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SELECTIVE RECYCLING OF METALS FROM SECONDARY RESOURCES

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Selective recycling of metals from secondary resources

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“The only way to do great work is to love what you do. If you haven't found it yet, keep looking. Don't settle. As with all matters of the heart, you'll know when you find it.”

Steve Jobs

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Maryam

Abstract

Metals are vital yet non-renewable raw materials in today's society. Either due to its natural scarcity or massive consumption, certain metals are increasingly becoming a potential development bottleneck for entire economies. Paired with pertinent environmental concerns, recovery of metals from wastes, i.e., recycling has become a strategically important step into a more circular economy. However, the recycling process itself needs to be environmentally sustainable. This thesis, therefore, was designed to explore and optimize recycling processes of several wastes, which possess significant amounts of economically relevant metals such as zinc (Zn), manganese (Mn), lanthanum (La) and platinum (Pt).

Three types of wastes were tested: spent alkaline batteries (containing Mn and Zn); spent fluid cracking catalysts (FCC) (rich in La) and finally petroleum refining spent catalysts (with Pt). A state of the art was created, highlighting current limitations in existing recycling techniques for these wastes, which provided guidelines and ideas and how to brake such limitations and improve upon current knowledge in the field.

In order to improve traditionally used recovery techniques, all studies followed the same basic principles: to test the influence of auxiliary energies (either ultrasound or microwave) and to create a flowsheet that is as complete and yet as simple as possible, with the least amount of reagent and time used.

For the recycling of alkaline batteries, several optimization tests were performed, testing different times, and concentration of acid, etc. It was concluded, however, that the best option would be a two stage ultrasound- and microwave-assisted leaching with sulphuric acid (and added glucose as a reductant for the second stage) followed by either selective oxidative precipitation of Mn or solvent extraction to dissolve and separate the two main metals – Zn and Mn, but also capable of recovering carbon black as co-product. The resulting process was significantly faster and more efficient than traditional methods, capable of producing end products with sufficient quality for reuse in alkaline batteries.

For the recycling of spent FCC, a similar thought-process was applied as before: after extensive optimization studies in which several variables were tested, it was found that a single stage microwave-assisted acid leaching with HCl followed by a two selective (alkaline followed by oxalate) precipitation stage was the best solution to recovery La as main final product at sufficient purity along with aluminum hydroxide and zeolite as potential co-products.

Finally, for the petroleum reforming catalyst, after an initial pre-treatment, it was found that the best combination of processes was a single stage microwave-assisted leaching with both HCl and hydrogen peroxide (H_2O_2) followed by ion exchange to isolate Pt from Al and Fe. This process successfully obtains high pure Pt for complete recovery in a simplified and faster version of traditional recovery methods.

Despite the significant differences between the three types of tested wastes, auxiliary energies such as ultrasound but especially microwave is a great tool to enhance the leaching process regardless of the situation, making it faster but also enabling the use of lower concentrations and overall quantities of harmful chemicals such as strong acids as well as contributing to an overall lower energy consumption, leading to several environmental and economic benefits. On the other hand, separation methods such as precipitation, solvent extraction and ion exchange, can and should be optimized to the specific characteristics of the waste to be recycled and computer models provide a great assistance in streamlining the process design.

This thesis provides three process flowsheets for a complete and environment friendly recycling of three important wastes, contributing to a more circular economy whilst simultaneously providing economic benefits at the operational level.

Keywords: spent alkaline batteries, spent fluid cracking catalyst, spent petroleum reforming catalyst, auxiliary energies, ultrasound, microwave, leaching, metal selective recovery, metal purification, solvent extraction, ion exchange.

Resumo

Na sociedade atual, os metais são matérias-primas vitais, não renováveis. Devido à sua escassez natural e consumo maciço, o acesso a esta matérias primas corre o risco de provocar graves constrangimentos no desenvolvimento de várias economias à escala global. Em paralelo com as preocupações ambientais pertinentes que se colocam, a recuperação de metais a partir de resíduos, ou seja, a sua reciclagem é estrategicamente relevante para uma economia mais circular. No entanto, o próprio processo de reciclagem precisa de ser ambientalmente sustentável. Deste modo, esta Tese foi delineada para explorar e otimizar processos de reciclagem de vários resíduos que possuem quantidades significativas de metais economicamente relevantes, como o zinco (Zn), manganês (Mn), lantânio (La) e platina (Pt).

Nesta Tese, foram utilizados três tipos de resíduos: pilhas alcalinas esgotadas (contendo Mn e Zn); catalisadores usados no *cracking* de hidrocarbonetos na indústria petroquímica (ricos em La) e finalmente catalisadores usados na refinação do petróleo (ricos Pt). Após uma revisão do estado da arte, que permitiu atualizar o conhecimento nas técnicas de reciclagem existentes para esses resíduos e destacar as limitações atuais das mesmas, foi possível desenhar novas estratégias de reciclagem que permitem ultrapassar essas limitações.

Com vista a melhorar a eficácia darecuperação de metais dos resíduos relativamente às técnicas tradicionalmente usadas, todos os estudos seguiram os mesmos princípios básicos: testar a influência de energias auxiliares (ultra-sons e microondas) no processo de extração dos metais dos vários resíduos e criar procedimentos simples que minimizassem o consumo de energia, reagentes e tempo utilizados. Para a reciclagem de baterias alcalinas esgotadas, foram realizados vários testes de otimização, testando diferentes tempos e concentração de ácido, etc. Concluiu-se, que a melhor opção seria uma lixiviação assistida em dois estágios (ultra-sons seguida de micro-ondas) com ácido sulfúrico (e adição de glucose, como redutor, para o segundo estágio) seguido de precipitação oxidativa seletiva de Mn ou extração porsolventes para separação dos dois metais (Zn e Mn). Foi também possível recuperar o carbono como um sub-produto.

O processo resultante é significativamente mais rápido e eficiente que os métodos tradicionais, capaz de produzir produtos finais com qualidade suficiente para a sua reutilização na produção de novas pilhas alcalinas.

Para a reciclagem dos catalisadores usados no *cracking*, foi delineado um procedimento semelhante ao aplicado anteriormente: após extensos estudos de otimização nos quais várias variáveis foram testadas. Verificou-se que uma única etapa de lixiviação ácida assistida por microondas com HCl seguida por duas etapas de precipitação seletiva (precipitação alcalina seguida de precipitação com oxalato) foi a melhor solução para a recuperação de La como produto final principal com pureza suficiente. Adicionalmente, hidróxido de alumínio e zeólito foram também recuperados como sub-produtos.

Finalmente, para o catalisador usado na refinação do petróleo rico em Pt, após um pré-tratamento inicial, verificou-se que a melhor combinação de processos seria uma lixiviação única assistida por microondas com HCl e péroxido de hidrogénio (H_2O_2) seguida de separação por permuta iónica para purificar a Pt do Al e Fe. Este processo permite recuperar totalmente a Pt com elevada pureza através da utilização de um procedimento muito mais simples e rápido do que os tradicionalmente descritos.

Apesar das diferenças significativas entre os três tipos de resíduos estudados, a utilização de energias auxiliares, como é o caso do ultra-sons e em particular do microondas, revelaram-se uma ferramenta excelente no processo de lixiviação na medida em que permitiram tornar o processo de extração muito mais rápido assim como reduzir aconcentração dos reagentes usados e consumo de energia, o que se reflete em enormes benefícios ambientais e económicos. Por outro lado, os processos separativos, como a precipitação, extração por solventes e resinas de troca iónica, foram otimizados para as características específicas de cada metal a ser reciclado de cada resíduo, o que associado à especiação química por modelação computacional permitiu contribuirpara a otimização do design do processo.

Esta tese fornece três novos fluxogramas de processo para uma reciclagem completa e ambientalmente mais amigáveldos principais metais existentes em três resíduos importantes, contribuindo para uma economia mais circular e, ao mesmo tempo, proporcionando benefícios económicos.

Palavras-chave: baterias alcalinas esgotadas, catalisadores usados no *cracking* de hidrocarbonetos, catalisadores usados na refinação do petróleo, energias auxiliares, ultra-sons, microondas, lixiviação, recuperação seletiva de metais, purificação de metais, extração porsolventes, resinas de troca iónica.

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Abbreviations

AAS-FA	Atomic absorption spectroscopy with flame atomization
BV	Bed volume
CMD	Chemical manganese dioxide
EAS	Emission atomic spectroscopy
EMD	Electrolytic manganese dioxide
EU	European Union
FCC	Fluid cracking catalyst
ICP-MS	Inductively coupled plasma mass spectrometry
LOD	Limit of detection
L/S	Liquid-solid ratio
O/A	Organic- aqueous ratio
PGMs	Platinum group metals
PTFE	Polytetrafluoroethylene
RPM	Rotation per minutes
SN	Separation Number
wt.	Weight
XRD	X-ray diffraction
XRF	X-ray fluorescence

List of publications:

The present thesis is based on the following papers:

- **Sadeghi, S.M.**, Vanpeteghem, G., Neto, I.F.F., Soares, H.M.V.M., 2017. Selective leaching of Zn from spent alkaline batteries using environmentally friendly approaches. Waste Manag. 60, 696–705. https://doi.org/10.1016/j.wasman.2016.12.002
- **Sadeghi, S.M.**, Jesus, J.M.O.M., Soares, H.M.V.M., 2018. Recycling spent fluid cracking catalysts for rare earth metal recovery - a review. Recycl. Sustain. Dev. 11, 43–52. https://doi.org/10.5937/ror1801043M
- **Sadeghi, S.M.**, Ferreira, C.M.H., Soares, H.M.V.M., 2019. Evaluation of two-step processes for the selective recovery of Mn from a rich Mn residue. Miner. Eng. 130, 148–155. https://doi.org/10.1016/j.mineng.2018.10.014
- **Sadeghi, S.M.**, Jesus, J.M.O.M., Pinto, E., Almeida, A.A., Soares, H.M.V.M.. A simple, efficient and selective process for recycling La (and Al) from fluid cracking catalysts using an environmental-friendly strategy (submitted for publication).
- **Sadeghi, S.M.**, Jesus, J.M.O.M., Soares, H.M.V.M.. A critical updated review of the hydrometallurgical routes for recycling zinc and manganese from spent zinc-based batteries (submitted for publication).
- **Sadeghi, S.M.**, Soares, H.M.V.M.. Pt recovery from spent reforming petroleum catalyst- a comprehensive and environment friendly approach (in preparation).

Chapter 1

Introduction

1.1. Relevance and aims

Raw materials form the base of any economy. Beyond their use as food sources, raw materials drive industrial productivity and enable the very existing and maintenance of modern society with its technological wonders. Throughout the recent decades, an immense increase in demand and extraction of metals occurred and metal extraction has increased by 133 % worldwide due to the economic growth, particularly, starting in 2002, as a consequence of the acceleration of demands of emerging economies, such as China and India.

Metals, along with other raw materials categories such fossil fuel carriers, are also non-renewable. Although metals are not exhausted upon use, most uses of these metals in the world economy can be considered dissipative (Gordon et al., 2006). Moreover, for certain metals, their properties can also cause a shortage in the future, i.e. some metals cannot easily and simply be replaced by other metals or raw materials in vital processes. This can create situations in which a more abundant metal becomes more essential than a rare one due to this uniqueness in function. Another very specific aspect regarding metal scarcity is its worldwide distribution.

Combining this aspect of regional scarcity with total scarcity, substitutability, losses, recyclability, etc., since 2011, the European Union (EU) identifies a list of critical raw materials (which are considered to have reached or exceeded threshold for both economic importance and supply) and updates this list periodically depending on changes of market and production of these raw materials. According to the most recent list of critical materials (EU Commission, 2018), lanthanum (La) and platinum (Pt) are considered critical metals and, among others applications, are used in the production of catalysts. Even though zinc (Zn) and manganese (Mn) are not identified as critical materials, nowadays, there are reports of scarcity of these two metals, namely for battery production.

In the context of the circular economy, wastes are considered as resources and, so, should be used in an efficient and sustainable way for producing new products (such as new batteries, catalysts, etc).

Based on these motivations, the main goal of this thesis was to develop new, simple and environmental-friendly processes to recycle the metals mentioned above from secondary sources: (i) La from spent fluid cracking catalysts (FCCs); (ii) Pt from spent petroleum reforming catalysts; (iii) Mn and Zn from spent alkaline batteries.

1.2. Organization of the Thesis

This thesis consists out of 6 chapters.

Chapter 1 delineates the framework of this thesis where the focus lies on the importance of the metals as raw material and the main goals of this Thesis. Furthermore, the organization of this Thesis is included in this chapter.

In chapter 2, the 'State of the Art' is outlined and mainly focusses on theoretical concepts and bibliographic reviews about the main topics studied throughout this thesis. This chapter is divided into subchapters with three different topics. The first subchapter describes the possible methods for recovering of metals from spent alkaline batteries. The second subchapter handles different techniques of metal leaching and several recovery methods for spent FCCs and the third subchapter explains common methods for Pt extraction from spent Pt catalyst.

Chapter 3 includes the methods, the materials and reagents used to perform the experiments for recovery of valuable metals from spent alkaline batteries. Furthermore, the evaluation of experimental results is described, and respective results are discussed and concluded.

Chapter 4 describe the processes performed for extraction and recover of valuable metals, mainly La from spent FCC and the results of the experiments are shown, discussed and concluded.

Chapter 5 deals with the possible methods as well as with the methods and materials applied during the experimental part for recovering precious metal (Pt) from spent platinum group metal (PGM) catalyst and the results of tested conditions are presented, discussed and compared with the literature and finally concluded.

At last, Chapter 6, ‘Conclusions’ compromises the main conclusions of the thesis based on the optimized results.

References

EU Commission, 2018. Commission Staff Working Document. Report on Critical Raw Materials and the Circular Economy. Brussels. https://ec.europa.eu/docsroom/documents/27348

Gordon, R.B.., Bertram, M.., Graedel, T.E., 2006. Metal stocks and sustainability. Proc. Natl. Acad. Sci. 103, 1209–1214. https://doi.org/10.1073/pnas.0509498103

Chapter 2

State of the art

2.1. Metals as raw materials

Raw materials can be divided into large sub groups, with varying possible designations, including: industrial minerals (a large range of non-metallic minerals, such as phosphate rock), wood, metals, fossil energy carriers, construction minerals (such as sand, gravel, natural crushed stone, etc.) and biomass (includes food and feed) (OECD, 2013). The extraction percentage of each of these groups worldwide is represented in Fig. 2.1.:

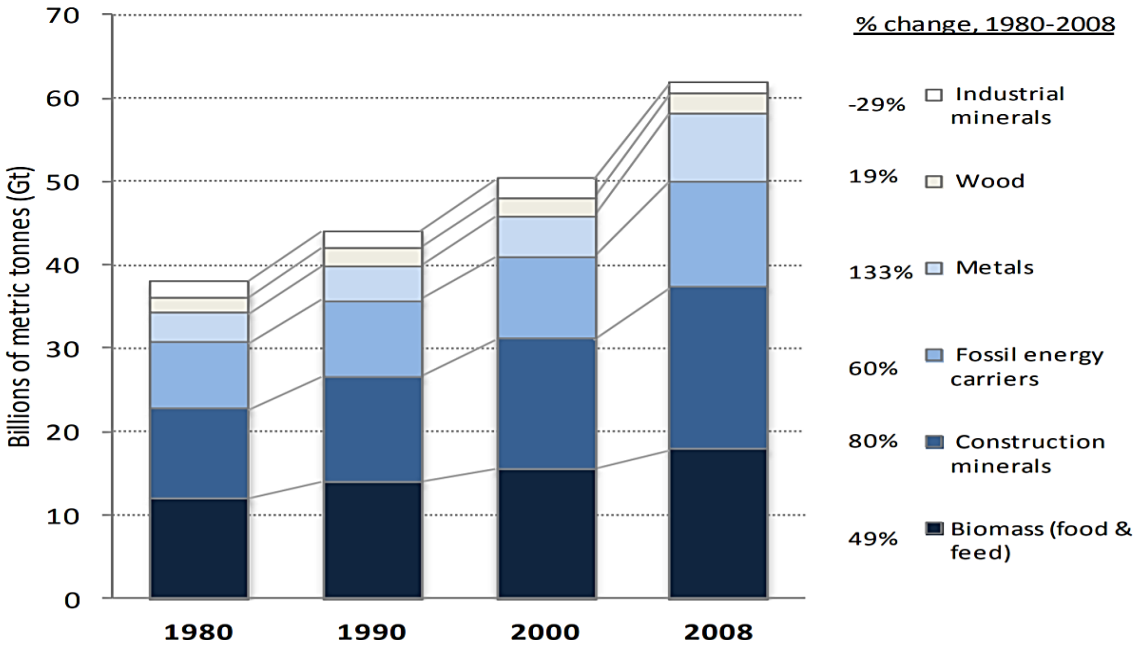

Fig. 2.1. *Worldwide raw material extraction (OECD, 2013).*

It worth to mention that, these values only account for extracted and used materials. However, unused extracted materials are extremely proper in the case of metals, with more than a 50 % increase to the values denoted in Fig. 2.1, if they were to be considered.

This large volume of unused metals is due to mining overburden and tailings (OECD, 2013), both of which can still contain appreciable amounts of metal but not economically feasible and therefore lost from the cycle. Another important key issue is resource productivity, i.e., the use

of less material per unit of gross domestic product (GDP), which is closely associated with another concept, decoupling material use (and, at times, associated environmental impacts) from economic growth (UNEP, 2016). In these two aspects, despite recent developments, the World in general and the EU in particular still have not achieved sustainable improvements. This problem can be explained, in part, by lack of efficient methodologies and poor to null exploration of secondary sources and wastes to increase productivity. Other losses include metals already in landfills for which recovery is technically complex and economically extremely disadvantageous (Gordon et al., 2006).

