extraction and recovery efficiency of base metals is also presented in Table 2. As expected, the main element in the recovered deposit was Cu (over 90%), which reached an extraction efficiency ca. 99% for both extraction matrices. Higher Cu recovery efficiencies were reached in the sulfate matrix due to longer deposition time. Some of the base metals extracted still remained in the solution at the end of the process. Note that ER is designed to be a continuous process and thus overall recovery will be higher in practice. For the rest of the base metals, higher extraction and recovery efficiencies were observed from experiments using HCl. The low recovery rate observed for less noble metals, such as Sn, Pb, Ni, and Zn, follows the order of nobility of these metals and it is explained by the negative reduction potential of these elements. Higher cathode polarization, which will translate in higher energy consumption, would be required to increase the recovery efficiency. However, it is hypothesized that the build-up of concentration, in the leaching solution after several extraction cycles, along with metal co-deposition with the more noble metals will keep controllable levels of such metals in the leaching solution. This has already been observed in longer term experiments using the same solution with multiple extraction columns. In the case of Ag, the higher solubility of Ag_2SO_4 compared to AgCl explains the higher concentration of silver obtained in the deposited material in the H_2SO_4 matrix process. The lower dissolution of the silver salt in the chloride matrix process is advantageous to the selective extraction and recovery of silver in a following process.

3.3 Precious metals recovery

To evaluate the benefit of base metal recovery, extraction of precious metals with acid thiourea was performed. The redox reaction describing the dissolution of gold is presented in Equation 4 [34]. Since Fe^{3+} can also oxidize thiourea to form formamidine disulphide (Equation 5), which can further be irreversible oxidized to form sulfur [35], freshly prepared 10 mL 0.4 M thiourea in 0.5 M HCl and 10 mL 0.2 M FeCl_3 solutions were mixed just before entering the extraction column at an equal flow rate of 0.5 mL min^{-1} . The effluent solution was collected. After feeding the total amount of thiourea and oxidant to the column, the outlet solution was recirculated through the column for two hours. Silver and palladium can also be extracted in the acidic thiourea solution by means of the oxidation with Fe^{3+} and complexation with thiourea.

Table 3 shows the effect of the ER process in the extraction efficiencies of precious metals in which base metals extracted material (treated), and fresh (untreated) are subject to acid thiourea extraction under the same conditions. The precious metals extraction experiments described in this section have not been performed under optimized conditions. These experiments were performed with the aim to assess the effect of the ER process in the efficiency of precious metals extraction. The optimization of the precious metals extraction and recovery is out of the scope of this paper and may be subject of another research paper. Nevertheless, it is clear that the presence of base metals significantly affect the extraction efficiency of the precious metals and

that the ER process considerably facilitates the extraction of precious metals from electronic waste.

3.4 Rare earths (REE) extraction

At the end of the RE extraction experiment (72 h) the pH of the leaching solution was 3.52 but no deposit (Fe_2O_3) was observed. Elemental analysis of the leaching solution showed the presence of metals such as Fe (83% of the total mass of metals present on the leaching solution), Zn (5.5%), and Ni (0.3%). Traces of other base metals (Cu, Sn, and Pb) < 0.005% were also observed. It should be noted that most of the leached Fe should originate from the NdFeB magnets, which suggests the benefits of the anaerobic leaching process for an efficient and selective extraction of REE. The composition of REs out of the total amount of metals extracted in the leaching solution was Pr (1.5%), Nd (8.9%), and Dy (0.9%). An overall REs extraction efficiency of 72.8% was achieved with the anaerobic extraction process. The individual extraction efficiencies are presented in Fig. 8. Extraction efficiencies, which seem to be higher for lighter REs, could have been affected by the pH increase caused by the corrosion of Fe and Zn.

Before the precipitation of rare earths sulfate double salts ($\text{NaRE}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$) from the leaching solution, concentrated H_2SO_4 was added to decrease the pH to 0.5. 5 M NaOH was slowly added until a pH of 2 was reached. The formation of ($\text{NaRE}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$) was allowed for more than 4 hours before filtration. The formation of ($\text{NaRE}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$) was verified using XRD as presented in Fig. 10. Over 90% of the leached Pr, and Nd were recovered as ($\text{NaRE}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$) as shown in Fig. 9. Finally, the rare earths sulfate double salts were converted to $\text{RE}(\text{OH})_3$ as an intermediate product for future calcination to form rare earth oxides or re-dissolution for REE separation. Fig. 10 also shows the XRD patterns obtained for the final

RE(OH)₃ product. Based on the peak's intensity, no significant contamination of other elements (e.g. Fe) can be observed.

