

PROCESS DEVELOPMENT FOR THE RECOVERY OF CRITICAL MATERIALS FROM ELECTRONIC WASTE

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PROCESS DEVELOPMENT FOR THE RECOVERY OF CRITICAL MATERIALS FROM ELECTRONIC WASTE

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ABSTRACT

As electronic technology continues to evolve there is a growing need to develop processes which recover valuable material from antiquated technology. This need follows from the environmental challenges associated with the recovery of raw materials and fast growing generation of electronic waste. Although present in small quantities in electronic devices, the availability of raw materials such as rare earths and precious metals becomes critical for the production of high tech electronic devices and the development of green technologies (i.e. wind turbines, electric motors, and solar panels). Therefore, the proper recycling and processing of electronic waste presents an opportunity to stabilize the market of critical materials, providing a proper disposal and treatment of a hazardous waste stream. This paper describes the development and techno-economic assessment of a comprehensive process for the recovery of value and critical materials from electronic waste. This hydrometallurgical scheme aims to selectively recover several value streams (base metals, precious metals, and rare earths) present in electronic waste. The economic feasibility for the recovery of rare earths from electronic waste is mostly driven by the efficient recovery of precious metals, such as Au and Pd (ca. 80 % of the total recoverable value). Rare earth elements contained in magnets (speakers, vibrators, and hard disk storage) can be recovered as a mixture of rare earth oxides which can later be reduced to the production of new magnets.

KEYWORDS

Rare earths, precious metals, electronic waste, recycling

INTRODUCTION

The fast evolution of electronic devices, which eventually become electronic waste (e-waste), provides an important resource which could be leveraged to produce a sustainable supply chain for scarce and critical materials (Baldé, Wang, Kuehr, & Huisman, 2015; Dodson, Hunt, Parker, Yang, & Clark, 2012). The diversity and high concentrations of elements, which exceed those found in mineral ores (Akçil et al., 2015), suggest an economic benefit from the recovery of different value streams. Extensive research efforts are currently under development for the recovery of precious metals (Ag, Pd, and Au) and base metals (Cu, Sn, Pb, Ni, and Zn) not just due to the economic value of such elements, but also motivated by the need of a proper handling and disposal of e-waste that mitigates its potential environmental risks (Sun, Xiao, Sietsma, Agterhuis, & Yang, 2015).

Electronic waste is classified in six different categories that includes: temperature exchange equipment, screens, lamps, large equipment, small equipment, and small IT (Baldé et al., 2015). Among them, small IT waste is showing the most accelerated growth, driven by rapid technology developments and fashion (Geyer & Doctori Blass, 2010). Small IT, which include mobile devices such as cell phones, personal computers, and tablets represent close to 10% of the total amount of e-waste generated in 2014 (Baldé et al., 2015). It can be estimated that almost 707 kt of small IT e-waste was generated in the United States.

Besides precious and base metals, small IT waste also contains rare earth elements, such as Nd, Pr, Dy, and Gd, which are considered critical for the development of renewable energy technologies by the U.S. Department of Energy (DOE, 2011). Although present in small quantities in speakers, hard disk drives, and vibrators (Lister, Wang, & Anderko, 2014; Tukker, 2014), the volume of generated small IT waste shows a significant opportunity for the stabilization of the REE markets, currently controlled by China (Tukker, 2014), by means of recycling. However, there are technological challenges for the development of a sustainable process to recover critical material from electronic waste. The compact nature of the small IT waste complicates the access and recovery of elements (Lister et al., 2014), and the low recycle rates of e-waste, which in the U.S. does not exceed 30% (Coalition, 2014), impacts the availability and price of the feedstock.

Current metal extraction technologies from electronic waste include pyrometallurgical, hydrometallurgical, or combinations of both process (Hagelukens, 2006). Nevertheless, several challenges exist for the cost-effective recovery of value and critical materials from electronic waste, such as high energy consumption, chemical requirements, and waste generation (Khaliq, Rhamdhani, Brooks, & Masood, 2014). On the other hand, based on the composition and distribution of value within the e-waste, close to 80% of the total recovery value falls over the precious metals (Diaz, Lister, Parkman, & Clark, 2015), which are less than 1 % of the total content. Thus over 90 % of the total content, which are less noble metals, have limited contribution to the total recoverable value in e-waste while consuming most of the chemicals required for the extraction in a hydrometallurgical process. As an alternative, we have proposed a comprehensive process for the recovery of value and critical materials which is based in an electrochemical-hydrometallurgical mediated approach (Diaz et al., 2015; Lister et al., 2014). An electrochemical recovery process (ER) was then proposed using a weak oxidant (Fe^{3+}), which can be generated at the anode of an electrochemical cell and re-generated after the extraction of base metals. Extracted metals are electrowon in the cathode of the electrochemical cell. The comprehensive process for the recovery of critical and value materials has been designed to operate at normal temperatures (ca. 25°C) and has been described in a previous work (Diaz et al., 2015). The comprehensive recovery of value metals includes comminution and separation of the ferromagnetic fraction for the extraction of REE, while the non-magnetic fraction follows the sequential extraction of base metals. A process flow diagram is shown in Figure 1.