This finite aspect to metals as a whole leads to several drawbacks: even a metal that is theoretically not rare can, through its wide use, may become scarce in the future with increased price, which impacts economy and, in excessive uses, leads to complete depletion (Backman, 2008). Several different types of assumptions are required to estimate reserves, and depletion are often debated and controversial. However, Table 2.1 denoted an example of such an estimation.

In Table 2.1, it can be seen that certain predictions did not occur, but this information provided a relative index of scarcity which combines metal reserves to metal use. In other words, Table 2.1 shows which metals are more likely to become scarce in nearer future than others regardless of their natural abundance.

The authors of this particular study (Backman, 2008) also highlighted the most presumably future scenario. They suggested that the physical depletion of metals does not occur (fixed stock paradigm) but certain metals will become too expensive to be extracted (opportunity of cost paradigm).

Table 2.1. *Life index (in years) of certain metals (Backman, 2008).*

Metal	Symbol	Life index (year)	Metal	Symbol	Life index (year)
Aluminum	Al	820	Nickel	Ni	51
Copper	Cu	31	Platinum group metal	PGM	150
Iron	Fe	72	Silver	Ag	14
Lead	Pb	10	Tin	Sn	24
Magnesium	Mg	4500	Uranium	U	96
Manganese	Mn	12	Zinc	Zn	22

Whether this aspect is sufficient to cause a future spike in metal price or even physical scarcity remains highly debated. It is possible (or even likely) that the tradeoff worth it, i.e., metal diminution in favor of reduced air pollution and climate change impacts. This perspective clearly highlights the importance of a proper management of metal reserves worldwide (EU Commission, 2018).

Another issue to be considered is that metals are not always extracted executively; in fact, a significant amount of scarce metals is a by-product of mining another more common metal (Fig. 2.2). This particular aspect can present several opportunities to improve or expand synergetic production and efficiency and applies both mining as shall be exemplified in this thesis.

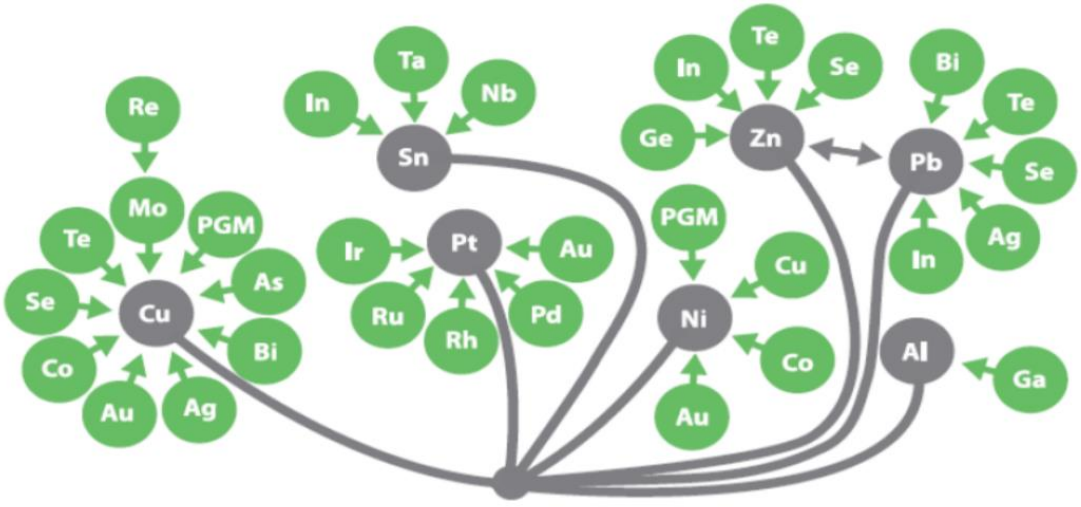

Fig. 2.2. *Sources of certain raw materials (green) mined in association to carrier metals (grey) (EU Commission, 2018).*

Finally, another very specific aspect regarding metal scarcity is its worldwide distribution. It means that a resource can be abundant in the earth crust but limited distribution and concentrated in a few countries leading to geopolitical issues. The quantity of REEs in China (Fig. 2.3.A) as compared to the rest of the world is one of the most well-known examples of this fact. Even though, despite its name, REEs are not particularly scarce in total quantities.

Fig. 2.3.B indicates that China is by far the biggest producer (as of 2018) and also the country with the biggest reserves. This brings about almost complete external dependency for several countries, including the EU.

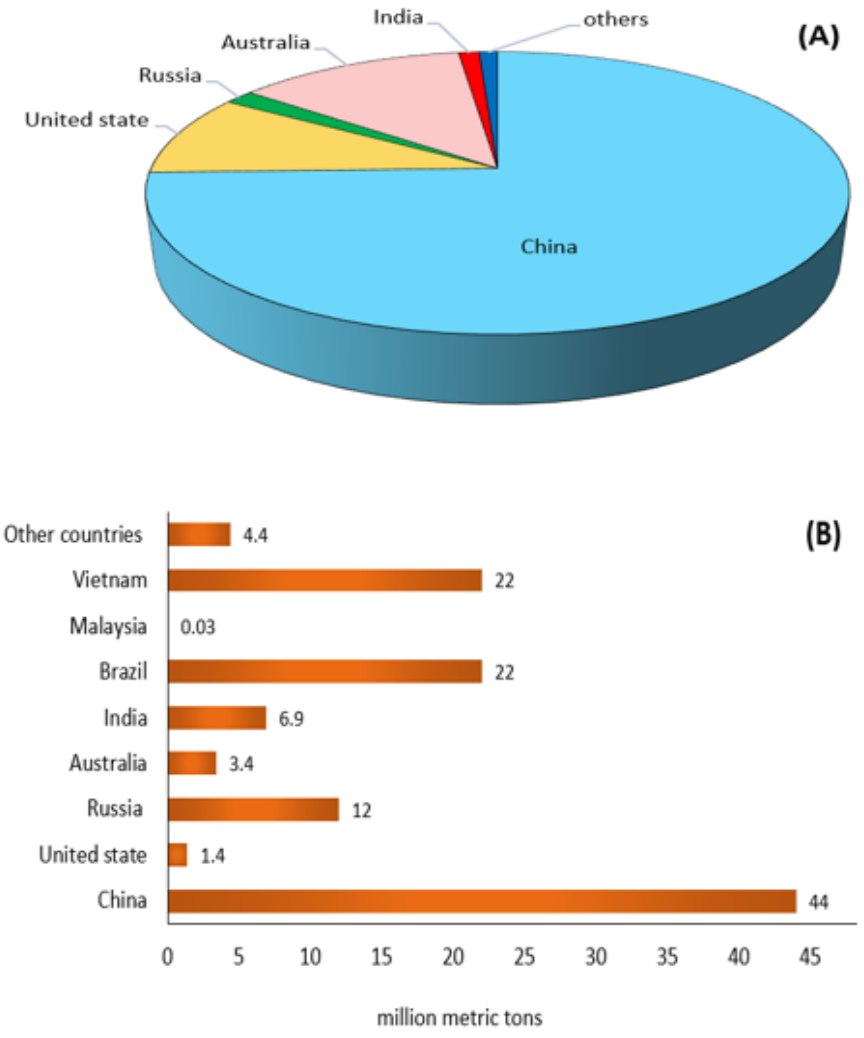

Fig. 2.3. *REEs production* ***(A)*** *and estimated reserves (million metric tons)* ***(B)*** *per country in 2018 (USGS. 2019a).*

Partly as a result of this and combining this aspect of regionals scarcity with total scarcity, substitutability, losses, recyclability, etc. the concept of critical raw material was developed and applied as a policy in the EU. These critical raw materials are limited to non-energy, non-agricultural raw materials and include metals and construction materials. They are often associated to high tech products and emerging innovations with special attention to the needs of the renewable energy sector. A complete list of critical raw materials as of 2017 include:

antimony (Sb), fluorspar, heavy rare earth elements (HREEs), light rare earth elements (LREEs), PGMs, phosphorus, baryte, gallium (Ga), Mg, scandium (Sc), beryllium (Be), germanium (Ge), natural graphite, silicon metal (Si), bismuth (Bi), hafnium (Hf), natural rubber, tantalum (Ta), borate, helium (He), niobium (Nb), tungsten (W), cobalt (Co), vanadium (V), coking coal, indium (In) and phosphate rock (EU Commission, 2018).

2.2. Economic importance of studied metals

In order to clearly characterize the economic interest and even geopolitical of the metals intended for recycling in this thesis, some basic economic concepts require to be introduced:

Relative supply risk - A calculated index by the Royal Society of Chemistry UK, which indicates, on a scale from 1 (very low risk) to 10 (very high risk), the risk to the supply of the analyzed metal. It integrates several parameters such as crustal abundance, reserve distribution and production concentration among others.

Substitutability - The availability of suitable concentration among others.

Production concentration -The percentage produced by the top country.

Reserve concentration -The percentage of the reserves located in the country with the largest reserves.

This section will focus on characterizing the five metals subject of study in this thesis by economic characterization followed by, when available, graphic details on its end-use, among other considerations. These metals are being presented in order of relevance to this thesis.

2.2.1. Zinc

Zn is the fourth most common consumed metals in the world after Fe, Al and Cu and the 24th most abundant element in the Earth's crust with crustal abundance of 72 ppm and recycling rate

of > 30 % (RSC, 2019a). It is found in several ores, mainly in silicate (calamine) and zinc sulfide (zinc blende) and is obtained from concentrating and roasting those ores and reduction to elemental Zn by pyrometallurgy. Identified Zn resources of the world are about 1.9 billion metric tons and Zn world mine production was estimated to be 13.2 million metric tons in 2017 with 5 % of increase from that of 2016 (USGS, 2018). World's biggest Zn mine production and reserve holders are presented in Fig. 2.4. As it is shown China is the top producer with 39 % of total mine production and Australia is the top reserve holder with 28 % of total reserves concentration among the other countries (USGS, 2018).

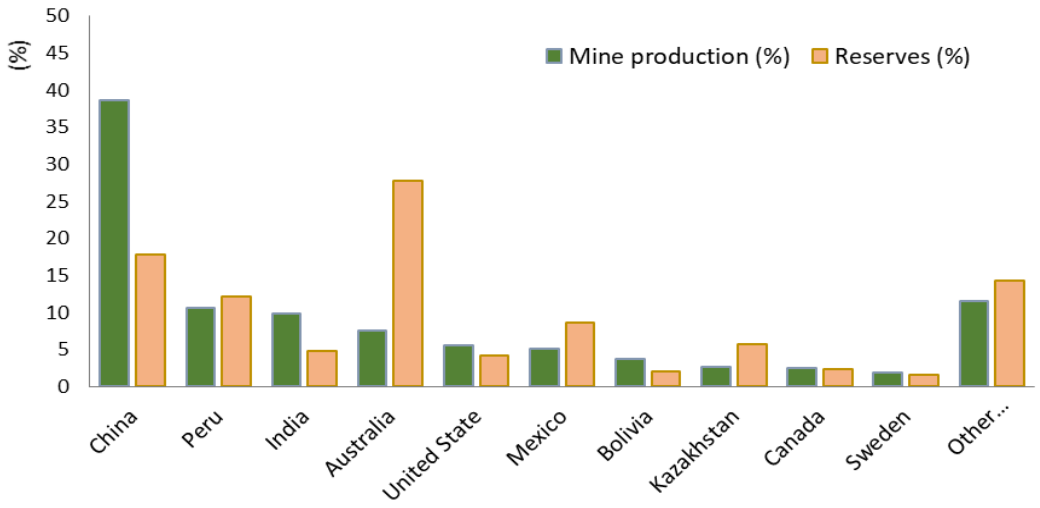

Fig. 2.4. *Zn major producers and reserve holders (by country) (USGS, 2018).*

Zn price had a great increase in 2007 and 2008, with a maximum value of 4500 USD per metric ton, but more recently (2018-2019) the price was around 3000-3500 USD per metric ton (Infomine, 2019a).

The main characteristics of the Zn market revolve around its low crustal abundance and its low substitutability for the uses that are currently attributed to this metal (Fig. 2.5). As it can be seen in Fig. 2.5, Zn is mostly used for galvanizing (60 %) following by die casting (15 %) and brass/bronze production (14 %) (Zinc One, 2018). Although the supply risk of Zn is not high (4.8),

its variety and competing uses in several aspects such as battery industry may lead to higher supply risk in the future.

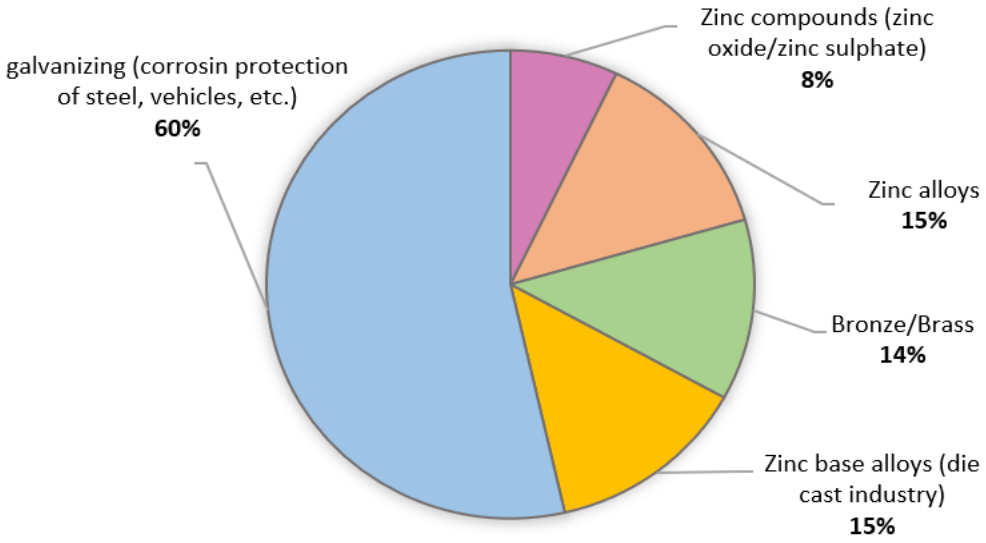

Fig. 2.5. *Zn uses distribution (Zinc One, 2018).*

2.2.2. Manganese

Mn is the fifth most abundant metals in the earth's crust (774 ppm), normally occurring as minerals, such as rhodochroiste (manganese carbonate) or pyrolusite (manganese dioxide). This metal is obtained either by electrolysis of manganese sulfate or by the reduction of its oxide form using sodium (Na), Mg or Al (RSC, 2019b). The top mining areas for Mn production is in South Africa (33 %), as it is shown in Fig. 2.6. As it can be seen in Fig. 2.6, South Africa (29 %), Ukraine (21 %) and Brazil (18 %) are the 3 top reserve holders (USGS, 2018). Despite its high abundancy, the relative supply risk for Mn is high (5.7), which might be, in part, connected to its widespread use in the steel industry (USGS, 2019b), and other chemicals such as those used as a colorant for automobile undercoat paints, bricks, frits, glass, textiles, and tiles (USGS, 2014).

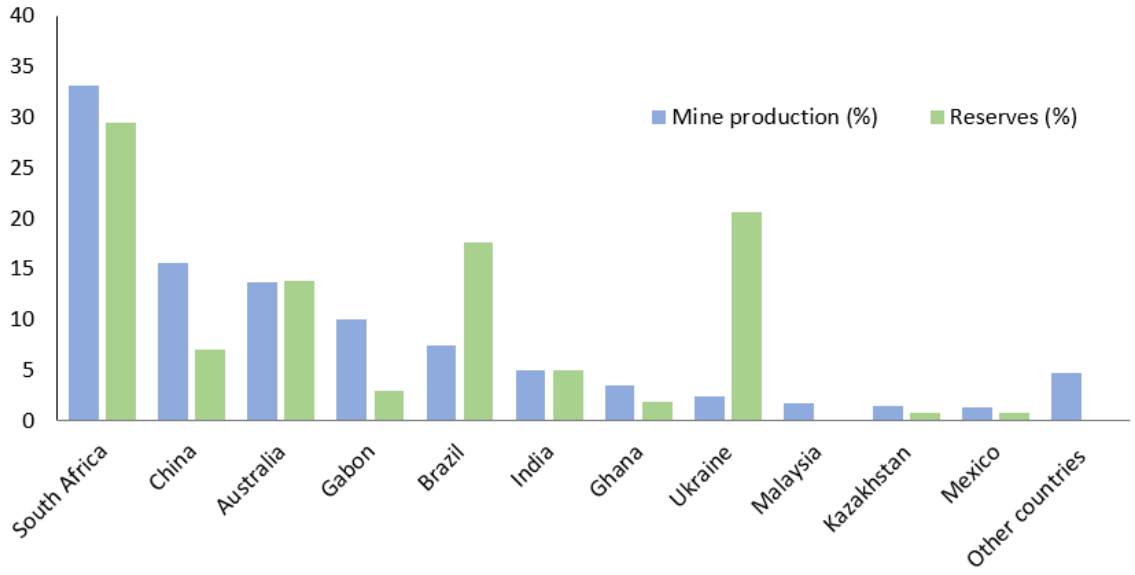

Fig. 2.6. *Mn major producers and reserve holders (by country)* (USGS, 2018).

As can be seen in Fig. 2.7, as much as 90 % of Mn consumption, in the US (as well as globally) is accounted for by the steel industry. Important nonmetallurgical uses include battery cathodes, soft ferrites used in electronics, micronutrients found in fertilizers and animal feed, water treatment. Fig. 2.7 also denotes a recent increase in Mn overall consumption in the US and particularly for batteries and alloys after a period of lower overall consumption. The end use of steel is likely linked to peaks in construction use in the US which have recently subsided.

In more than last 10 years, Mn price has been varying between 1300 to 2000 USD per metric ton but the price jumped to 4600 and 3500 USD per metric ton at 2008 and 2011, respectively (Metalary, 2019).