Total recovery efficiency of the process was over 80% for base metals, while the recovery of critical materials was 91.7%, 66.7%, and 54.9% for Pr, Nd, and Dy, respectively. The extraction efficiency of the precious metals was significantly enhanced by the previous removal of the base metals. Although it is still necessary to perform optimization in each one of the extraction and recovery steps, the general flow diagram shown in Fig. 1 can be used as a comprehensive approach for the recovery of value and critical elements

Conclusions

A comprehensive process for the recovery of critical and value metals from electronic waste has been developed. By separation of the magnetic and non-magnetic fractions of electronic waste, and the implementation of selective extraction/recovery processes, it was possible to obtain different value streams (base metals, precious metals and REE) from electronic waste. The implementation of a packed bed extraction column in the ER process, allowed an efficient extraction and recovery of base metals, by enhancing contact between the leaching solution and the e-waste. Galvanic reactions taking place inside the extraction column could permit the separation of base metals leaving the extraction column in the galvanic series order. Moreover, the use of the ER process, for precious metals enrichment in the e-waste, significantly reduces the chemical consumption and waste generation, as the oxidant and leaching solution used in the base metals extraction can be re-used to process new material. The significant increase in the precious metals extraction from the ER treated e-waste also contributes to a more efficient metal extraction process. Finally, the anaerobic extraction of REE from e-waste magnets has been

shown as an efficient and selective alternative for the recovery of critical materials from electronic waste.

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List of figures

Figure 1. Value distribution of metals and critical materials in a) cell phones and b) laptops.

Figure 2. Flow diagram for the comprehensive recovery of value and critical materials from electronic waste.

Figure 3. Experimental set-up for the electrochemical recycling of base metals. V1 and V2 represent the sample ports.

Figure 4. Breakthrough curves for the oxidant Fe^{3+} in the extraction of base metals from cell phone materials on a packed bed. BTP = break through point.

Figure 5. Elution curves for base metals extraction and percentage of the total extracted for each sample in 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ + 1 M H_2SO_4 a) and c) and 0.2 M FeCl_3 + 0.5 M HCl b) and d).

Fig. 6. XRD patterns of the precipitates obtained after metals extraction in H_2SO_4 matrix. PbSO_4 and SnO_2 were identified using the software EVA and a 2010 ICDD data base.

Fig. 7. Concentration profiles for Fe^{3+} for the column inlet ($\blacktriangle$), column outlet ($\blacksquare$) and inside the electrochemical reactor ($\blacklozenge$) for the ER processes at 0.5 A and flow rate of 3 mL min^{-1} in a) 0.1 M $\text{Fe}_2(\text{SO}_4)_3$ + 1 M H_2SO_4 , and b) 0.2 M FeCl_3 + 0.5 M HCl . Decrease on the measured concentrations for a) at 26, and 49 hr, and b) at 25 hr is due to the replenishment of water to replace water lost to evaporation.

Fig. 8. a) Composition of the metal deposited through the ER process. b) ER process recovery and extraction efficiency.

Fig. 9. Extraction and recovery efficiency of REE from ferromagnetic fraction of cell phone waste. Recovery efficiency was calculated based on the amount of REE precipitated from the leaching solution.

Fig.e 10. XRD patterns of the precipitated sodium rare earth sulfate double salt extracted from the ferromagnetic fraction of cellphone materials, before and after conversion to $\text{RE}(\text{OH})_3$. Peaks were identified using the software EVA and a 2010 ICDD data base.

Fig. 1. Diaz, Lister, Parkman, and Clark

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Fig. 9. Diaz, Lister, Parkman, and Clark

Fig. 10. Diaz, Lister, Parkman, and Clark

Table 1 Composition of value and critical material in cell phones

Metal	wt% Cell phone Measured^a	wt % non-magnetic fraction^a	wt % Ferromagnetic fraction^a	wt % Cell phone literature
Cu	22.62	19.38	2.68	16 ¹³
Sn	3.075	1.95	-	0.61 ¹
Zn	-	1.40	0.60	0.59 ¹
Pb	-	0.17	0.006	0.3 ⁹
Fe	-	0.94	78.78	5 ⁹
Ni	13.49	0.82	6.84	0.1 ⁹
Ag	0.26	0.3	-	0.3 ¹²
Au	0.053	0.06	-	0.03 ¹²
Pd	0.0273	0.01	-	0.01 ¹²
Pr	0.0095	-	0.11	0.01 ¹²
Nd	0.0818	-	0.90	0.05 ¹²
Dy	0.0137	-	0.10	-

^a Experimental values obtained after digestion in aqua regia and/or 50% HNO₃

Table 2. Results for the ER process in H₂SO₄ and HCl matrices

	0.2 M FeCl₃ / 0.5 HCl	0.2 M Fe₂(SO₄)₃ / 1 M H₂SO₄
Process time (h)	35	52
Extraction efficiency⁺	93%	89%
Dissolution Efficiency	77%	55%
Deposit Weight (g)	13.35	13.75
Recovery Efficiency⁺	77%	79%
Faraday Efficiency	67.7%	47.1%
Power consumption (kWh/kg_{deposit})	3.45	5.00

⁺ Overall efficiency based on (Cu, Sn, Ni, Fe, Zn, Pb)

Table 3. Precious metals extraction efficiencies with acid thiourea leaching

	Un-treated Material	Treated Material
% Ag Extracted	0.04	20.72
% Au Extracted	1.92	54.81
% Pd Extracted	0.79	29.6