This paper reports a preliminary techno-economic assessment of the comprehensive recovery process of (critical and value metals). A base of 10 t/day of cell phone material has been taken to assess the processing of small IT waste, representative of a regional processing facility. A brief description of the

extraction steps of the process is presented as well as the analysis of the ER process effect in operational costs and economic feasibility of the process.

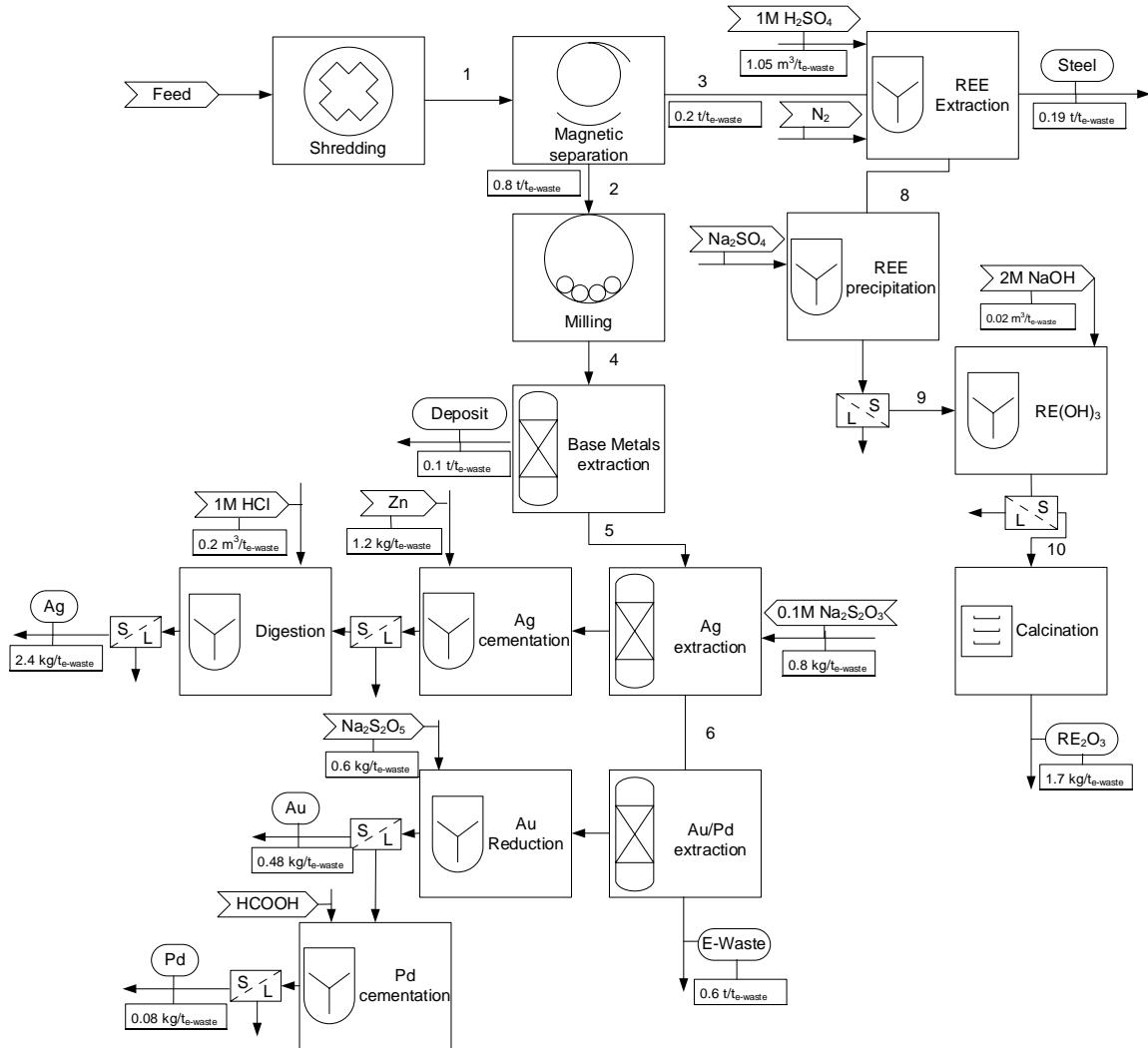


Figure 1 – Process flow diagram for the comprehensive recovery process of critical and value materials from electronic waste