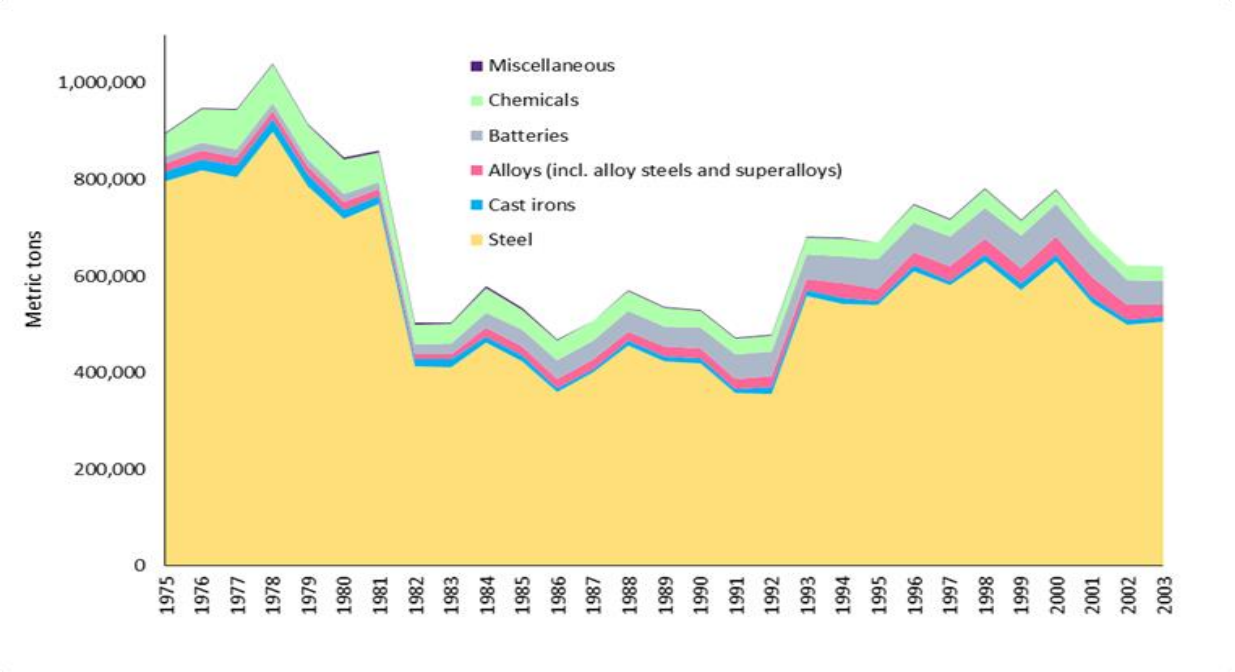

Fig. 2.7. *Mn end-use statistics in the US between 1975-2003 (USGS, 2019b).*

2.2.3. Lanthanum

The REEs represent 17 different elements, which have similar physical and chemical properties. These 15 elements (Lanthanides) coupled with scandium (Sc) and yttrium (Y) are split into 2 groups of LREEs and HREEs (Connelly et al., 2005). Among LREEs, La with an average crustal abundance of 0.3 ppm, occurs mainly in minerals, such as bastnaesite (38 % La) or monazite (25 % La). To properly isolate this metal from these minerals, a combination of techniques that include solvent extraction and ion exchange are required (RSC, 2019c). In the case of La, despite its high substitutability, the relative supply risk is almost the maximum value (9.5). This is due to a combination of factors: its low crustal abundance, its geographic concentration in terms of production and reserves, mainly China and low recycling rate (<10 %). In this aspect, as is the case for every other rare metal, new deposits in other areas should be procured and explored but also, in the short term, an increase of its recycling rate would also alleviate this high supply risk.

In 2008, a total of 38700 metric tons of La was used in a variety of applications (Fig. 2.8.). FCC represents the majority of La end-use at 46 %, followed by batteries at 16 % (Goonan, 2011).

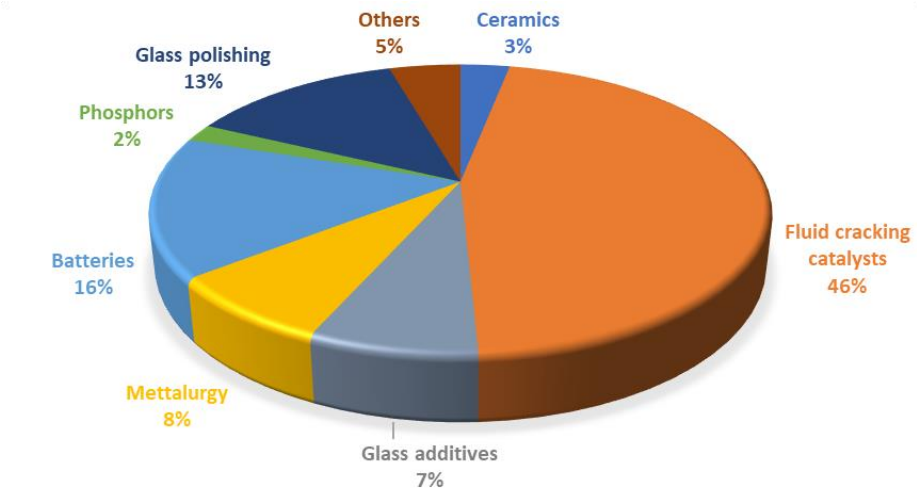

Fig. 2.8. *Distribution of La_2O_3 consumption by market sector in 2008 (Goonan, 2011).*

The price for La is strongly associated to lanthanum oxide (La_2O_3) as it is the most commonly used form, which peaked in 2011 at almost 99000 USD per metric ton but has since being reduced to 7000 USD per metric ton in 2019 and it is predicted to further decrease slightly (Statista, 2019a).

2.2.4. Platinum

Pt can mainly be found in alluvial deposits or as platinum sulphide (cooperite mineral) in South Africa. To a lesser extent, some Pt can also be obtained as a by-product from Ni and Cu refining (RSC, 2019d).

Similar to La, but not so high, Pt also has high relative supply risk (7.6), and even lower crustal abundance (3.7×10^{-5} ppm). The top producer and reserve holder in the World are South Africa, which increases supply risk. Pt is mostly used for auto catalysts (37%), followed by jewellery (26 %) as it shown in Fig. 2.9. (Statista, 2019b).

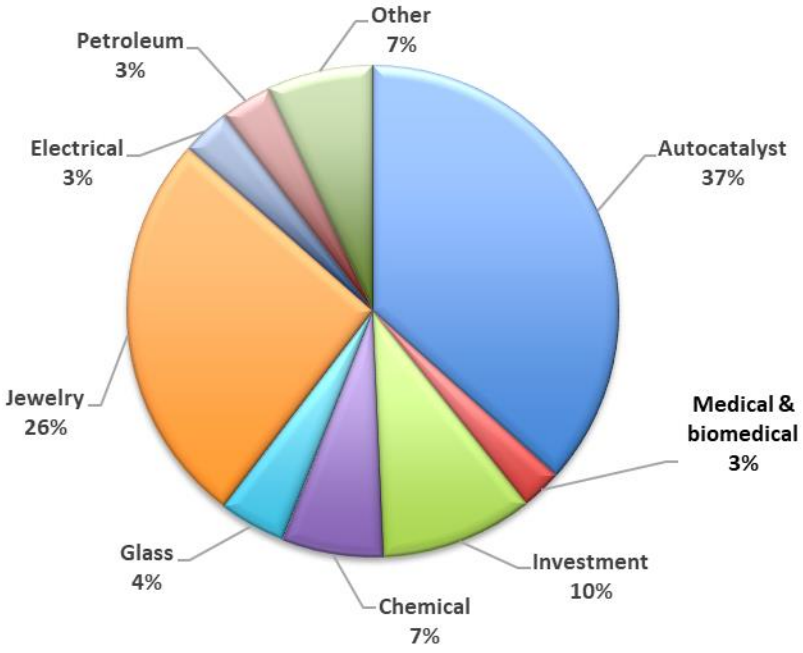

Fig. 2.9. *Platinum global demand in 2019 by area of applications (Statista, 2019b).*

In the last 15 years, Pt prices per Kg peaked at 67000 USD in 2008 but, also as of 2019, it has been reduced to 30000 USD per Kg (Bullionvault, 2019).

2.2.5. Aluminum

Al is the most abundant metal in the Earth's crust (84149 ppm) but is normally only found in such minerals like cryolite, or bauxite (raw rocky material), which are aluminum silicates. The hall-Héroult process is one of the most widely applied processes to commercially extract Al but is a very energy intensive. Al has particular properties, such as low density, non-toxicity, high thermal conductivity, excellent corrosion resistance and easily casting and forming, which makes it attractive in large variety of applications. These applications include: aircrafts and cars construction, foils, cans, toys, food packaging, windows frame, power lines, paints, etc. (RSC, 2019e). Its oxides are also used in industrial catalysts, absorbents or abrasives. Five top world smelter productions for Al are placed in China, Russia, Canada, India and United Arab Emirate.

However, bauxite with 15 to 25 % Al is the only ore that is used for commercial extraction of Al today. Fig. 2.10 shows major producers and reserve holders for this ore (USGS, 2018).

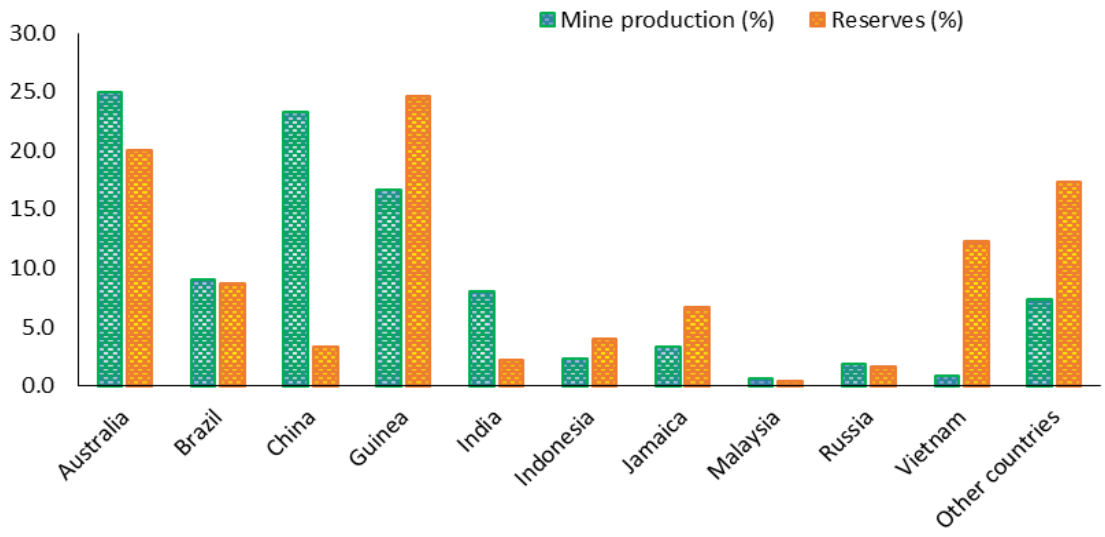

Fig. 2.10. *Bauxite major producers and reserve holders (by country) (USGS, 2018).*

Despite Al crustal abundance is very high, its relative supply risk is medium (4.8) because of its widespread use (78.8 million metric tons by 2015) in a variety of different industries as well as medium substitutability (RSC, 2019e). The main uses of Al are in transport at 27 % followed by construction at 25 % as well as a variety of other uses and industries (Fig. 2.11) (ECONOMICS, 2019).

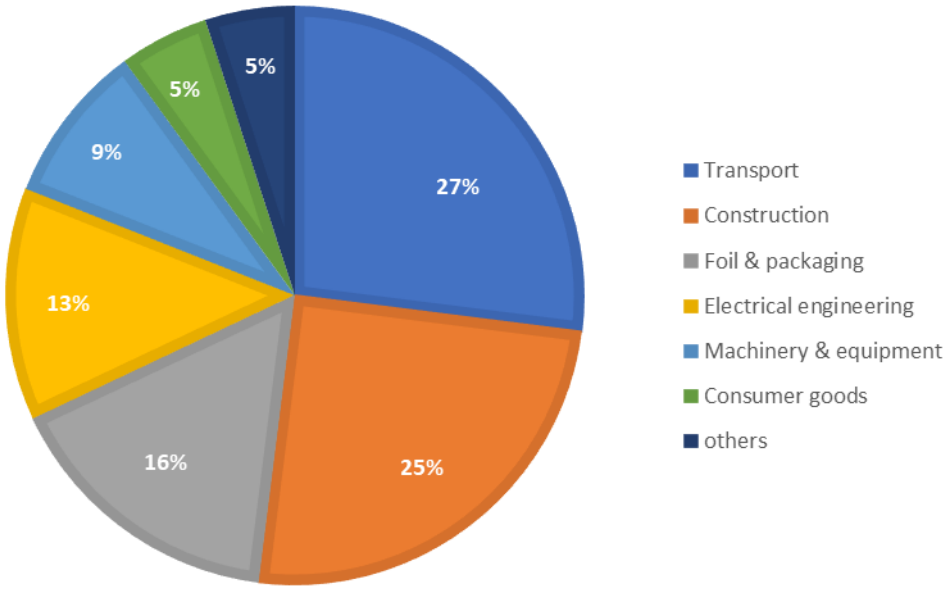

Fig. 2.11. *Al consumption by industry (ECONOMICS,2019).*

Al prices, in the last 15 years, have peaked at around 3000 USD per metric ton in 2008 but it has been reduced to 1750 USD per metric ton in 2019 (Infomine, 2019b).

2.3. Wastes as secondary sources of metals

Based on the difference in nature of wastes in study, they will be separately analyzed below. Also due to their nature, there is a vast gap between available information for them, particularly because there is specific legislation for batteries and also because catalysts are more shrouded in company confidentiality. This explains the different volume and nature of discussed topics below.

2.3.1. Batteries

2.3.1.1. Battery basic structure and types

Chemical cells convert chemical energy into electrical energy. Batteries are composed of two or more cells joined together in series or parallel or in a combination of both. Each battery is made of two unlike material called electrodes; in which anode is the negative and cathode is the positive electrode, electrolyte, which is capable to move ions within the electrodes, separator which has to be made of polymeric or nonwoven permeable membrane chemically stable regarding to the electrolyte material and can or enclosure which the internal components of the battery are protected from the environment. All portable batteries have similar yet slightly distinct design. As an example, an alkaline battery is represented below in Fig. 2.12.

Batteries have a wide variety of different materials, such as metals (in the case of alkaline batteries, Zn and Mn), plastic, graphite, etc. The outside is mainly constituted by a stainless steel can or container that acts as the cathode current collector (Fig.2.12, red outside line). Beyond that, the cathode itself, electrically connected to the can wall and which, for alkaline batteries, is made of graphite particles and with high pure MnO_2 powder [known as electrolytic manganese dioxide (EMD)], potentially mixed with coal dust (Fig.2.12, blue dotted line) (Lumen, 2019; Johansen, 2007).

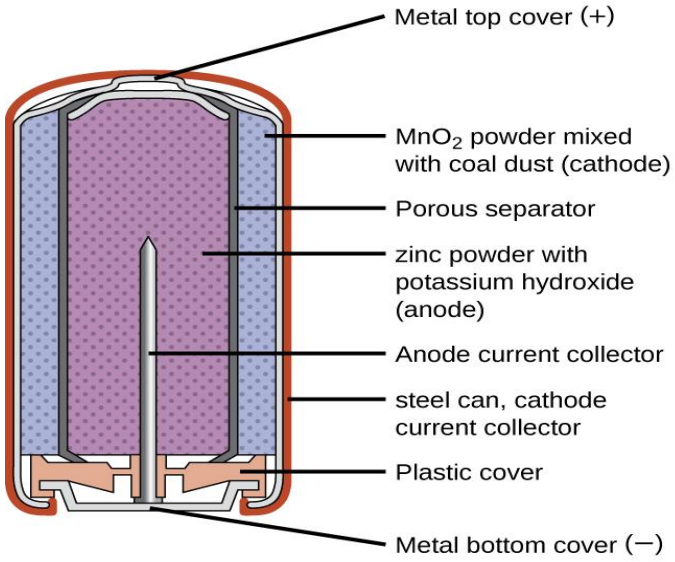

Fig. 2.12. *Schematic representation of an alkaline battery (Lumen, 2019).*

A porous separator acting as insulator separates the cathode from the anode (Fig.2.12, grey line). Finally, the anode lays in the center of the battery, made of Zn powder with potassium hydroxide (KOH) to serve as electrolyte (Fig.2.12, pink dotted line). At the center, there is the anodic current collector mainly made up with brass , separated from the metal bottom cover by a plastic cover in order to prevent short circuiting (Lumen, 2019; Johansen, 2007).

As it can be seen in Fig. 2.13, alkaline batteries are the most commonly used portable batteries. Due to the non-rechargeable nature of this type of battery, huge amounts of spent batteries wastes are produced, which need to be recycled.

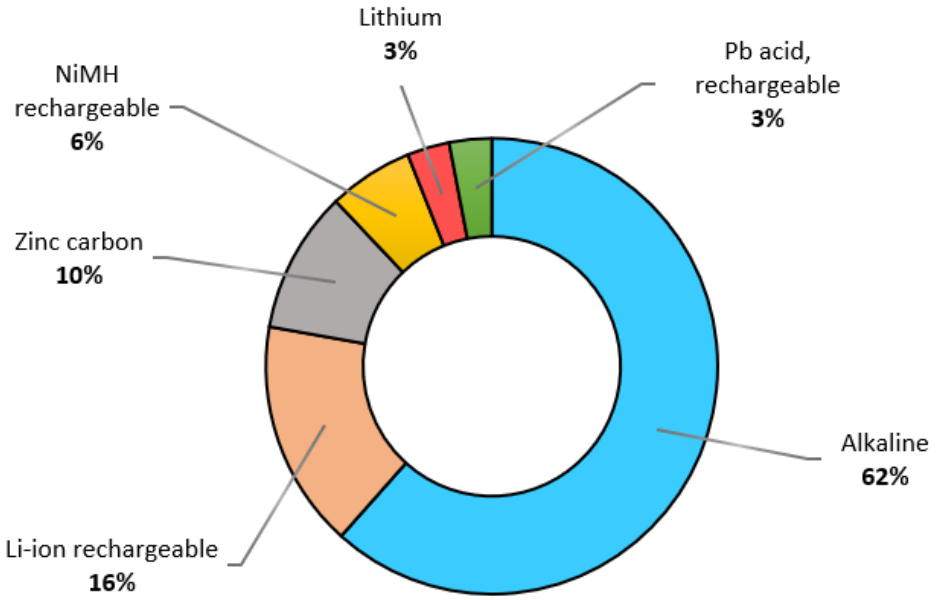

***Fig. 2.13**. Portable batteries placed on the market in the EU (based on values from Germany) in 2015 by weight (Hartmut et al., 2018).*

2.3.1.2. Battery collection and recycling in the European Union

In the EU, a Batteries Directive was adopted in 2006 and has been subject to several revisions, with the latest amendments being incorporated in 2013. This was intended to uniform collection rate objectives and way to quantify such collection rate for all types of batteries. With this directive, a set of other incentives to collect and ultimately recycle batteries have been established. This directive also enabled a more direct monitoring of the production cycle and potential losses as described in Fig. 2.14.

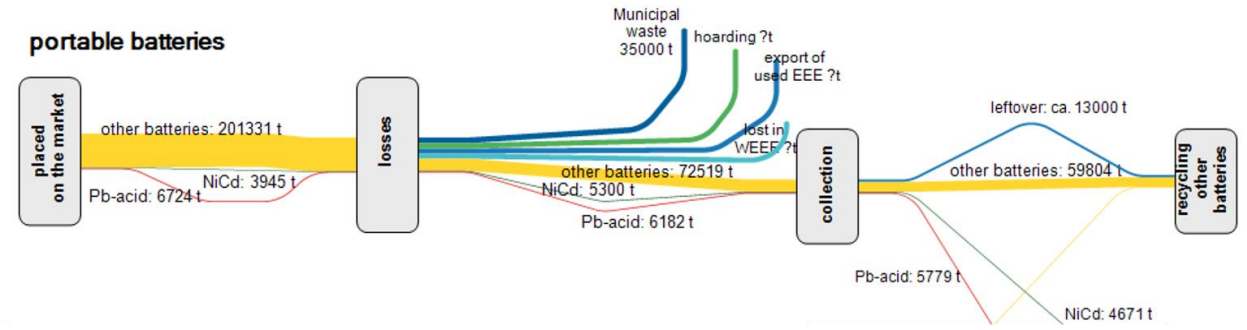

Fig. 2.14. *Portable batteries placed on the market mass flow diagram for EU in 2015 (Hartmut et al., 2018).*

The difference between the quantity of portable batteries placed on the market and not collected throughout the cycle is roughly 128 thousand tons of these type of batteries in 2015. Of these losses, 27 % is found in municipal waste and presumably taken to landfill or incineration. There is, however, other potential explanations (Hartmut et al., 2018):

- Losses through electronic wastes, i.e., batteries that were not removed from their appliances when these were discarded and therefore shredded together;

- Exports of used appliances with batteries still inside to outside the EU;

- Hoarding of batteries by end consumers.

In Fig. 2.14, alkaline batteries are part of the other batteries denomination. They are considered to be less hazardous to the environment compared to Pb-acid and nickel-cadmium (Ni-Cd) batteries, which, as the schematic suggest, are separated and recycled in some other process. Only around 30 % of these batteries arrive at the recycling center.

To further complicate the issue, the recycling of the collected alkaline batteries remains challenging from an environmental and economic standpoint. For that purpose, the EU defines the term BAT – Best Available Technique defined in the IPPC Directive 2008/1/EC, which briefly explained defines the best, i.e, the most effective in terms of environmental protection, available techniques, i.e, in techniques developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions (EU Commission, 2009).

Table 2.2 denotes the most relevant battery recycling processes and selected representative companies in the EU for alkaline battery recycling.

Table 2.2. *Most relevant alkaline battery recycling process in EU and companies that carry out said processes (EU Commission, 2009).*

Designation of the process	**Select companies carrying out the process**
Mechanical separation and subsequent Waelz process	Redux GmbH; DELA GmbH
Thermal treatment separation and subsequent Waelz process	Fernwärme Wien GmbH
Pyrolysis and pyrometallurgical treatment	Batrec Industrie AG
Thermal treatment for button cells and hydrometallurgical	Pilagest S.L.
treatment for Zn-C and Alkaline batteries (primary)	Revatech
Pyrometallurgical treatment for Zn-C and AlMn batteries	AFE Valdi
Oxyreducer: Thermal process under reductive atmosphere	Citron AG
Room temperature recycling process	Recupyl

As can be seen in Table 2.2, most processes are based on pyrometallurgical treatment or possess a stage with thermal pre-treatment. These pyrometallurgical techniques are often seen as less expensive routes, capable of high metal recovery with a rapid reaction rate without the necessity of complex pre-treatment process and allow the separation of materials in form of molten metal or gases from other products that can be high value by-products. However, due to the high temperatures required, these techniques tend to be extremely energy intensive and may emit dust and release harmful gases, requiring expensive cleaning and dust collecting system to prevent air pollution.

These limitations help explain the recent development of further research on alternatives methods, namely hydrometallurgical methods for wastes and/or low grade ores in particular,

which have been proved to limit air pollution by comparison (Briffaerts et al., 2009), and shall be, therefore, the focus of testing in this thesis.

2.3.2. Spent fluid cracking catalysts

There are several types of catalysts currently in use in the oil refinery industry. As demonstrated in Fig. 2.15, FCC is one of the most prevalent types catalytic processes used today worldwide.

FCCs are components used for hydrocarbon processing in the petroleum industry. These catalysts aid in the cracking of large molecules from feedstocks, such as heavy or vacuum gas oil.

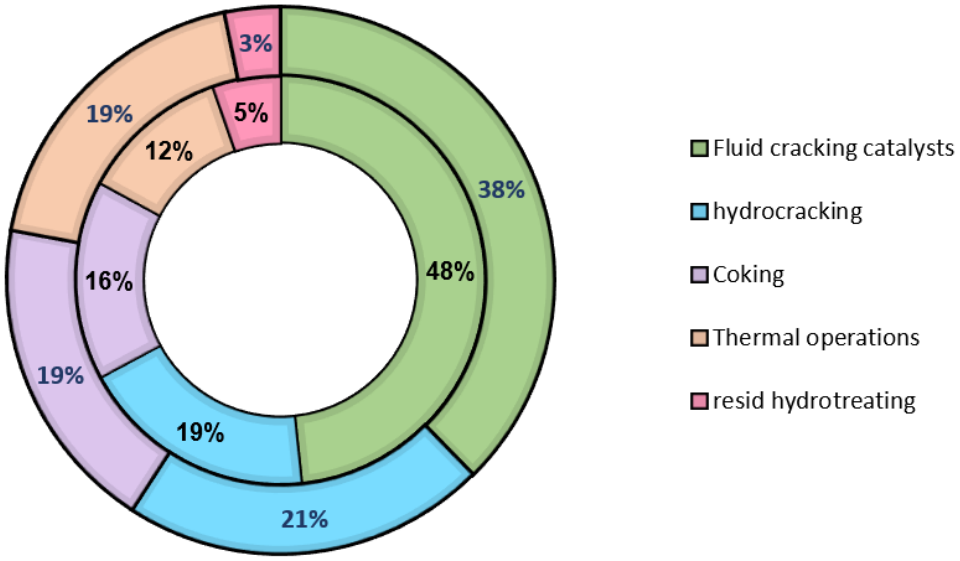

Fig. 2.15. *Installed capacities in % of barrels per day for major conversion processes in the refineries (outer circle) and % of refineries with major conversions processes installed (inner cycle). Refineries can have more than one technology installed (Vogt and Weckhuysen, 2015).*

Although their constitution can vary (Fig. 2.16), they are mainly made of crystalline microporous aluminosilicates also known as zeolites, which are synthetized in such a way to increase its potential as a catalyst. The zeolite is responsible for cracking due to its acid sites that can convert molecules to the shorted and desired gasoline range. However, other components are required

to pre-crack larger molecules as well as to act as binding agent (Vogt and Weckhuysen, 2015). Zeolite Y is one of the main types of zeolites used in the industry and is stabilized with REEs, such as La and cerium (Ce). These metals not only enhance the catalyst activity but also prevent loss of acid sites due to metal poisoning, mostly V and Ni.

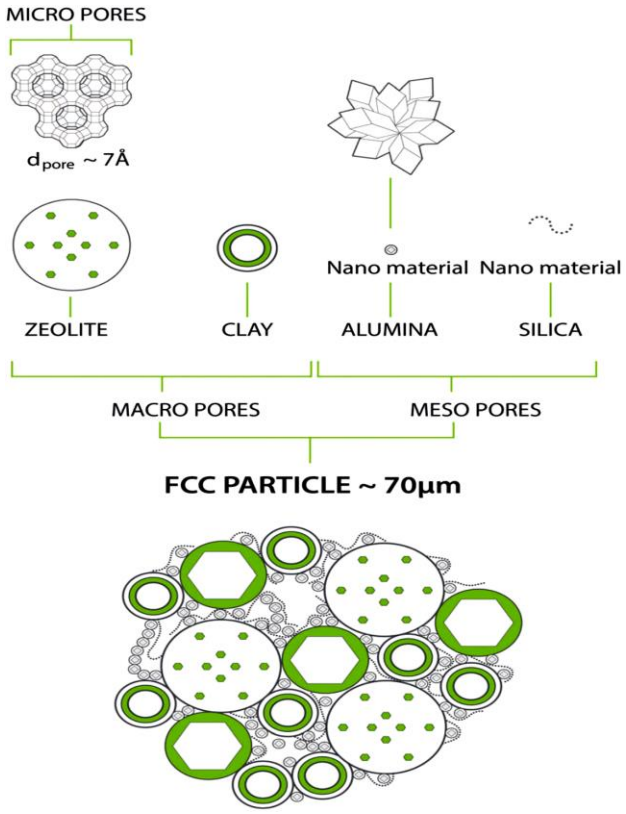

Fig. 2.16. *Representative structure of FCC particles (Vogt and Weckhuysen, 2015).*

A simplified schematic of how FCC are used can be seen in Fig. 2.17. As the reaction is endothermic, there is a need of a feed to increase the temperature and enable the beginning of the process.

After reaction at high temperatures, the FCCs are separated from the products ('spent cat') and regenerated by burning off the carbon ('regen cat'), also known as coke, that has been deposited; therefore, FCCs are continuously regenerated. However, this process cannot be repeated endlessly; due to the harsh temperature and pressure conditions in the reactor, a complete

catalyst deactivation eventually occurs. Thus, fresh catalyst ('fresh') needs to be added to sustain the conversion reactions (Ferella et al., 2016), substituting exhausted catalyst ('ecat').

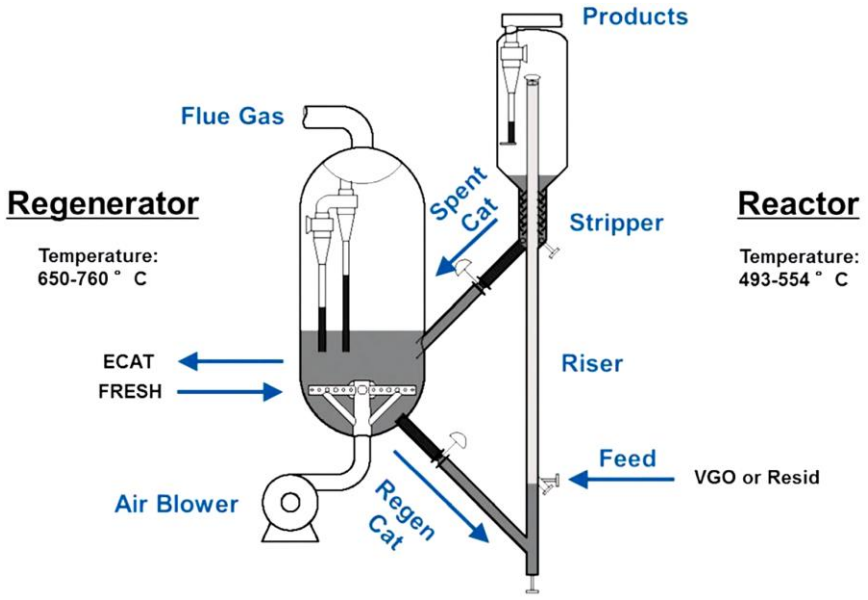

Fig. 2.17. *Schematic representation of the catalytic process using FCC (Vogt and Weckhuysen, 2015).*

This exhausted catalyst can be rejuvenated mostly by removing impurities, such as V and Fe, which concentrate in the outer surface and reduce the active surface available for reaction. However, despite several developed methods, rejuvenation is not always an option and has limited commercial application, namely due to associated costs (Marafi and Stanislaus, 2008). Once rejuvenation is no longer a possibility, spent FCCs can be reused in other applications without the need of any further processing. One of such reuse options is its application in cement production. It is estimated that FCCs can replace up to 15–20 % of cement content or 10 % of sand without adverse effect (Al-Jabri et al., 2013) although some disadvantages of this reuse are also reported (Soriano et al., 2016). As a last resort, spent FCCs are still being sent for disposal in landfills. However, the price of such option has been increasing steadily. Spent FCCs sometimes can be classified as hazardous waste depending on the metals that accumulated. Therefore, it

requires several pre-treatments to ensure its safe disposal and to reduce heavy metal leaching (Ferella et al., 2019; Marafi and Stanislaus, 2008).

Before opting for landfill disposal, metal recovery of spent FCCs should be considered due to the sheer volume of REEs used in the catalyst; in 2008, 1980 tons of cerium(IV) oxide (CeO_2) and 17800 tons of La_2O_3 were used for FCC production and it is expected that these values have increased since then (Akah, 2017).

Unlike alkaline batteries, there is yet to be established a clear European Directive and information, as a whole, on the waste management of this rather specific waste is extremely scarce. Regardless, as a waste containing several important REEs, one of the most critical raw materials in the EU, as well as its importance to the oil industry, its recycling is of paramount importance.

2.3.3. Platinum group metals catalyst

Yet another type of catalyst, PGM bearing catalysts have the function of performing catalytic reforming, a chemical process used to convert petroleum refinery naphthas distilled from crude oil into reformates, liquid high octane products. These materials may contain Pt, palladium (Pd), rhodium (Rh), rhenium (Re), iridium (Ir), ruthenium (Ru), gold (Au), and/or Ag, with precious metal concentrations ranging from less than 40 ppm (parts per million, or grams per ton) to greater than 15 % by weight. Fig. 2.18 presents an example of a reforming catalyst contating PGMs.

Fig. 2.18. *Example of a reforming catalyst containing PGMs (MCR, 2019).*

These catalysts tend to have a similar life cycle in industrial setting as the one described above for FCC; so, there is little need to repeat the information. This is to say that in a refinery, PGM catalysts also are associated with zeolites and operate in similar way with loss of activity due to metal poisoning leading to the need of regeneration and, eventually, rejuvenation. However, the main difference with FCC lies with its content in PGM metals, namely Pt and Rh, which are extremely precious metals

To illustrate the importance of the presence of these precious metals in the catalyst, the influence of a Ni based catalyst compared to a PGM one in tar reforming can be found in Fig. 2.19. As the figure suggests, using PGMs in the catalyst leads to faster kinetics when compared to the use of Ni (Steele et al., 2013). In addition, catalyst with PGMs are typically more active than Ni based catalyst. This suggests that, although these metals can be replaced (high substitutability for Pt as referred above) this will come at a high cost in terms of efficiency not only for this sector but for all sectors that use this catalytic process. Furthermore, these type of catalysts are also present in automobiles or even factories to control and limit pollution by enhancing the reactions that occur within motors (Saguru et al., 2018).

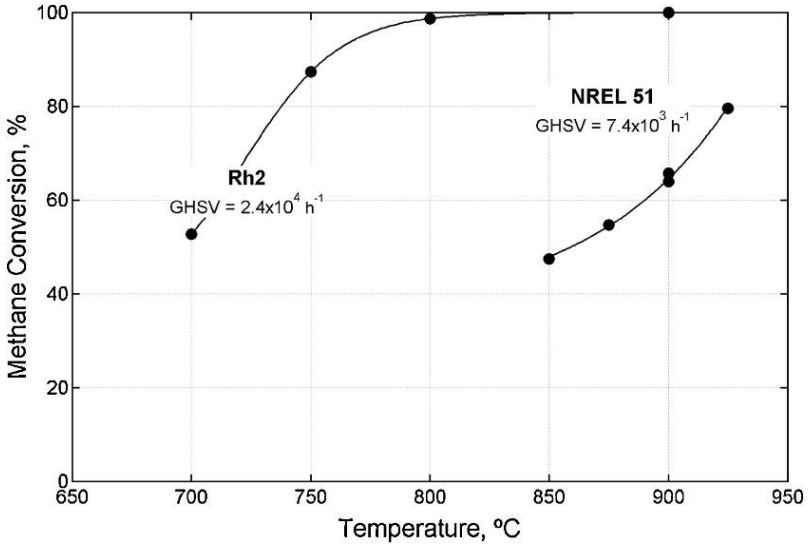

Fig. 2.19. *Methane conversion % in tar reforming at different temperatures for a PGM bearing catalyst ('Rh2') compared to a Ni based catalyst ('NREL 51') (Steele et al., 2013).*

This not only increase its demand, but also plays a vital role in further controlling environmental damages. Recycling of such precious metals is therefore of vital importance not only due to its price but also to its use.