BASE AND PRECIOUS METALS EXTRACTION

Electrochemical Recovery (ER) Process

In the ER process (Diaz et al., 2015; Lister et al., 2014) the milled non-magnetic fraction of small IT waste is packed in extraction columns. The leaching solution, composed of $FeCl_2$ and HCl , leaves an electrochemical reactor after contact with the anode of the electrochemical cell where the oxidant (Fe^{3+}) is generated. The leaching solution, with the oxidant, is fed to the bottom of one of the packed columns to oxidize the base metals without attacking Au and Pd. While the oxidant can oxidize several metals, galvanic processes define the metal ions exiting the column such that the least noble metals are first to leave. The metal rich solution leaving the columns is directed back to the cathode side of the electrochemical cell where the extracted material is electrowon. A series of three columns (Figure 2) have been tested with the aim of keeping the mass transfer zone (Reaction zone) inside the packed columns.

This allows a complete reduction of the oxidant, enhancing the current efficiency towards the deposition of the extracted metals. After complete extraction of base metals is achieved in the first column, this column can be replaced by a fresh column, which will take the last position in the series allowing for a semi-continuous operation. A parametric optimization of the flow rate, applied current density, and iron concentration was performed for the ER process reducing the energy consumption to as low as 1.94 kWh/kg of deposit (Diaz, Clark, & Lister, 2016).

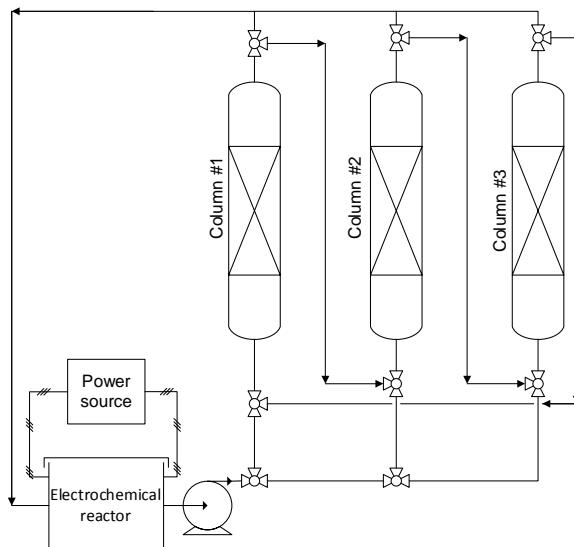


Figure 2 – Process description of the electrochemical recovery (ER) process for base metals from electronic waste

Silver can also be oxidized by Fe^{3+} in chloride media to produce AgCl . Taking advantage of the low solubility of AgCl , most of the Ag is kept inside the extraction column and can be extracted in a separate stage by complexation with $\text{Na}_2\text{S}_2\text{O}_3$. Elemental analysis of the recovered base metals deposit presented in Figure 3a show that a small fraction of Ag is deposited with the base metals. However based on the initial composition of Ag on small IT e-waste reported previously (Diaz et al., 2015) and the production rate of deposit, this represents only 13% of the total available Ag.

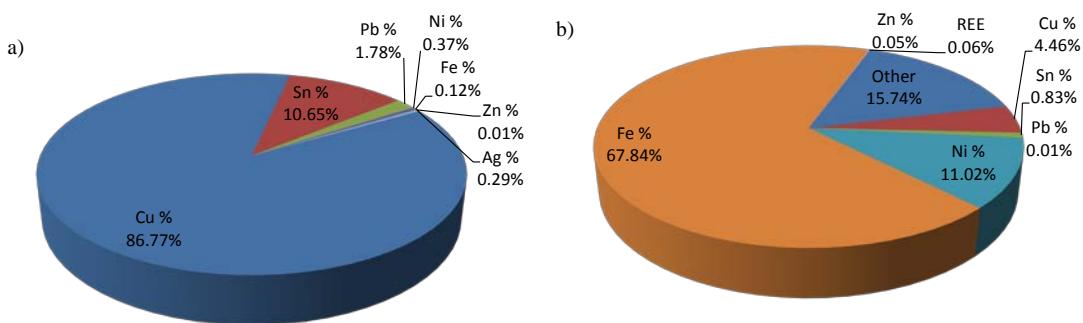


Figure 3 – Composition of a) recovered base metals, and b) steel stream from electronic waste

The composition of metals in the deposit shown in Figure 3a also indicates that it can be appraised as bronze or leaded tin bronze (lead is now mostly engineered out of electronics). This characteristic is going to be used to assign a revenue value for the base metals extraction process.