2.4. Metal recovery

2.4.1. Hydrometallurgical recycling of spent batteries

After the collection of spent batteries and before their chemical treatment, some mechanical/physical pre-treatments are required. These may include shredding or cut-crashing, thermal procedures, separation of ferrous metal from inert compounds (paper, plastic, ferrous and non-ferrous scraps) by the use of magnets as well as powder sieving.

Subsequently, hydrometallurgical processes are applied, usually in small scale plants and involves several basic steps, such as leaching, separation and metal recovery. The aim of the leaching is

to extract the metals from the solid matrix into the aqueous phase. Usually, strongly acidic or alkali solutions, with or without the presence of reducing agents, are used.

Due to the complex nature and numerous parameters that might affect the efficiency of leaching and the subsequent separation step(s), these processes still remain an important research avenue.

The leaching processes described in the literature can be divided into four simplified main types: neutral, acid (or acid-reductive), alkaline and complexation leaching. As the name suggests, these processes depend on the type of chemicals applied and reactions can vary from simple dissolution to dissolution plus reductive reactions.

2.4.1.1. Leaching

Neutral leaching

Neutral leaching corresponds to the use of deionized water to leach out the electrolyte and other soluble components of the spent batteries. In the case of alkaline batteries, this electrolyte is KOH while for zinc- carbon (Zn-C) batteries is ammonium chloride (NH_4Cl) (Buzatu et al., 2013). In the case of a subsequent acid leaching implementation, neutral leaching is previously used to leach these and other water-soluble components of the spent batteries in order to avoid excessive use of acid as well as to avoid interferences with other later processes, such as electrolysis (Buzatu et al., 2014). During the neutral leaching, the KOH and NH_4Cl dissolve in the deionized water and may later be recovered, ready for reuse as electrolytes for new batteries (Abid Charef et al., 2017).

Alkaline leaching

Alkaline leaching is mostly applied using a strong base (e.g. sodium Hydroxide (NaOH)), which reacts according to the following Eqs. (Shin et al., 2007):

$$\mathrm{Zn(s) + 2\ NaOH(aq) + 2\ H_2O\ (aq) \rightarrow 2Na^+(aq) + Zn(OH)_4^{2-}(aq) + \ H_2(g)} \qquad (2.1)$$

$$ZnO(s) + 2\ NaOH(aq) + 2H_2O\ (l) \rightarrow 2Na^+(aq) + Zn(OH)_4^{2-}(aq) + \ H_2O\ (l) \qquad (2.2)$$

It is important to note that there is no reactivity for Mn oxides nor for hetaerolite ($ZnMn_2O_4$), which are usually present in the alkaline batteries, when using NaOH as a leaching agent. This was confirmed by several X-ray diffraction (XRD) analyses by different research groups (Abid Charef et al., 2017; Sadeghi et al., 2017). As a result, alkaline leaching is only applicable for selective leaching of Zn. It can be followed by a second acid reductive leaching to recover Mn at a later stage, as it has been used in this Thesis.

Acid leaching

Acid leaching is most often conducted using mineral acids, such as hydrochloric acid (HCl), nitric acid (HNO_3) and mostly sulphuric acid (H_2SO_4) due to its low cost.

The reactions of the main Zn and Mn forms that may be present in alkaline spent batteries after leaching with acid, such as H_2SO_4, are represented below (Buzatu et al., 2014):

$$ZnO(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + \ H_2O\ (l) \qquad (2.3)$$

$$Zn(s) + H_2SO_4(aq) \ \rightarrow ZnSO_4(aq) + \ H_2(g) \qquad (2.4)$$

For Mn, several compounds can be present, which react with H_2SO_4 according to the following Eqs. (Buzatu et al., 2014):

$$MnO(s) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + \ H_2O\ (l) \qquad (2.5)$$

$$Mn_2O_3\ (s) + H_2SO_4(aq) \ \rightarrow MnSO_4(aq) + \ MnO_2(s) + \ H_2O\ (l) \qquad (2.6)$$

$$Mn_3O_4\ (s) + H_2SO_4(aq) \ \rightarrow 2MnSO_4(aq) + \ MnO_2(s) + \ 2H_2O\ (l) \qquad (2.7)$$

As it can be seen from the Eqs., manganese oxide (MnO) is the only readily soluble manganese oxides. The dissolution of other manganese oxides, such as Mn_2O_3 and Mn_3O_4, is partial due to

the formation of insoluble MnO_2 in the leaching process. This was verified by XRD analysis of the final residue in studies where only acid was applied (Sadeghi et al., 2017).

Yet another possible form that Zn and Mn can occur is as $ZnMn_2O_4$. This compound reacts with H_2SO_4 originating its partial solubilization according to the following Eq. (Abid Charef et al., 2017):

$$ZnMn_2O_4(s) + 2H_2SO_4(aq) \rightarrow ZnSO_4(aq) + MnSO_4(aq) + MnO_2(s) + H_2O\ (l) \qquad (2.8)$$

Complexation-assisted leaching

Besides acid or alkaline leaching, complexation- assisted leaching is another type of leaching that has been described in the literature. As the name suggest, this method implies the use of complexing agents, such as ammonium carbonate [$(NH_4)_2CO_3$] or NH_4Cl as leaching agents.

The ability of these leaching agents derives from the formation of soluble complexes of Zn with the added ligands, which enable selective dissolution of Zn from the battery waste. This reaction occurs at much lower pH conditions than when alkaline leaching is used. Eqs. below represent the formation of the most dominant forms of complexes formed between Zn with the complexing agents added (Nogueira and Margarido, 2015):

$$ZnO\ (s) + 2\ NH_4{}^+(aq) + 4\ Cl^-(aq) \rightarrow\ ZnCl_4{}^{2-}(aq) + 2\ NH_3(aq) +\ H_2O\ (l) \qquad (2.9)$$

$$ZnO\ (s) + 2\ NH_4{}^+(aq) + 3\ NH_3(aq) \rightarrow\ Zn(NH_3)_4{}^{2+}(aq) +\ H_2O\ (l) \qquad (2.10)$$

Although other complexes can be formed, these are the most dominant under higher concentrations of ammonia (NH_3) or NH_4Cl.

Comprative analysis of different leaching conditions

Table 2.3 evidences that when alkaline leaching was applied less than 1% of Mn was leached for all cases studied. These results are in agreement with theoretical predictions and evidences the high selectivity of the alkaline leaching process for Zn over Mn. Table 2.3 also shows that Zn leaching efficiency varied widely (from 38 to 82 %) even if seemingly similar conditions were used,

possibly due to differences in the types or even brands of batteries tested. Nevertheless, the highest performance extraction requires a very high molar quantity of base in order to guarantee pH conditions adequate to solubilize totally Zn; pH values $\geq$ 14.4 are needed in order that Zn will be solubilized as a complex of tetrahydroxizincate [$Zn(OH)_4^{2-}$] (Machado et al., 2010). This might not be a convenient concentration of base to be implemented at industrial scale due to the cost, use of very corrosive conditions and the potential dangers for the workers.

Literature also describes examples of leaching of Zn by complexation (Table 2.3). Only three complexing agents were tested. As described above, both ammonia (NH_4^+) and chloride (Cl^-) ions form complexes with Zn but carbonate anion (CO_3^{2-}) may also form weak complexes. Considering that the use of this complexation-assisted leaching may originate comparable Zn extraction efficiency yields, as it was described in the work of (Shin et al., 2007) under mild alkaline conditions, this fact constitutes an important advantage of this strategy relatively to the alkaline one.

Relatively to acid leaching, H_2SO_4 was the acid mainly used probably due to its low cost whereas HCl was only described in one study (Table 2.3). Under these conditions, the Mn leaching efficiency varied widely (between 13 and 82 %) (Table 2.3).

Table 2.3. *Detailed performance of complexation, alkaline and acid leaching strategies tested on spent alkaline and/or Zn-C batteries. Data were normalized in function of both the molar quantities of leachant per g of waste.*

Source	L/S ratio (mL/g)	Leachant (M)	mol leachant / g waste	Time (h)	Particle size (µm)	T (°C)	Mn (%)	Zn (%)
Alkaline leaching*								
(Kim, 2008)	10	NaOH (4)	0.04	1	< 2380	80	0.1	63.4
(Shin et al., 2009)	10	NaOH (4)	0.04	0.5	< 2380	80	< 0.1	82
(Sadeghi et al., 2017)	10	NaOH (4)	0.04	3	< 1000	80	< 0.01	38
(Sadeghi et al., 2017)	10	NaOH (4)	0.04	0.05	< 1000	**	< 0.01	82
(Sadeghi et al., 2017)	10	NaOH (4)	0.04	0.23	< 1000	***	< 0.01	81
(Buzatu et al., 2013)	10	NaOH (6)	0.06	2	< 1250	80	-	> 64
(Abid Charef et al., 2017)	10	NaOH (6.5)	0.065	3	-	80	0	52
Complexation leaching*								
(Shin et al., 2007)	10	$(NH_4)_2CO_3$ (2)	0.02	1	< 2380	60	< 0.1	83.4
(Senanayake et al., 2010)	10	NH_3 (2.5)	0.025	1.5	< 2380	60	< 1	39
(Nogueira and Margarido, 2015)	20	NH_4Cl (5)	0.1	4	< 3970	100	< 1	72
Acid leaching*								
(Senanayake et al., 2010)	10	H_2SO_4 (1)	0.01	1.5	< 2380	30-32	35	98
(Sadeghi et al., 2017)	10	H_2SO_4 (1)	0.01	3	< 1000	80	15	86
(Sadeghi et al., 2017)	10	H_2SO_4 (1)	0.01	$8x10^{-3}$	< 1000	**	19	94
(Sadeghi et al., 2017)	10	H_2SO_4 (1)	0.01	$3.3x10^{-2}$	< 1000	***	13	92
(Ferella et al., 2008)	10	H_2SO_4 (1.5)	0.015	3	< 1000	80	19.3	98.8
(Abid Charef et al., 2017)	10	H_2SO_4 (2)	0.02	3	-	80	82	100
(Buzatu et al., 2013)	10	H_2SO_4 (2)	0.02	1	<1250	60	40	96
(Shin et al., 2007)	10	H_2SO_4 (2)	0.02	-	< 2380	60	35	92
(Deep et al., 2011)	10	HCl (5)	0.05	2	-	70	28.8	96.1

* The data are organized in increasing order of molar quantity of the reagents; **Microwave-assisted; *** Ultrasound-assisted.

As it can be seen in Eqs. (2.5) -(2.7), the solid phase containing Mn(II) (MnO) is the only one that dissolves totally in the presence of acid. Thus, different proportions of Mn(IV), Mn (III) and Mn(II) solid phases, which can be present in the spent batteries residues, may explain the variability of leaching results reported.

2.4.1.2. Separation techniques

Solvent extraction

Data from Table 2.4 indicates that most studies used cationic extractants, namely Cyanex 272 [bis-(2,4,4-trimethylpentyl) phosphinic acid], Cyanex 301 [bis(2,4,4-trimethlpentyl) dithioohosphinic acid], Cyanex 302 [bis(2,4,4-trimethylpentyl) monothiophosphonic acid], PC88A or EHEHPA (also known as Ionquest 801) [2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester] and D2EHPA [di-(2-ethylhexyl) phosphoric acid] (which, unlike the others, is a phosphoric rather than phosphinic acid) while some other studies used, either alone or in combination, neutral extractants, such as Cyanex 923 =TRPO [trialkyl phosphine oxide] and TBP [tributyl phosphate]. As the name suggest, these two types of extractants have different reactions with the metal to be extracted, according to the following two Eqs. for cationic extractants (Eq. 2.11 (Ahmadipour et al., 2011; Falco et al., 2014) and neutral extractants (Eq. 12 (Deep et al., 2011; Ibiapinaa et al., 2018) respectively:

$$\mathrm{n\ M^{2+}\ (aq) + (RH)_2(org) \rightarrow MR_2(RH)_{2n-2}(org) + \ 2H^+(aq)} \qquad (2.11)$$

$$\mathrm{MX_2(aq) + nR\ (org) \rightarrow MX_2.nR\ (org)} \qquad (2.12)$$

In which M is the metal being extracted, R is the molecule of extractant, H^+ is the hydrogen ion, X is an anion (equal to 1 for chloride and ½ for sulphate) and n is the stoichiometric coefficient of the metal in the extraction and can only be determined experimentally for particular situations. These different extraction reactions can impact the performance of the extractant as, for example, the cationic extractant lead to unwanted pH reduction, limiting the process to a point.

Before any comparison, it is also important to point out that, to base a comparison on Zn extraction efficiency alone, might be misleading. For instance, in Tanong et al. (2018) Zn extraction was only 60 %. However, this fact might be due to a combination of high initial of Zn and Mn. Under these conditions, for each mol of extractant, 0.13 mol of Zn were extracted; this amount of Zn is much more than in other studies (Biswas et al. 2016; Hosseini et al. 2010), where a higher percentage of Zn extracted was recorded.

With such limitations in mind, general trends can be highlighted based on the results detailed in Table 2.4. In particular, as mentioned above, it is possible to detect some differences between phosphoric and phosphinic acid cationic extractants as well as between cationic and neutral extractants. It would seem that phosphoric acid extractants, in particular D2EHPA, have more affinity for Mn than Zn and lacks selectivity when compared to phosphinic acid extractants. This results in Mn extraction over Zn as detailed in Biswas et al. (2016) but without sufficient selectivity. Simultaneously, this also means that when D2EHPA is mixed with other cationic extractants, it leads to higher Mn extraction, therefore decreased the selectivity and diminishing the potential for synergetic extraction of the mixture. Therefore, it can be concluded that D2EHPA is not suitable for separation of Mn and Zn, either alone or combined with other cationic extractants.

On the other hand, results suggest that neutral extractants perform better than cationic extractants: Cyanex 923 is the best performing in terms of Zn extraction with 0.41 mol of Zn per mol of extractant and with negligible amounts of Mn co-extracted, i.e, highly selective. In addition, TBP, another neutral extractant, when added in combination with cationic extractants, seemingly also produces a synergetic positive effect; when added with Ionquest 801 (which has the same formula than PC88A) it leads to higher separation effect and lower Mn co-extraction (when compared to 40 % PC88A) and similar increase can also be seen when comparing D2EHPA performance with or without TBP added. However, the same cannot be said for TBP added to Cyanex 272, so this synergetic effect is inconclusive. Regardless, it can be seen that the best performing tests are with Cyanex 923 (Deep et al., 2011) with 87 % Zn extraction and < 1 % Mn

co-extraction as well as with 30 % Ionquest 801 + 5 % TBP (Li et al., 2010) with 96 % Zn extraction and 1.5 % Mn co-extracted.

Regardless, neutral extractants are considerably more expensive. As an alternative, the extractant Cyanex 302, for example, without the added D2EHPA, is in fact the best performing cationic extractant with only 10 % Mn co-extraction and can be obtained at a more reasonable price. However, the choice of a solvent does not lie solely on the performance, but it is also dependent of the costs and objectives that are set up. Another important aspect is the stripping and its efficiency. The stripping efficiencies reported in the same articles referenced in Table 2.4, do not vary significantly; values varying from 82 to 100 % using H_2SO_4 between 0.4 and 2 M are described.

Table 2.4. *Zn and Mn extraction, expressed in percentage, as well as molar quantities of Zn and Mn extracted applied (Zn/ extractant; Mn/ extractant) from different studies. The differences between the pH at which 50 % of Zn and Mn are removed ($\Delta pH_{0.5}$) as well as separation factors (β) are also reported with corresponding relevant conditions. Aqueous-organic (A/O) ratio of 1:1.*

Sources	Extractant (v/v)	Diluent	ΔpH 0.5	pH	β (Zn/Mn)	T (°C)	[Zn] g/L	Initial [Zn]/[Mn] (M)	Zn %	Zn / extractant	Mn %	Mn / extractant
(Falco et al., 2014)	16% Cyanex 272	Kerosene	1.4	4	4010	25	6	3.36	100	0.18	20	0.01
(Ahmadipour et al., 2011)	15% Cyanex 272 + 5% D2EHPA	Kerosene	1.7	3	52	25	-	-	99.8	-	38.5	-
(Tanong et al., 2018)*	20% Cyanex 272 + 2% TBP	Kerosene	-	3.5	366	50	19.9	0.61	60	0.13	3.7	0.01
(Biswas et al., 2016)	40% Cyanex 272	Kerosene	1.4	3	208	25	2.2	0.26	98.5	0.03	24	0.01
(Lee et al., 2010)	30% D2EHPA + 5% TBP	Shellshol D70	4.1	3	222	40	22	0.66	97.1	0.29	13	0.06
(Lee et al., 2010)	30% Ionquest 801 + 5% TBP	Shellshol D70	3.75	3	1578	40	22	0.66	96	0.29	1.5	0.01
(Biswas et al., 2016)	40% PC88A	Kerosene	1.81	4	563	25	2.2	0.26	98	0.03	8	0.06
(Hosseini et al., 2010)	15% Cyanex 302 + 5% D2EHPA	Kerosene	2.3	5	12687	60	4	0.84	100	0.10	62	0.08
(Biswas et al., 2016)	40% Cyanex 302	Kerosene	2.75	4	1793	25	2.2	0.26	99.5	0.03	10	0.01
(Biswas et al., 2016)	20% Cyanex 301	Kerosene	2.75	1.8	483	25	2.2	0.26	99	0.06	17	0.04
(Deep et al., 2011)	4% Cyanex 923	n-hexane	-	0	-	25	2.9	1.21	87	0.41	< 1	-
Mn extraction												
					β (Mn/Zn)			Initial [Mn]/[Zn] (M)				
(Biswas et al., 2016)	40% tech grade D2EHPA	Kerosene	0.85	2	7	25	2.2	3.81	65	0.03	93	0.14
(Biswas et al., 2016)	40% analytical grade D2EHPA	Kerosene	0.7	2.5	9	25	2.2	3.81	69	0.02	95	0.10

* A/O ratio of 1:2

Chemical precipitation

Another technique that may be used to separate Mn and Zn from spent batteries leachates is chemical precipitation. This technique can be applied in a variety of different ways, depending on the objectives.

One such way is to attempt to selectively precipitate Zn and Mn, and, therefore, separating these metals in order to recover them. Chen et al. (2017) were able to selectively precipitate Mn at pH 13 and then reduced the pH to 10 to precipitate Zn. Both metals were precipitated as $Mn(OH)_2$ and $Zn(OH)_2$ respectively, by adding NaOH, and were subsequently calcinated into MnO_2 and ZnO at high purities. However, this process implies to use very alkaline (pH 13) conditions.

Sayilgan et al. (2010) was able to obtain complete precipitation of Zn at pH 8 and of Mn at pH 10 with either KOH or NaOH and while using a variety of different leachants and reductants. Kursunoglu and Kaya (2014) obtained almost identical results for the same range of pH. However, although not mentioned, the purity of the Zn and Mn precipitates is likely to be low as the pH range of precipitation of both metals are close (Sadeghi et al., 2019) resulting, as mentioned in the studies referenced above, in Mn co-precipitation with Zn.

Alternatively, co-precipitation of Mn and Zn is also proposed (Kim, 2008; Sobianowska-Turek et al., 2016) but this strategy does not enable the recovery of these metals separately.

There is also the possibility of using oxidative precipitation to separate Zn and Mn, by oxidizing Mn to Mn(IV) and precipitate as insoluble MnO_2 while Zn remains in the solution at lower pH values.

Furthermore, chemical precipitation can also be used as an auxiliary technique in the recovery of Zn and Mn, by precipitation of impurities, most commonly iron (Ferella et al., 2008).

2.4.2. Hydrometallurgical recycling of spent FCC

The process of FCC recycling can be roughly divided in two major steps. The initial step is the leaching process, in which strong acid solutions are used to transfer the metals into a liquid phase. A second step (or series of steps) involves the separation of the REEs from contaminants and, eventually, between them, if desirable, in order to enable their complete recovery. Aspects, such as leaching efficiency and the influence of temperature, type of acid, etc. will be firstly discussed. Subsequently, separation methods, namely solvent extraction and selective precipitation, will be focused.

2.4.2.1. Leaching strategies

The first stage of REEs recovery from spent FCC or other derivatives is the acid leaching. There is a variety of numerous inorganic acids studied, which may exhibit different leaching efficiencies. To better assess the performance of different acids as well as other varying conditions, a comparative performance of several different works dedicated to this matter was done, where some screening parameters were used to ensure the quality and relevance of potential comparisons. All studies included in Table 2.5 have the following characteristics: (i) studies of leaching of spent FCC or FC slag and (ii) studies that have individual leaching efficiency values for La and Ce.

Furthermore, to enable a more comprehensive comparison of the data, the molar quantity of the leachant per gram of waste is also reported. Table 2.5 summarizes the results compiled from studies on FCC acid leaching, reported by increasing order of molar acid used per g of waste. By analysing Table 2.5, it can be seen that the lowest values of Ce leaching efficiencies (25 and 53.5 %, respectively) were obtained when HNO_3 and H_2SO_4 were used as leachants. However, the same pattern cannot be found for La leaching efficiency. Furthermore, Zhao et al. (2017) also details that preliminary tests indicate that H_2SO_4 and HNO_3 up to 4 M in similar conditions as described in Table 2.5 are only able to recover around 70 % of existing REEs while HCl is able to obtain 84.3 %. One possible explanation for this difference presented by Zhao et al., (2017) was that chloride (Cl^-) ions have a higher coordination effect than nitrate (NO_3^-) or sulphate (SO_4^{2-}).

Another aspect is that HNO_3 and H_2SO_4 are also reported to lead to Ce precipitation, which would require a secondary leaching in order to increase the recovery of this rare metal (Zhao et al., 2017). From the data in Table 2.5 little to no conclusions can be made regarding the time and temperature required for leaching. Based on the results of Zhao et al. (2017), 0.5 h is clearly insufficient for leaching and higher temperatures (60 °C) are preferable. The experimental setup and conditions can be difficult to compare. For instance, Wang et al. (2017b), used a preliminary caustic selective leaching of aluminium before the acid leaching, which seemingly increases the efficiency of the latter. Other aspects can also be seen in Table 2.5, like the influence of varying the liquid- solid (L/S) ratio.

In Zhao et al. (2017), for the same H^+ content (the same number of H^+ moles), it was found that the efficiency of the leaching of REEs decreased with the L/S ratio; i.e., the lower volume of acid, which corresponded to a more concentrated acid but for the same quantity of H^+ originated a higher efficiency. Further studies are therefore needed to confirm that acid concentration, not just its molar quantity, affects the leaching process and how. Yet another aspect is the prospect of leaching both spent FCC as well as the slag from its production and other wastes of similar characteristics. This aspect was explored in depth by Wang et al. (2017a). These authors found similar recovery values of La and Ce from spent FCC, FCC slag and Rey Zeolite despite their different initial compositions. However, the extremely high HCl concentration used can be unpractical. This might be mitigated by decreasing the L/S ratio and/or the temperature. Most studies do not report the extraction efficiency of other metals (e.g. Al) also present in the spent FCCs.

Table 2.5. *Acid leaching of FCC or FC related wastes for La and Ce recovery.*

Source	Type	L/S ratio (mL/ g)	Leachant (M)	mmol H^+ / g waste	Time (h)	T (°C)	Initial Concentration (%)	La (%)	Initial Concentration (%)	Ce (%)
(Nguyen et al., 2018)	FCC	3	HNO_3 (2)	6	1	80	1.82	88.0	0.06	25.0
(Zhao et al., 2017)	FCC	5	HCl (2)	10	2	60	1.92	84.0	0.29	83.0
(Zhao et al., 2017)	FCC	11	HCl (1)	11	9	25	1.69	76.6	1.57	95.5
(Zhao et al., 2017)	FCC	10	HCl (2)	20	2	45	1.92	83.5	0.29	86.4
(Zhao et al., 2017)	FCC	10	HCl (2)	20	2	30	1.92	76.0	0.29	81.0
(Zhao et al., 2017)	FCC	10	HCl (2)	20	0.5	45	1.92	68.1	0.29	72.8
(Zhao et al., 2017)	FCC	10	HCl (2)	20	2	60	1.92	92.0	0.29	96.0
(Zhao et al., 2017)	FCC	11	HCl (2)	22	9	25	1.69	75.8	1.57	94.5
(Zhao et al., 2017)	FCC	20	HCl (1)	20	9	25	1.69	71.38	1.57	90.3
(Innocenzi et al., 2015)	FCC	6.7	H_2SO_4 (2)	26.7	3	25	3.02	61.2	0.23	53.5
(Innocenzi et al., 2015)	FCC	6.7	H_2SO_4 (2)	26.7	3	80	3.02	89.0	0.23	81.7
(Wang et al., 2017a)	FC slag	4	HCl (9)	36	2	20	1.20	91.0	2.40	92.2
(Wang et al., 2017a)	FCC	4	HCl (9)	36	2	20	0.38	86.18	1.60	82.3
(Wang et al., 2017a)	Rey Zeolite	4	HCl (9)	36	2	20	1.10	97.94	4.00	99.9
(Wang et al., 2017b)	FC slag	-	HCl (3)	-	3	20	3.80	98.6	0.25	98.8

2.4.2.2. Separation techniques

Following the leaching step, the recycling process for FCC moves into a separation and recovery step: a series of different processes to separate the REEs from contaminants, such as Al, as well as between the REEs, if needed. Up to now, the two most widely used processes correspond to solvent extraction and consecutive precipitation.

Solvent extraction

The separation of REEs from each other and other elements by liquid-liquid extraction techniques have been applied for decades. However, the processes are more complex than for other metals (as it will be explained below) and even more so considering the impurities that are associated in the pregnant solutions of FCC leaching. Simple solvent extraction with commercially available extractants has very limited extraction capabilities when applied to REEs. This is because of the characteristics of the metals and its reactions with most extractants as demonstrated below: using EHEHPA as an example, REEs react with simple extractant (represented as H_2L_2) according to the following Eq. (Hou et al., 2016) :

$$\mathrm{REE^{3+}(aq) + 3H_2L_2\ (o) \leftrightarrow RE(HL)_3L_3(o) + 3H^+(aq)} \qquad (2.13)$$

Considering that most extractants are acidic, the release of H^+ promotes the reverse reaction; therefore, the formation of the REE complex with the extractant is limited. One way to overcome this problem is to partly saponify the extractant. For the same example of EHEHPA, Hou et al. (2016) was able to determine the molar ratio and the complex formed when the extractant was saponified with ammonia hydroxide (NH_4OH), enabling the description of the following Eq. 2.14:

$$\mathrm{2REE^{3+}(aq) + 3H_2L_2\ (o) + \ 6NH_4L\ (o) \leftrightarrow 2RE(HL)_3L_3(o) + 6NH_4{}^+(aq)} \qquad (2.14)$$

In which NH_4L represents the saponified portion of the extractant. This reaction leads to the release of NH_4^+ instead of H^+, therefore not limiting the reaction as previously mentioned. Other saponification reagents include magnesium oxide (MgO) and calcium hydroxide [$Ca(OH)_2$] (Liu et al., 2017). Saponified solvent extraction is one of the most widely used purification method for

REEs, including La and Ce from both primary and secondary sources (Wu et al., 2010). However, this approach raises some problems. On the one hand, it leads to the production of wastewaters with high quantities of NH_4^+, which requires treatment prior to discharge into the environment (Chang et al., 2010). On the other hand, this approach is limited by the saponification rates, i.e., the extent of saponification: a low saponification rate might mean that the reaction will remain limited while a high saponification may lead to emulsification of the extractant and, therefore, the formation of a third phase, which is also negative and affects the extraction efficiency (Zhao et al., 2017). Furthermore, several impurities also affect emulsion formation, leading to lower extraction capacities. Several of these impurities are present in spent FCC wastes, such as silica (SiO_2) as well as Fe and most notably Al, which directly and indirectly (for instance, due to the precipitation as $(Fe(OH)_3SiO_2{\cdot}NH_2O)$ increase and stabilize emulsification (Wu et al., 2010). Due to the limitations of the saponified solvent extraction method, several other avenues have also been explored in liquid-liquid extraction of REEs. One such possibility is the complex induced extraction. This method aims to replace saponification as a solution to the abovementioned issue of H^+ production by adding a complexing agent. One such complexing agent is lactic acid, which forms several complexes with the REEs and enables the following extraction reaction, Eq. 2.15 (Yin et al., 2013) :

$$\mathrm{RE(Lac)_x^{(3-x)+}(o) + 3\ H_2L_2\ (o) \leftrightarrow REA_3 3HA\ (o) + (3-x)H^+(aq) + xLAC\ (aq)} \qquad (2.15)$$

In which 'x' represents the number of the moles of the ligand in the REE complex and 'Lac' represents the lactate ion. The higher the 'x' the lower the H^+ produced. Several other compounds have been tested, such as citric acid, acetic acid, ethylenediamine tetraacetic acid (EDTA), etc. to name a few (Kashi et al., 2018). It is reported that the addition of these complexing agents enhances the selectivity among different REEs as well as improves the overall extraction efficiency. For instance, Zhang et al. (2016) found that the presence of 0.6 M of lactic acid combined with the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester P_50_7 increased the distribution ratio up to 8 times for Ce (at pH 2) and up to 25 times for La (at pH 3.5). Another strategy that might even allow the use of unsaponified extractant is the synergetic extraction. As the name suggests, it involves the synergetic combination of two or more different

extractants in such a way that the extraction efficiency is improved, being higher than the sum of the individual extractants (Song et al., 2009). For instance, a combination of the extractant 8-hydroxyquinoline (HQ) with Cyanex 301 has a La distribution ratio up to 3.3 times higher than the ones observed for HQ and Cyanex 301 when tested independently (Tian et al., 2013). Zhang et al. (2014) combined both principles using a complex induced synergetic solvent extraction – a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP) and D_2EHPA, as extractants, and lactic and citric acids, as complexing agents. In this study, it was found that lactic acid was able to increase the extraction capacity of Ce and La by two-fold for both extractants separately. However, this value decreased when the two extractants tested were mixed. Mixing the two extractants with the lactic acid increases the separation factor. Only a few recent studies have analyzed the potential and limitations of liquid-liquid extractions when applied to FCC recycling and metal recovery (Table 2.6). There are only 4 studies that incorporate liquid-liquid extraction into a spent FCC recycling flowsheet. Based on Table 2.6, D2EHPA is the most tested extractant with n-hexane being the solvent that seems to enable a better extraction performance when compared to kerosene and n-octane. However, with n-octane and added TBP, a high extraction is possible even at low pH; this extraction was extremely selective to the REEs with no Al being co-extracted. Saponification, as demonstrated in Ye et al. (2017), leaded to very high extraction, but not selective to REEs; under these conditions, all Al was also co-extracted. Stripping performance varies with the different studies, likely a reflection of the different quantities being extracted in the first stage of the process.

Table 2.6. *Solvent extraction applied to FCC pregnant solutions containing La and Ce. (pH_e – equilibrium pH; SE – stripping efficiency).*

Source	(Innocenzi et al., 2015)	(Zhao et al., 2017)	(Nguyen et al., 2018)	(YE et al., 2017)
Extractant	20 % D2EHPA (v/v)	16 % D2EHPA (v/v)	D2EHPA + TBP (4:1 ratio)	EHEHPA (20 % saponified w/ammonia)
Solvent	n-hexane	kerosene	n-octane	kerosene
pH_e	2.25	2.5	< 1	3.17
Time (min)	-	10	10	-
A/O ratio	-	1	-	2
La extraction (%)	95	85	72	100
Ce extraction (%)	98		89	100
Al extraction (%)	-	50	0	100
Stripping agent	HNO_3 (4 M)	HCl (2 M)	-	HCl (1 M)
SE (%) – La	82	62.88	-	96
SE (%) – Ce	79		-	

Consecutive selective precipitations

Another strategy to recover the REEs present in the FCCs leachates is to selectively precipitate them. However, as is the case for solvent extraction, research on this issue remains scarce. There are two main issues to be addressed: (i) to separate the REEs, La and Ce, from the rest of the impurities and (ii) separate La and Ce from each other. The choice of one over the other depends on the end use and the necessary purity; a precipitated containing both La and Ce can still be used as a mischmetal for several applications, whilst specific needs require pure La or pure Ce. To accomplish the second option, Ce^{3+} can be selectively precipitated from La and Al by oxidation whilst Al and La remain in the solution.

However, this strategy, should only be applied if an appreciable amount of Ce is present in the leachate and the ultimate goal is to recover Ce and La with high purity. For the separation of La and Ce from the rest of the impurities in the pregnant solution, two main precipitation options are described in the literature: (i) the precipitation of double sulphate salts– $NaRE(SO_4)_2 \cdot H_2O$ and oxalate precipitation in the form of $RE_2(C_2O_4)_3$. In this case, the main precipitates are either $NaLa(SO_4)_2$ or $La_2(C_2O_4)_3$ for the double salt precipitation or the oxalate precipitation strategies, respectively.

Although scarcely, literature describes application of these two precipitation methods for recovering REEs from FCCs leachates. For example, Innocenzi et al. (2015) initially precipitated La and Ce as double sulphate salts by increasing the pH up to 2 after extraction with sulphuric acid. This led to a precipitation yield of 100 %, with a RE purity between 75 and 80 %. These authors have also tested oxalic acid precipitation, achieving a precipitate with 37-47 % La and 3.06-3.11 % Ce (w/w) content. However, this precipitation was only performed after solvent extraction; even though an absolute comparison between the different precipitation approaches is extremely difficult, results suggest that oxalic acid precipitation is capable of yielding a precipitate with higher purity in REEs.

Wang et al. (2017b) performed oxalic acid precipitation prior to any other separation method and was able to achieve a final product with 98.7 % RE purity after calcination. These results suggest that oxalic acid precipitation is capable of producing a final product with high purity. However, since this precipitation was performed at pH 1.5, it is likely that a significant portion of oxalic acid was unused as it remains in protonated form. Finally, Wang et al. (2017a) tested a sequence of precipitation steps for recovering REEs from a HCl leachate. Initially, REEs were precipitated, as $NaRE(SO_4)_2 \cdot H_2O$, using Na_2SO_4 at 300 % of its stoichiometric proportion with 99 % efficiency; under these conditions, only 2 % of Al co-precipitated together with REEs. Subsequently, this precipitate was converted into $RE(OH)_3$ by reacting with NaOH and then to $RECl_3$ by dissolution in HCl; a final product with a total recovery of 90.2 % of the REEs ready for immediate and direct reuse in zeolite production was achieved. Even though high total REEs recovery with high purity was achieved, the recycling procedure is not simple containing several steps, which consume a huge amount of reagents.

In conclusion, further studies are needed in order to better assess the potential of consecutive and selective precipitations, particularly considering its potential to substantially simplify the process and reduce operational costs without compromising the final purity of the recycled REEs.

2.4.3. Hydrometallurgical recycling of spent Pt catalyst

Table 2.7 details the results of several studies with a variety of chemicals, conditions and even source material. This is not intended as a completely through analysis of all existing studies in this field but only the most relevant and diverse of the existing options. In certain instances, it is not possible to convert concentrations values in % v/v as the studies do not provide enough information, which, along with other information limitations such as lack of reporting of L/S ratio or even concentration used, limits the comparison possibilities.

Therefore, comparisons between different studies require caution also because different catalyst have widely different characteristics even within the same type. As an example of such, tests performed in Patel and Dawson (2015) with the same fuel cells before and after use have widely different requirements in terms of time and L/S ratios to achieve similar Pt leaching efficiency even though the same reagents, concentration, temperature and pre-treatment are used in both case. Another example can be found in the work of Sasaki and Maeda (2014), in which unused and used car catalytic converters are tested and compared – in this scenario it was found the reverse trend, i.e, used converter are easier to leach with more than 3 times the leaching efficiency for both aqua regia and just HCl, for the same leaching time and temperature.