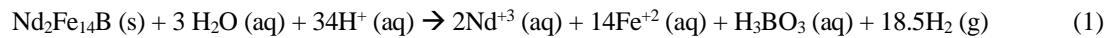
Precious Metals Extraction

As formerly mentioned, silver can be recovered from the extraction columns after complexation with $\text{Na}_2\text{S}_2\text{O}_3$. Experimental tests have been performed using a 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ solution with a liquid to solid ratio of 1:1. After extraction, Ag is cemented on Zn powder and the cemented silver is digested with 1 M HCl to obtain pure Ag. Recovery efficiencies have reached over 80% after considering the amount of Ag lost in the base metals extraction. Reagent requirements for the process based on the amount of e-waste material process are presented in Figure 1.

The process for Au and Pd extraction and recovery is still under development. For the techno economic analysis, a 100% recovery efficiency is assumed based on promising results obtained with the extraction chemistry reported elsewhere (Cheng et al., 2013). As Au and Pd represent the highest revenue value of the metal recovery process, a sensitivity analysis based on the extraction efficiencies is included in the techno economic assessment.

RARE EARTH EXTRACTION

Extraction of REE has been performed on the ferromagnetic fraction of small IT e-waste as reported elsewhere (Diaz et al., 2015). The REE extraction takes place in an anaerobic environment where water acts as the oxidant based on Equation 1. The suppression of oxygen in the leaching environment should suppress Fe corrosion as described in Equation 2.



Preliminary studies in 1M H_2SO_4 leaching solution also reported in our previous work (Diaz et al., 2015) show that an overall REE extraction efficiency of 73% was achieved. Extraction percentages of the different metals present in the ferromagnetic stream are presented in Figure 4. As can be observed Fe extraction is low compared with the REEs. The amount of Fe extracted is close in proportion to what is expected from $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets, which indicates that most of the Fe extracted comes from the magnet alloy.

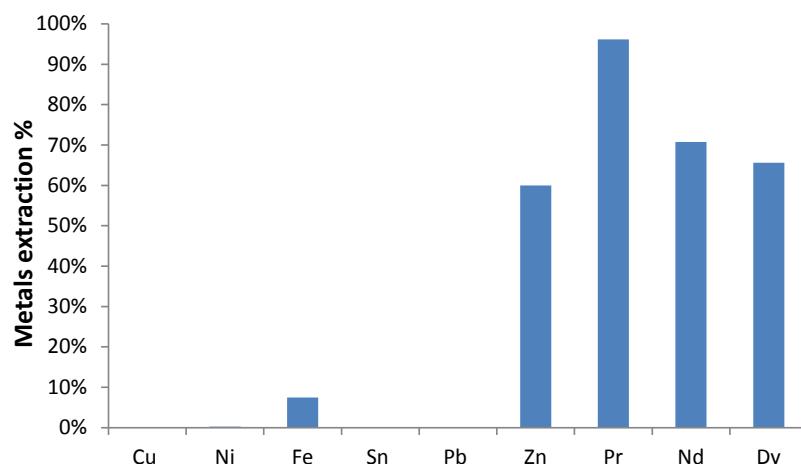


Figure 4 – Extraction rates of metals from the ferromagnetic fraction after REE anaerobic extraction process

After REE extraction the composition of the ferromagnetic fraction is as presented in Figure 3b where other elements refer to plastics and fibreglass. The final ferromagnetic stream is appraised as scrap steel for the techno economic analysis. REE in the leachate can be recovered after precipitation as $(\text{NaRE}(\text{SO}_4)_2 \bullet x\text{H}_2\text{O}$ with the addition of Na_2SO_4 (D Abreu & Morais, 2010). Recovery efficiencies as high as 95% have been achieved for Pr and Nd, while Dy recovery efficiency was close to 40% (Diaz et al., 2015). In the final stages $(\text{NaRE}(\text{SO}_4)_2 \bullet x\text{H}_2\text{O}$ are converted to $\text{RE}(\text{OH})_3$ by means of reaction with stoichiometric amounts of 2M NaOH at 70°C, and finally to RE_2O_3 after calcination at 500°C for three hours. Chemical requirements per ton of small IT e-waste are shown in Figure 1.

TECHNO ECONOMIC CALCULATIONS

The techno economical assessment of the comprehensive recovery of metals based on the ER process was performed for the process flow diagram shown on Figure 1. A complete hydrometallurgical alternative (Figure 5) was also evaluated to compare the profitability of both processes. A facility processing 10 t/day of small IT e-waste was assumed for the calculations.