Table 2.7. *Detailed performance of acid leaching tested on spent Pt catalyst.*

Source	Type of catalyst	Crushed ?	Roasted ?	L/S ratio (mL/g)	T (°C)	Reagents used	Time (min)	Leaching efficiency Pt (%)
(Sun and Lee, 2013)	petroleum refinery	N	Y	20	70	10% HCl + 1% H_2O_2	120	100
(Kizilaslan et al., 2009)	car catalytic converter	Y	N	20	80	10% HCl + 1% H_2O_2	120	95
(Shams et al., 2004)	paraffin dehydrogenation	N	N	2	60	1% NaCN	180	76.3
(Jafarifar et al., 2005)	petroleum refinery	N	Y	2	-	Aqua regia	5	98.3
(Duclos et al., 2016)	PEM fuel cell catalyst	N	N	-	25	HCl (12M) + 3% H_2O_2	1440	91
(Patel and Dawson, 2015)	polymer electrolyte fuel cells untested	N	N	2000	90	potassium iodide 5 mM	20	98.7
(Patel and Dawson, 2015)	polymer electrolyte fuel cells end of life	N	N	666	90	potassium iodide 5 mM	60	96.7
(Sasaki and Maeda, 2014)	car catalytic converter unused	Y	N	-	60	Aqua regia	30	22
(Sasaki and Maeda, 2014)	car catalytic converter used	Y	N	-	60	Aqua regia	30	85
(Sasaki and Maeda, 2014)	car catalytic converter Zn pre-treatment	Y	N	-	60	Aqua regia	30	100
(Sasaki and Maeda, 2014)	car catalytic converter unused	Y	N	-	60	HCl (12M)	30	30
(Sasaki and Maeda, 2014)	car catalytic converter used	Y	N	-	60	HCl (12M)	30	90
(Sasaki and Maeda, 2014)	car catalytic converter Zn pre-treatment	Y	N	-	60	HCl (12M)	30	92
(Zanjani and Baghalha, 2009)	spent naphtha reforming catalysts	Y	N	20	25	I_2 30 g/L, 0.66 M HCl	60	28.3
(Zanjani and Baghalha, 2009)	spent naphtha reforming catalysts	Y	N	30	25	I_2 30 g/L, 0.66 M HCl	180	31.8
(Zanjani and Baghalha, 2009)	spent naphtha reforming catalysts	Y	N	30	75	I_2 30 g/L, 0.66 M HCl	180	76.2
(Zanjani and Baghalha, 2009)	spent naphtha reforming catalysts	Y	N	30	95	I_2 30 g/L, 0.66 M HCl	180	48.3

Further difficulties arise from the use of different leaching techniques. In Table 2.7, aside from what might be considered conventional leaching, there is two other treatment types represented:

-Microwave-assisted leaching (Jafarifar et al., 2005); this technique seems quite promising considering that enables very high leaching efficiency and a very low L/S ratio and low leaching time.

- Zn vapor pre-treatment (Sasaki and Maeda, 2014), – as the name suggests this technique involves the use of Zn vapor to react with the catalyst in such a way as to improve its leachability. This is possible because the formed PGM-Zn alloys (including Pt) is more susceptible to dissolution. This pre-treatment improved the efficiency of leaching with HCl slightly, but its effect on aqua regia was more significant, leading to 15% more Pt leached.

Although temperature of leaching is clearly an important parameter, this aspect can be more noticeable in the work of Zanjani and Baghalha (2009) (Table 2.7) in which the same conditions of iodine (I_2) 30 g/L; 0.66 M HCl and L/S ratio of 30 and time of 180 min were tested fosr Pt leaching with different temperature; 25, 75 and 95 °C. There is a clear increase of leaching at 75 °C when compared to 25 °C (more than double) but there is also a clear decrease when leaching was extended up to 95 °C. The authors suggest that this decrease may be due to precipitation. Regardless of the reason, these results seem to suggest that the relation between temperature and Pt leaching is not necessarily linear and simple and therefore it is an aspect to be optimized in each specific case, particularly if a novel leaching technique is being tested.

Based on Table 2.7, HCl is the most usually studied reagent, either alone or in combination with other reagents, due to its low cost. One such combination is HCl with hydrogen peroxide (H_2O_2) with demonstrably acceptable results for petroleum refinery catalysts (Sun and Lee, 2013) as well as car catalyst (Kizilaslan et al., 2009). In the case of the study by Duclos et al. (2016) the leaching time is 24 h (1440 min), which is likely due to the use of room temperature but also lack of control of leaching time as leaching efficiency would likely be similar with significant lower time. Another combination is the

use of aqua regia – which, despite its considerably strong acidic nature, does not guarantee high leaching as seen in, for example, (Sasaki and Maeda, 2014).

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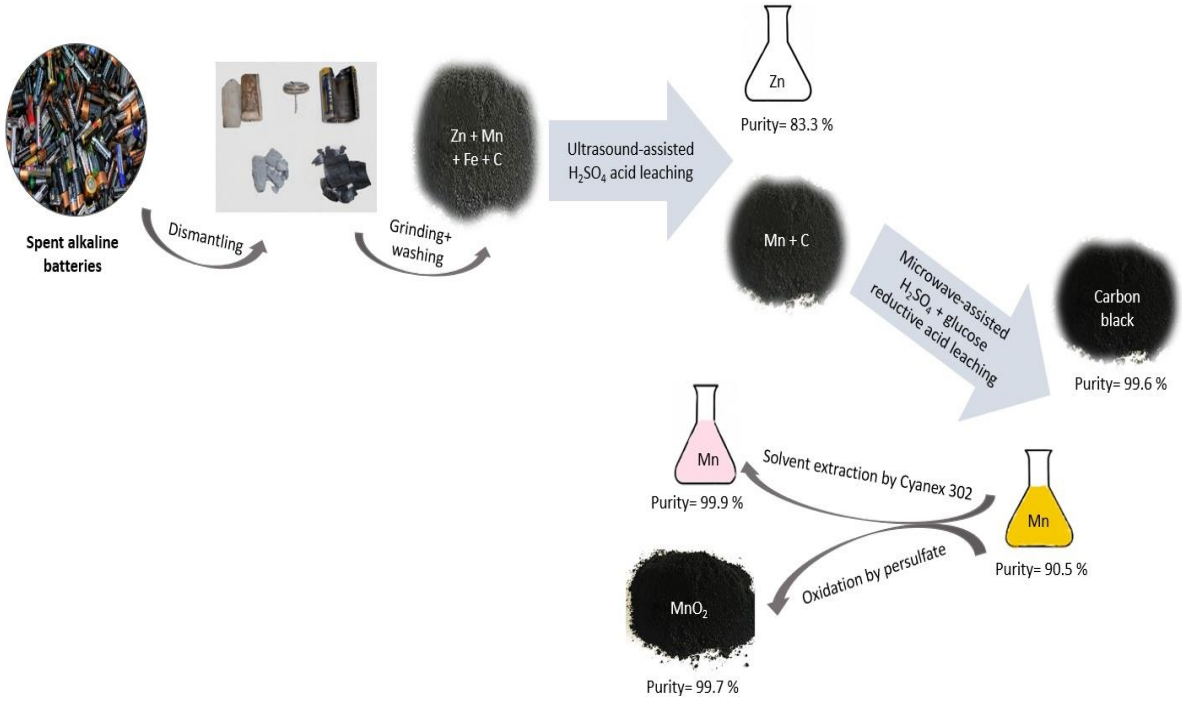
Chapter 3

Recovery of zinc and manganese from spent alkaline battery



Abstract

In this work, initially, the potential of microwave or ultrasound to assist on the efficient and selective acid leaching of Zn from alkaline spent batteries was evaluated and the results compared with the conventional method. For that goal, the acid leaching using microwave- or ultrasound-assisted leaching increased the extraction of Zn from the spent washed residue when compared with the best results attained with the conventional leaching (1.5 M H_2SO_4, 3 h, 80 °C): 90 % of Zn extraction. 94 % of Zn was extracted with microwave-assisted leaching (1 cycle, 30 s, 1 M H_2SO_4) while 92 % of Zn with ultrasound-assisted leaching (2 min, 0.1p 20 % amplitude, 1 M H_2SO_4). Ultrasound-assisted leaching resulted in a more selective (Zn/Mn ratio 5.1) Zn extraction than microwave-assisted leaching (Zn/Mn ratio 3.5); both processes generated a concentrated Zn solution (≥18.7 g/L) with a purity (83.3 %) suitable for electrowinning. Afterwards, leaching from the residue that remained after this first leaching step, which is an enriched Mn residue, was tested. For this purpose, reductive acid leaching using different methods (conventional, ultrasound- and microwave-assisted) were evaluated. The results showed that microwave-assisted leaching was the most effective in terms of the percentage of metal leached (with 98 and 100 % of Mn and Zn, respectively) as well as the effectiveness of time and reagent consumption. Subsequently, two different strategies for purification of Mn from the leachate were considered: oxidative precipitation of Mn with persulfate and solvent extraction with Cyanex 302 as the extractant. Both Mn purification strategies were found to be effective; with oxidative precipitation, a 99.7 % pure MnO_2 precipitate and 3.30 g/L Zn solution with a purity of 99.9 % were obtained at a global yield of 83.5 and 85.1 %, respectively. Solvent extraction resulted in a 32.6 g/L Mn solution with a purity of 99.9 % and 35.2 g/L Zn solution with a purity of 98.4 %, with global yield of 83.6 and 90.6 %, respectively. Based on these conclusions, a process flowsheet is herein proposed, which fulfills the principles of circular economy since both metals (Mn and Zn) were almost completely recovered with high purity from spent alkaline batteries, which allows their effective reuse. A final residue containing 99.6 % carbon black can also be used for combustion.

3.1. Introduction

Alkaline batteries are non-rechargeable (primary cells) and, therefore, designed to be fully discharged. These alkaline cells have a longer lifetime than Zn–C cells and consist of an electrochemical system in which Zn and manganese dioxide (MnO_2) serve as the anode and cathode, respectively. Powdered Zn is mixed with a corrosion inhibitor, and a compacted cathode composed of MnO_2 is mixed with graphite, acetylene black, and a concentrated KOH electrolyte solution (De Souza and Tenório, 2004). In this work, alkaline batteries were chosen because sales trends indicate increasing consumption of alkaline over Zn–C batteries. Moreover, alkaline batteries are predominantly consumed in industrial countries compared to Zn-C batteries (Salgado et al., 2003).

3.1.1. Waste management of spent batteries

Waste management of spent batteries involves collection, transport, treatment and disposal, as well as the monitoring and legal regulation associated with these activities. Some countries have guidelines for the appropriate disposal of spent batteries that include landfill deposition, stabilization by incineration (with certain restrictions) and recycling (Deep et al., 2016).

In Europe, the waste management of spent batteries and accumulators is regulated by Directive 2006/66/EC, which was conferred to all national member states (MS) (Official Journal of the EU, 2006). This Directive regulates the market placement and subsequent collection, treatment, recycling and disposal of batteries in the EU, with the aim of improving the environmental performance. In the framework of this Directive, collection and recycling are mandatory for all portable batteries regardless of a hazardous or non-hazardous classification. This Directive defines a collection rate of spent batteries of 45 % to be reached by 2016 (EU Commission, 2019) and increased 1 % in 2017 (Eurostat, 2019). Ideally, all batteries should be collected and recycled. Collection schemes for each type of battery are more difficult to implement due to difficulties in identification by the consumer of the various types of batteries (Xará et al., 2015). For countries, where an established flux of collection, transport and recycling of batteries is not implemented,

batteries are sent for landfilling and/or incineration. Dumping of batteries at municipal solid waste landfills still occurs and leads to leaching of metals, which increases the metal content from the plot (Tarasova et al., 2012). However, safe disposal in landfills of spent batteries becomes increasingly expensive due to the high amounts of waste as well as the limited sanitary landfill storage capacity (Ruffino et al., 2011; Salgado et al., 2003; Veloso et al., 2005). On the other hand, the incineration of batteries is restricted by environmental legislation because it can release Hg, Cd and dioxins to the atmosphere (Cruz-díaz et al., 2015; Provazi et al., 2011). In recent years, interest in the recycling of spent batteries has grown. In 2013, in China, which is the biggest world producer of batteries, the production of Zn-based batteries reached 3.2×10^{10} (1.3×10^{10} corresponded to alkaline batteries) units; this amount corresponds to 5 times the total production of the others portable batteries (Sun et al., 2015).

The recovery of metals from spent alkaline batteries is based on pyrometallurgical or hydrometallurgical operations (Salgado et al., 2003). Pyrometallurgical processes are very energy intensive, and some emissions of dust and gases are expected (El-Nadi et al., 2007; Pedrosa et al., 2009; Salgado et al., 2003). Hydrometallurgical routes are commonly more economical and efficient than pyrometallurgical methods. The hydrometallurgical option is more versatile considering the final metal species produced, the lower energy consumption and the lack of air pollution since there are no particles produced. As it was already discussed in chapter 2 (section 2.4), hydrometallurgical processes are usually based on the dissolution of metal phases (essentially Zn and Mn oxides) in aqueous alkali (Buzatu et al., 2013; Shin et al., 2007, 2009) or acidic (Buzatu et al., 2014; El-Nadi et al., 2007; Wang et al., 2014) media. However, concentrated solutions, high temperatures and long reaction times are usually used, which are great disadvantages of these processes. To overcome these shortcomings, metal dissolution can be assisted by auxiliary energies, such as ultrasound and microwave irradiation, which have proven to be successful in the minimization of energy and optimization of reaction conditions (Marafi and Stanislaus, 2011; Pinto and Soares, 2013, 2012). In fact, several studies have shown the inherent advantages of these strategies over the conventional process for metal leaching from ores and spent residues. For example, Li et al. (2008) achieved an increase of 20 % in Mn extracted

from slag using an ultrasound-assisted method compared with the conventional method. Similarly, Wang et al. (2014) increased Zn extraction by 13 % using ultrasound-assisted H_2SO_4 leaching. In addition, ultrasound is used to promote selective leaching, as demonstrated by Li et al. (2010), who attained a more selective extraction (by approximately 10 %) of Cu, Zn and Ni over Fe and Cr when ultrasound was applied to an electroplating sludge.

On the other hand, some authors have suggested that the same metal recovery is achieved when microwave or conventional methods are applied, but shorter processing times are necessary for microwave leaching. Bayca et al. (2013) leached boron oxide from colemanite with an acid solution and obtained a recovery close to 100 % using microwave and conventional methods, but the leaching time was significantly smaller when the microwave was used. Chen et al. (2013) achieved high recovery of Au after leaching refractory ores with sodium cyanide for 12 min using microwave leaching, whereas 24 h were required under conventional conditions. Wu et al. (2009) obtained similar Cu removal yields from industrial sludge using traditional (48h) and microwave-assisted (30 min) acid extraction.

Moreover, the application of microwaves can improve the selective dissolution of metals, as demonstrated by Pinto and Soares (2012); these researchers showed that the extraction of Mo from hydrodesulphurization catalysts resulted in a more selective and higher dissolution of the metal using mild alkaline conditions and shorter processing times than when the conventional method was used. In the context of the battery industry, the production of new batteries based on recycled materials from spent batteries is the most energy efficient strategy and maximizes the reuse of the recycled materials. However, this strategy assumes that the metals recycled from spent batteries are obtained in high purity and can be reused to produce new batteries.

Based on these facts, the main aims of this work were to first evaluate the possibility of using ultrasound and microwaves to assist the selective leaching of Zn in high yield from spent alkaline batteries and to compare the results with those obtained using the conventional leaching procedure. For this purpose, acid leaching using H_2SO_4 was employed. In a second attempt, our aim was to recycle Mn efficiently and selectively

from the remained enriched Mn residue using a simple environmentally friendly two-step process based on efficient leaching of the metals and the subsequent purification of Mn (and Zn).

Considering the huge amount of alkaline batteries sold per year, the work developed herein will certainly contribute for recycling Zn and Mn from an important solid waste produced every year using more efficient and greener management strategies.

3.2. Experimental

3.2.1. Reagents

Analytical grade H_2SO_4 (Fluka, 96 %) was used as leaching agent alone or together with anhydrous D(+)-glucose (Merck, ≥ 99.5 %), which was used as reducing agent. NaOH (Eka, p.a) was used for acid neutralization while ascorbic acid (Merck, extra pure) was used for total digestion of solid samples. Sodium persulphate ($Na_2S_2O_8$, Sigma-Aldrich, >99.0%) was used for the oxidative precipitation of Mn while Cyanex 302 (Sigma-Aldrich, 85%) and kerosene (Alfa Aesar) were used for solvent extraction.

3.2.2. Metals quantification

Metals were determined in solution by atomic absorption spectroscopy with flame atomization (AAS-FA) with an air-acetylene flame using a PerkinElmer AAnalyst 400 (Norwalk, CT, USA) or an Analytik Jena novAA 350 spectrometers (Konrad-Zuse, Germany).

3.2.3. Preparation of the spent alkaline batteries residue and characterization of the residues

For this work, spent alkaline batteries of different sizes, brands and origins were used. Spent alkaline batteries were manually dismantled using an electrical saw to recover the

parts that were rich in Zn (anode) and Mn (cathode). Plastics, paper films and ferrous and nonferrous scraps were discarded.

The obtained paste was dried in air at 105 °C for 24 h, crushed in a domestic miller and finally sieved to obtain a fraction smaller than 1 mm. The grain size was selected based on the literature (Ferella et al., 2008).

Part of the powder was subjected to a two-step washing process using deionized water. The washing process was performed in a shaking bath with temperature control (OLS200, Grant) for 1 h at 80 °C with 200 rotations per minute (RPM) using a L/S ratio of 5. Between the two washing steps, the powder was dried in air at 105 °C overnight. Then, the powder was dried for 24–48 h at 105 °C until the moisture was removed, and a constant weight was obtained. The weight loss was calculated.