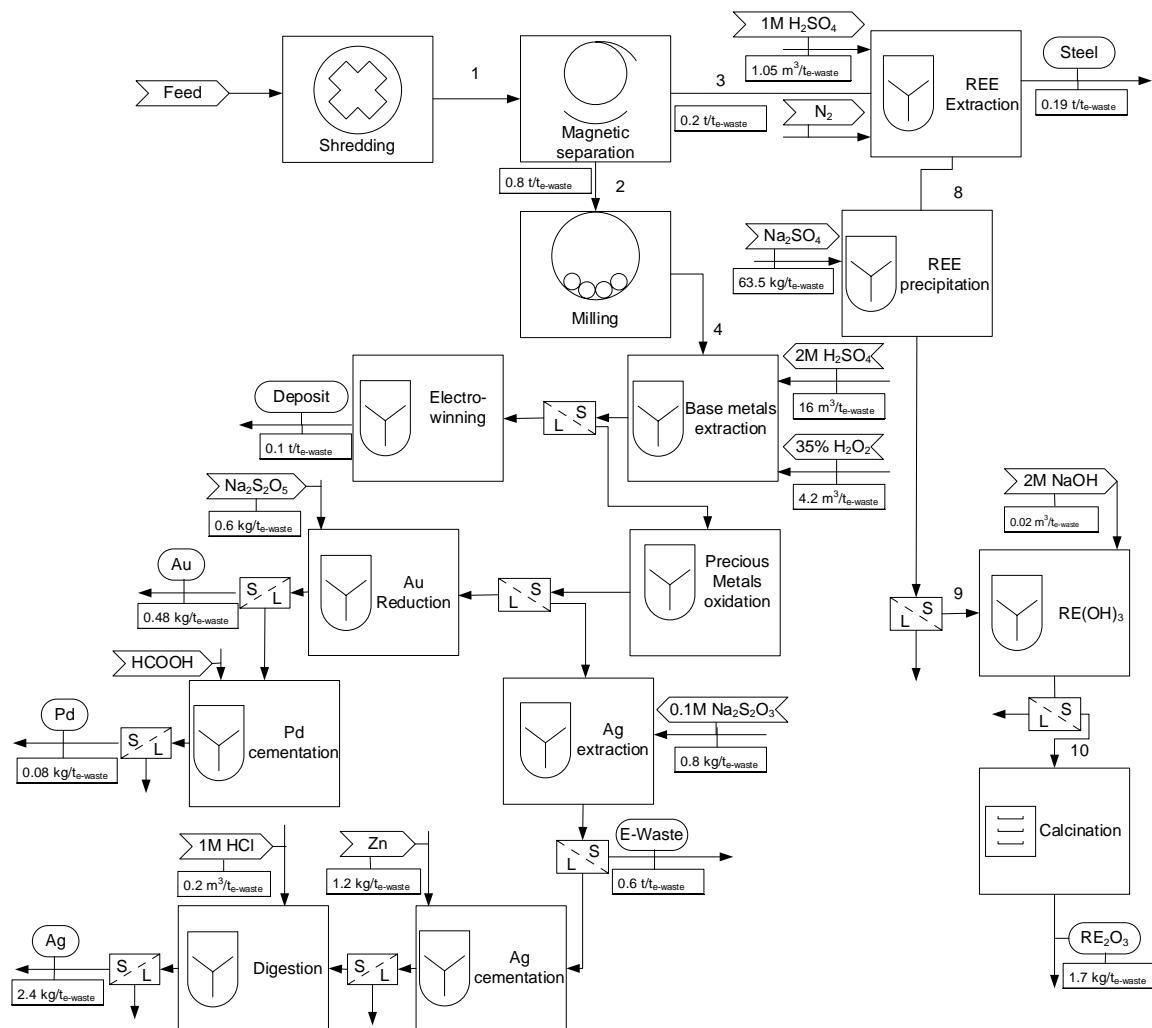


Figure 5 – Process flow diagram for a completely hydrometallurgical recovery process of critical and value materials from electronic waste

Mass and energy balances generated from bench scale experiments and from results previously reported on (Behnamfard, Salarirad, & Veglio, 2013; Cheng et al., 2013; Diaz et al., 2015) were used for the calculation of equipment specifications and the operating costs for the two process alternatives. Energy consumptions for pumps, heat exchangers, and agitation tanks were calculated using heuristic rules (Peters & Timmerhaus, 1991; Smith, 2005; Walas, 1990). Pressure drop of the fluid through the packed beds were calculated based on the bulk density of the milled cell phone material (0.827 kg/L) and the particle density obtained using the ASTM D845 method (1.43 kg/L).

Equipment cost estimation was performed based on cost-capacity charts, and applying proportions estimating methods (Peters & Timmerhaus, 1991; Smith, 2005). The price upgrade was performed using available indexes ("Financial Calculator," 2015). Total capital costs include multiplying factors for installation, piping, instrumentation, and a 10% contingency cost. The estimated capital costs of the two processes are shown in Table 1. Calculated prices are expected with an accuracy of $\pm 30\%$ (Smith, 2005). A summary of the main assumptions considered to obtain the cash flow of the processes for the economical assessment are shown in Table 2.

Table 1 – Estimated Cost of equipment

	ER process	Hydrometallurgical process
	Cost \$/t _{e-waste}	Cost \$/t _{e-waste}
Shredder	4.91	4.91
Mill	7.80	7.80
Electrolyzer	2.78	2.78
Columns	10.52	
Batch reactor 1		97.57
Batch reactor PM extraction		18.97
Reactor Ag cementation and digestion	13.55	13.55
Reactor Au/Pd precipitation	9.76	9.76
Vacuum filter	66.63	66.63
Vacuum pump 10 kW	4.87	4.87
Pump ER	1.82	
Pump PM	1.08	
Balance pumps	2.61	2.61
REE Extraction system	10.52	10.52
REE precipitation tank	16.26	16.26
REE(OH)3 tank	2.71	2.71
Oven	13.33	13.33
Equipment cost	169.16	272.27
Total capital cost	405.98	653.46

Table 2 – Plant assumptions for the techno-economic assessment

Assumption	Assumed value
Plant financing debt/equity	100% Capital investments + 40 % First year operational costs
Term of debt financing	5 years
Interest for debt financing	10% annually
Evaluation period for IRR	5 years
Depreciation term	7 years
Income tax rate	35%
Inventory	10% Reagents and feedstock
Startup time	6 months
Revenue and costs during startup	Revenue= 50% of normal Operational costs = 50 % normal Administrative costs = 100% of normal
Operating time	300 days a year (7200 hours)

TECHNO ECONOMIC ASSESSMENT RESULTS AND DISCUSSION

A simple comparison of the process flow diagrams on Figures 1 and 5 shows that the implementation of the ER process allows for the removal of several separation steps as the material can be treated through the whole process while being kept inside the extraction columns. However, a better assessment of both processes for economic decisions can be obtained from the comparison of the cumulative cash flow during the project's evaluation period. Figure 6 shows the cash flow patterns for both projects during the five year period assuming a 100% recovery of Au and Pd. Similar cash flows after the first year of operation are a result of the estimated amount of borrowed money for the hydrometallurgical project being almost 1.4 times the amount of money borrowed for the ER based process (\$8,567,675 vs. \$6,084,769).

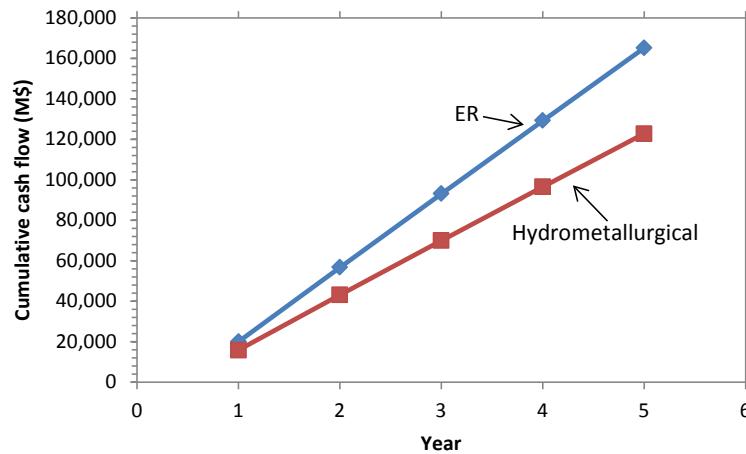


Figure 6 – Estimated cash flow patterns for the ER based and hydrometallurgical processes

To calculate the cash flow shown in Figure 6, the revenue streams for both processes are the same (\$63,321.385/year) from which 85% and 7% correspond to Au and Pd streams, respectively. The contribution of the REE to the total revenue is just 0.53% (\$336,900/year), which support that the financial

viability of the REE extractions depends on the recovery of precious metals, mainly gold. The differences in the cash flows for both processes observed in Figure 6 are mostly due to the production cost of each one of the processes. Figure 7 shows a graphical comparison of the main operational costs for the ER based and the hydrometallurgical processes. A comparison of the capital costs is also included in Figure 7. Significant reductions in energy, water and capital costs were observed as anticipated. However, one of the most important advantages of the ER based process is that the extraction chemicals are kept within the cycle loop, and no addition of chemicals, beyond that necessary to start the process, is required. This significantly reduces the chemical consumption of the overall process, therefore lowering the operational costs.

Other important conclusions can be extracted from the analysis of the operational cost distributions presented in the inserts of Figure 7. It is observed that for the ER based process the value of the feedstock, which was estimated as \$7.79/kg ("SCRAPREGISTER," 2015) represent almost 90% of the total operational costs. Thus an efficient e-waste collection chain can significantly reduce costs. A cost incentive can be used to encourage the proper recycling of e-waste. However, high incentives can significantly affect the economic performance of the recovery process.

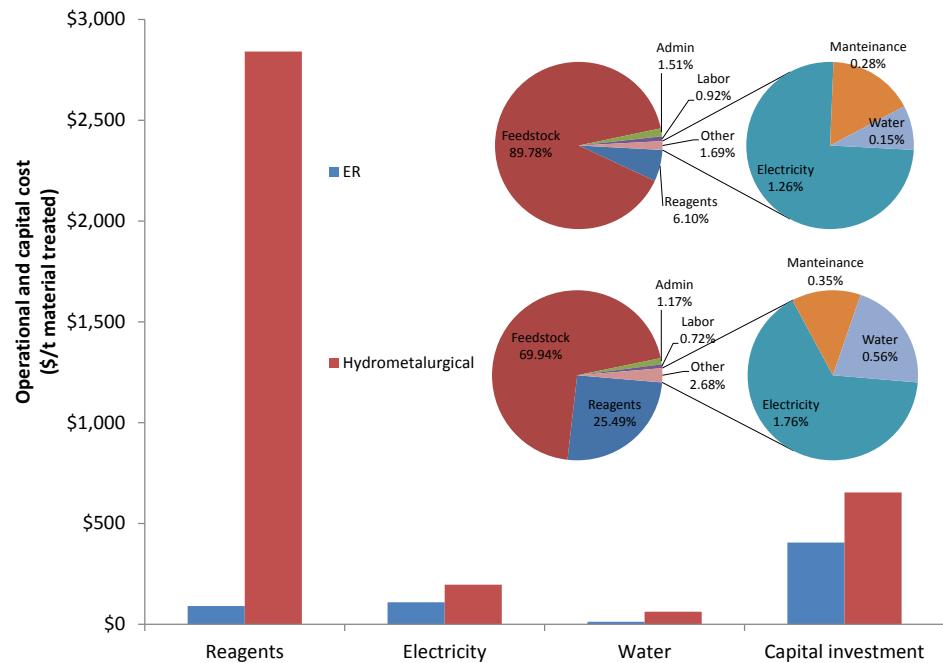


Figure 7 – Comparison of operational and capital costs for the ER based and hydrometallurgical processes.
Inserts distribution of total operational cost for the ER based a) and hydrometallurgical process b)

Sensitivity Analysis

A sensitivity analysis was performed recognizing the dependence of the precious metals streams in the process revenues, and the feedstock price in the operational costs. Figure 8 a and b show the effect of the Au/Pd recovery efficiencies and feedstock cost, respectively, in the internal rate of return (IRR) of the ER based process for the five years evaluation period. Results show that on average a 60% Au recovery efficiency is required to break even during the five year period. Pd recovery efficiency is significant at Au recovery concentration below or equal to 60%. In the last case at least a 60% Pd recovery is required to break even during the five year period. Effect of the recovery efficiencies were estimated at the quoted price of e-waste.

The second sensitivity analysis for the feedstock cost assumes an scenario where 60% recovery efficiencies are achieved for both Au and Pd (Figure 8b). It is clearly observed that a feedstock price reduction as low as 10% can increase the IRR from 10% to 86.7% within the first five years.

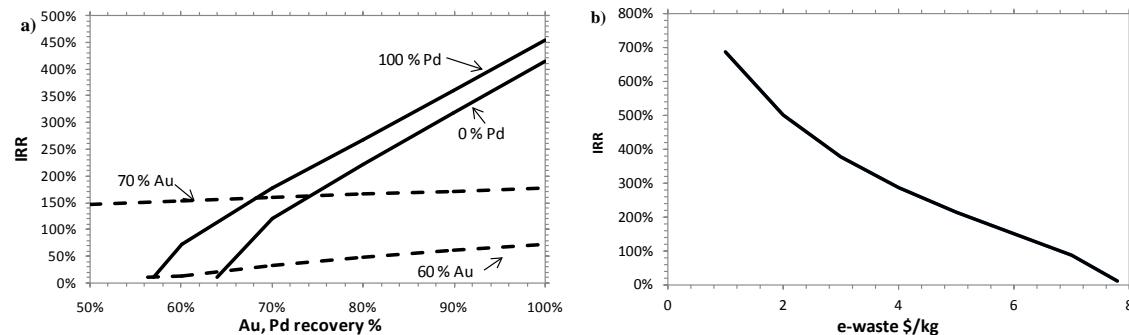


Figure 8 - Sensitivity analysis for the IRR for the recovery process based on recovery efficiencies for the precious metals revenue streams a), and the cost of the electronic waste b)

CONCLUSIONS

A techno-economic analysis that established the economic potential of the comprehensive recovery of value and critical materials from electronic waste was performed. The beneficial impact of an efficient process, centered on the electrochemical recovery of base metals, was demonstrated. Finally a sensitivity analysis provides a framework to define minimum recovery scopes in the precious metal streams and in the development of more efficient e-waste collection strategies.

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REFERENCES

- Akcil, A., Erust, C., Gahan, C. S., Ozgun, M., Sahin, M., & Tuncuk, A. (2015). Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixivants – A review. *Waste Management*, 45, 258-271.
- Baldé, C. P., Wang, F., Kuehr, R., & Huisman, J. (2015). The global e-waste monitor – 2014: United Nations University, IAS – SCYCLE,.
- Behnamfard, A., Salarirad, M. M., & Veglio, F. (2013). Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation. *Waste Management*, 33(11), 2354-2363.
- Cheng, Y., Shen, S., Zhang, J., Chen, S., Xiong, L., & Liu, J. (2013). Fast and Effective Gold Leaching from a Desulfurized Gold Ore Using Acidic Sodium Chlorate Solution at Low Temperature. *Industrial & engineering chemistry research*, 52(47), 16622-16629. doi: 10.1021/ie4026852
- Coalition, E. T. (2014). Facts and Figures on E-Waste and Recycling. Retrieved December 10 2015, from http://www.electronicstakeback.com/wp-content/uploads/Facts_and_Figures_on_EWaste_and_Recycling.pdf
- D'Abreu, R., & Morais, C. A. (2010). Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide. *Minerals Engineering*, 23(6), 536-540.

- Diaz, L. A., Clark, G., & Lister, T. E. (2016). Optimization of the Electrochemical Recovery of Metals Using Response Surface Methodology. (*Submitted*).
- Diaz, L. A., Lister, T. E., Parkman, J., & Clark, G. (2016). Comprehensive process for the recovery of value and critical materials from electronic waste. *Journal of Cleaner Production*, (*Accepted manuscript*). DOI: [10.1016/j.jclepro.2016.03.061](https://doi.org/10.1016/j.jclepro.2016.03.061)
- Dodson, J. R., Hunt, A. J., Parker, H. L., Yang, Y., & Clark, J. H. (2012). Elemental sustainability: Towards the total recovery of scarce metals. *Chemical Engineering and Processing: Process Intensification*, 51, 69-78.
- DOE. (2011). Critical materials strategy. Report PI-0009. http://energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf. U.S. Department of Energy.
- Financial Calculator. (2015). Retrieved December 11 2015, from <http://hydrogen.pnl.gov/tools/financial-calculator?canprint=false>
- Geyer, R., & Doctori Blass, V. (2010). The economics of cell phone reuse and recycling. *The International Journal of Advanced Manufacturing Technology*, 47(5-8), 515-525. doi: 10.1007/s00170-009-2228-z
- Hageluken, C. (2006, 8-11 May 2006). *Improving metal returns and eco-efficiency in electronics recycling - a holistic approach for interface optimisation between pre-processing and integrated metals smelting and refining*. Paper presented at the Electronics and the Environment, 2006. Proceedings of the 2006 IEEE International Symposium on.
- Khaliq, A., Rhamdhani, M. A., Brooks, G., & Masood, S. (2014). Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. *Resources*, 3(1), 152-179.
- Lister, T. E., Wang, P., & Anderko, A. (2014). Recovery of critical and value metals from mobile electronics enabled by electrochemical processing. *Hydrometallurgy*, 149, 228-237.
- Peters, M. S., & Timmerhaus, K. D. (1991). *Plant design and economics for chemical engineers*. New York: McGraw-Hill
- SCRAPREGISTER. (2015). Retrieved November 15 2015, from <http://www.scrapregister.com/scrap-prices/united-states/260>
- Smith, R. M. (2005). *Chemical process: design and integration*. Chichester, UK: John Wiley & Sons.
- Sun, Z., Xiao, Y., Sietsma, J., Agterhuis, H., & Yang, Y. (2015). A Cleaner Process for Selective Recovery of Valuable Metals from Electronic Waste of Complex Mixtures of End-of-Life Electronic Products. *Environmental science & technology*, 49(13), 7981-7988. doi: 10.1021/acs.est.5b01023
- Tukker, A. (2014). Rare Earth Elements Supply Restrictions: Market Failures, Not Scarcity, Hamper Their Current Use in High-Tech Applications. *Environmental science & technology*, 48(17), 9973-9974. doi: 10.1021/es503548f
- Walas, S. M. (1990). *Chemical Process Equipment: Selection and Design*. Newton, MA, USA: Gulf Professional Publishing.