The metal compositions of the washed residue, the residue after ultrasound-assisted leaching (residue after first leaching) and the residue after the microwave-assisted leaching (residue after the second leaching) were determined in the solutions that resulted from acid digestion with 2 M H_2SO_4 and 26 g/L ascorbic acid. The digestion assays were performed in a shaking bath with temperature control (OLS200, Grant) for 3 h at 70 °C and 200 RPM with a L/S ratio of 20, and after filtration, each metal in solution was quantified by AAS-FA.

XRD on a Philips X'Pert X-ray diffractometer using Cu Kα radiation under operating conditions of 40 mA and 45 kV with a step size of 0.04° and a scan step time of 30 s was used to identify the forms of Zn and Mn in the washed residue.

3.2.4. Acid leaching tests

Three different leaching strategies were evaluated: (i) conventional leaching, (ii) microwave-assisted leaching, and (iii) ultrasound-assisted leaching.

The conventional leaching assays were performed using Falcon tubes in a shaking bath (OLS200, Grant) with temperature control and agitation (200 RPM). The microwave-assisted leaching assays were performed in a domestic microwave oven (800 W, 2.45 GHz) with polytetrafluoroethylene (PTFE) bombs (container volume of 23 mL).

Ultrasound-assisted leaching was carried out using a Bandelin Sonopuls HD 2200 ultrasonic homogenizer (power of 200 W and output frequency of 20 kHz ± 500 Hz) with a 3 mm titanium microtip (Berlin, Germany) and a control panel for power selection to change the size of the electrical pulse and the amplitude of the ultrasound pulse, which create different pressures in the liquids; falcon tubes with conical bottoms were used because this geometry is considered to minimize dead zones in sonochemistry (Capelo-Martinez, 2009).

The metal leaching yield was determined by quantifying each metal in the leaching solutions by AAS-FA, as previously mentioned, after filtration. All experiments were performed at least in triplicate.

3.2.4.1. First acid leaching

The acid leaching tests were performed under different conditions using H_2SO_4. For conventional leaching, variations in the H_2SO_4 concentration (between 0.5 and 2 M) and time (1 and 3 h) were evaluated at 80 °C. For microwave-assisted leaching, variations in the H_2SO_4 concentration (between 0.5 and 2 M) and time (30 and 60 s) were studied using one-cycle assay. Samples were allowed to cool for 20 min before filtration. For ultrasound-assisted leaching, the concentration of H_2SO_4 was varied between 0.5 and 1.5 M as well as the time of the assay (between 1 and 6 min). In all experiments, the (L/S) ratio was maintained at 10.

3.2.4.2. Second (reductive) acid leaching

A second reductive leaching step was applied to the residue after the first leaching (i.e. the residue resultant from the best previous experimental conditions: ultrasound-assisted leaching), which resulted in the highest Zn extraction) to evaluate the potential ability for leaching Mn totally from the residue. Glucose was chosen as reductant for solubilizing Mn(IV) to Mn(II). At this stage, the same three different strategies (conventional method, ultrasound- and microwave-assisted leaching) were tested under the following conditions:

(i) Conventional leaching was conducted at 70 °C for 4 h with 1.5 M H_2SO_4 and 20 g/L glucose; two L/S ratios were tested: 10 and 20.

(ii) For ultrasound-assisted leaching, ultrasonic parameters were kept at 0.1 s and 20 % for pulse time and wave amplitude, respectively. The leaching experiments were conducted using 1.5 M H_2SO_4 and 20 g/L glucose for a L/S of 20 for two different times (2 and 14 min).

(iii) Microwave heating was performed with different L/S ratios (between 5 and 20), H_2SO_4 concentrations (1 and 1.5 M), glucose concentrations (15 and 20 g/L) and times (60 and 90 s).

3.2.5. Manganese purification

Two procedures for Mn purification were applied to the microwave-assisted second stage leachate: a purification by oxidation and a solvent extraction procedure.

The recovery of Mn, as MnO_2, was accomplished by oxidation adding $Na_2S_2O_8$ to the leaching solution in varied $Na_2S_2O_8$:Mn molar ratios (between 1 and 2) after previous pH adjustment to approximately 5 using NaOH. All recovery tests were conducted in a shaking thermostatic bath at 90 °C and agitation (150 RPM) for 3 h. Then, the solid was separated from the liquid by filtration and dried subsequently at 105 °C for 24 h. The structure of the dried solid as well as its total metals characterization was performed as described above, and the metal content in the resulting liquor was evaluated by AAS-FA, as described above.

The recovery of Mn with Cyanex 302 liquid-liquid extraction was performed using kerosene as diluent. First, the pH of the leachate solution was adjusted to 3, and a 1:1 v/v solution of Cyanex 302 and kerosene was added to the leachate in an aqueous/organic (A/O) ratio of 5:1. This mixture was vigorously shaken (~30 min) to promote the capture of Zn by Cyanex 302. The pH was controlled at 2.7 throughout the whole procedure. Because the pH continuously decreased in the extraction process, NaOH was added to restore the initial pH of 2.7.

At the end, the organic and aqueous phases were allowed to separate and settle. The Zn in the organic phase was then stripped using 4 M H_2SO_4 with an A/O ratio of 1:2, under vigorous shaking. The Mn, Zn, and Fe contents in both the aqueous phase and stripped solution were measured by AAS-FA, as described above.

3.2.6. Chemical computer simulations

Metal chemical speciation calculations were evaluated using the computer program Visual MINTEQ (Ver. 3.0, KTH, Sweden). All chemical equilibrium concentrations of all species considered in the model by the program reactions were generated based on component stability (Martell and Smith, 2004) and molar concentrations.

3.3. Results and discussion

3.3.1. Water washing and characterization of the spent alkaline batteries residues

In addition to metallic oxides, such as ZnO and Mn_xO_y, potassium superoxide (KO_2) is present in the spent alkaline batteries residues. KO_2 results from the oxidation by air of the electrolyte solution containing KOH during the pretreatment step (De Souza et al., 2001).

Because Zn and Mn oxides are insoluble in water, KO_2 can be separated by washing the powder with deionized water. This process is often performed as a pretreatment step in processes in which the main leaching step consists of acidic conditions because it reduces the consumption of acid (De Michelis et al., 2007). Later, this alkaline washing water can be evaporated to obtain KOH salt, and the recycled salt can be reused (Veloso et al., 2005).

The water content of the original powder, determined from the weight loss after drying at 105 °C, was 8.4%, which agrees with the contents reported in the literature (Ferella

et al., 2010, 2008, 2006; Moscardini et al., 2009; Salgado et al., 2003). After both deionized water washing steps, the contents of K, Zn and Mn present in the washing water were determined, and the pH was measured. The pH values and the amounts of metals removed are presented in Table 3.1.

The first washing water had a pH of 12, and the second had a pH of 11. Additionally, K removal was higher in the first washing step than in the second [(7.4 ± 0.6) and (3.7 ± 0.3) mg/g, respectively].

Table 3.1. *pH in the washing waters and removal amounts of Mn, Zn and K, expressed in mass of metal per gram of residue, from the spent residue after the first and second deionized water washing steps. Weight loss of the original spent residue after the washing processes. Each value represents the average of three replicates with respective standard deviations.*

	First step	**Second step**	**Total**
pH	12.0	11.0	-
Mn(μg/g)	2.7 ± 0.7	4 ± 1	6 ± 2
Zn (μg/g)	6.6 ± 0.3	2.7 ± 0.8	9.3 ± 0.8
K (mg/g)	7.4 ± 0.6	3.7 ± 0.3	11.2 ± 0.8
Weight loss (%)	5.8 ± 0.5	1.4 ± 0.2	7.2 ± 0.5

Mn and Zn were not significantly removed in either washing step; a total of 6 and 9.3 μg of Mn and Zn, respectively, were removed from each gram of the original powder after completion of both steps (Table 3.1). The weight loss from the residue after the first and the second washing steps was (5.8 ± 0.5) and (7.2 ± 0.5) %, respectively. Ferella et al. (2006) reported a weight loss of 5.7 % after only one washing step, which agrees with our results (Table 3.1).

Fig. 3.1 presents the diffractogram of the washed spent alkaline battery residue. ZnO was the main Zn compound detected (41 %), followed by $ZnMn_2O_4$ (27 %). However, a small (approximately 6 %) amount of Mn_3O_4 was also detected. According to Eqs. 2.3

and 2.5 (De Michelis et al., 2007), H_2SO_4 reacts with Zn and Mn oxides to produce Zn and Mn sulphate compounds, which are soluble in water.

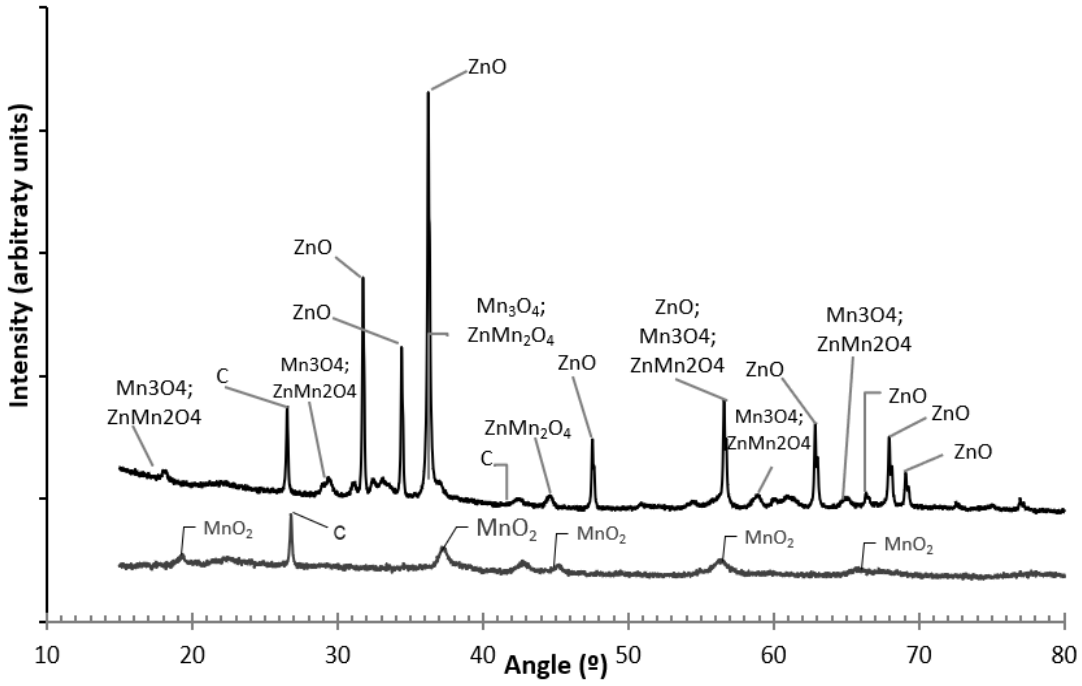


Fig. 3.1. *XRD analyses of the washed residue before (black line) and after leaching (grey line).*

Moreover, acidic treatment causes the disproportionation of other Mn compounds (Mn_2O_3, Mn_3O_4, and $ZnMn_2O_4$) [chapter 2 (section 2.4), Eqs. (2.6)– (2.8)], forming insoluble Mn oxides (MnO_2 and Mn_2O_4) and other soluble Zn and Mn oxides [chapter 2 (section 2.4), Eqs. (2.6) and (2.8)].

As mentioned above, Mn can be present in different oxidation states (Mn^{2+}, Mn^{3+} and Mn^{4+}) in various solid forms. Since aqua regia does not solubilize all solids containing the highest oxidation states (Mn^{3+} and Mn^{4+}), a stronger reductant, such as ascorbic acid, is needed to solubilize all Mn forms to Mn^{2+} and then quantify the total amount of Mn. In this work, ascorbic acid was selected, as the reductant, since it completely dissolves the Mn oxides with a high oxidation state present in spent alkaline battery residues according to the following Eq. (Kursunoglu and Kaya, 2014):

$$10\ MnO_2\ (s) + 10\ H_2SO_4\ (aq.) + C_6H_8O_6 \leftrightarrow 10\ MnSO_4\ (aq.) + 6\ CO_2\ (g) + 14\ H_2O\ (l) \quad (3.1)$$

Next, the total amounts of the metals were determined in the washed spent alkaline battery residues after complete digestion with H_2SO_4 and ascorbic acid, as described in the experimental procedure, and are presented in Table 3.2. The total amounts of Zn (20 %) and Mn (28 %) represented almost half of the total weight of the spent alkaline battery residues, which agrees with the XRD results discussed above. Considering that the cathodic part of the alkaline batteries was constituted by Mn oxides and graphitic C, the latter also represented a significant component (25 %, determined by XRD) of the residue.

The levels of Cd were below the maximum values allowed by Directive 2006/66/EC, which prohibits the sale of batteries containing more than 0.002 % Cd (Official Journal of the EU, 2006). Minor amounts of Fe and Ni were also present. The amount of Pb present in the powder was very low (≤0.01 %). The composition of the powder is in good agreement with the compositions determined in previous studies (De Souza and Tenório, 2004; Salgado et al., 2003; Sayilgan et al., 2009; Veloso et al., 2005).

Table 3.2. *Average chemical composition, expressed in %, of the washed spent alkaline battery residues. Each value represents the average of three replicates with respective standard deviations.*

Element	Zn	Mn	Fe	Ni	Cd
	20 ± 3	28 ± 5	0.35 ± 0.09	0.0052 ± 0.0002	0.01 ± 0.001

3.3.2. First acid leaching of the washed residue

As explained above, H_2SO_4 cannot reduce all Mn oxides. Considering the composition of the Mn oxides in the residue described above, much of the Mn present in the spent alkaline batteries would not be expected to be converted to a soluble Mn form and, thus, would not be leached from the residue when using only H_2SO_4 as the leaching agent. Therefore, since our goal for the first stage was to recover Zn from the residue in

high yield and with the best selectivity compromise (higher [Zn]/[Mn] ratio), different acid assisted leaching processes were evaluated.

First, the conventional method was used for comparative purposes. Table 3.3 presents the amounts of Mn and Zn leached after 1 and 3 h using 0.5 M H_2SO_4. The leaching of both metals increased with time, which indicates that equilibrium had not been established after 1 h. More time (3 h) was needed for the leaching. Nevertheless, after this long period of time, only approximately 61 % of the total Zn was leached. To increase the leaching efficiency, further experiments with increasing H_2SO_4 concentrations were performed (Fig. 3.2.A). As observed, the leaching of Zn and Mn increased with the acid concentration.

At 1 M H_2SO_4, an increase in Zn leaching of 25 % (from 61 to 86 %) was observed compared to that at 0.5 M H_2SO_4. At 1.5 M H_2SO_4, 90 % of the Zn was removed (similar to the leaching yield obtained with 2 M H_2SO_4). As expected, Mn leaching was less than Zn leaching. The maximum removal of Mn was 20 % with 2 M H_2SO_4.

Table 3.3. *Zn and Mn extraction from the washed residue, expressed in %, using the conventional procedure (H_2SO_4 0.5 M, at 80 °C, agitation of 200 RPM and L/S of 10) and Zn leaching selectivity, expressed as [Zn]/[Mn] ratio. Each value represents the average of at least three replicates with respective standard deviations.*

Time	Zn	Mn	[Zn]/[Mn]
1 h	52.2 ± 0.7	8.13 ± 0.03	4.6
3 h	61± 1	11.5 ± 0.2	3.8

The Zn leaching selectivity, expressed as the [Zn]/[Mn] ratio, was also affected by the concentration of H_2SO_4; when the H_2SO_4 concentration was increased from 0.5 to 1 M, the [Zn]/[Mn] ratio increased from 3.8 to 4.2, respectively. However, higher concentrations of H_2SO_4 decreased the Zn leaching selectivity to 3.5 and 3.3 when 1.5 and 2 M H_2SO_4 were used, respectively. In addition to the decrease in selectivity at higher H_2SO_4 concentrations, the amount of Zn that was leached increased, which is more favorable for the aim of the leaching process.

The Zn extraction yield obtained in this work was of the same order of magnitude as those described by El-Nadi et al. (2007) (87.7 % of Zn leached) using similar conditions of acid leaching (2 M H_2SO_4, 50 °C, 2 h). On the other hand, Buzatu et al. (2013) obtained a value of 96 % of Zn leached at a lower temperature (60 °C) and in less time (1 h) but using a high concentration of H_2SO_4 (2 M), and the process was less selective because of the high amount (43 %) of Mn leached. De Souza and Tenório (2004) reported complete Zn extraction from spent alkaline battery residues using 0.13 M H_2SO_4 (L/S of 60) at 70 °C for 4 h. However, 40 % of the Mn was also extracted.

To improve the extraction yield of Zn in a shorter leaching time, microwave- and ultrasound-assisted leaching experiments were tested using H_2SO_4 as the leaching agent. As a first attempt, microwave-assisted leaching tests were performed in a single cycle of 30 or 60 s.

The removal of Mn was much less effective, but a similar removal profile was observed: the leaching increased from approximately 13 to 19 % when the H_2SO_4 concentration was doubled from 0.5 to 1 M, with no increases at higher H_2SO_4 concentrations. The lowest efficiency of Mn leaching resulted from the fact that the residue was constituted by Mn oxides with oxidation states that were higher than +2, which do not completely dissolve in the presence of H_2SO_4, as stated previously.

For both metals, no difference in leaching was observed when cycles of 30 or 60 s were used (Fig. 3.2.B). Therefore, increasing the leaching time was not advantageous under these experimental conditions.

Comparative analysis of the results obtained from conventional and microwave-assisted leaching using 1 M H_2SO_4 evidences that the latter promotes increased Zn (86 and 94 %, respectively) and Mn (15 and 19 %, respectively) leaching. However, a slight decrease in selectivity ([Zn]/[Mn] ratio of 4.2 and 3.5 for conventional and microwave-assisted leaching, respectively) occurred as a consequence of the greater increase in Mn removal compared with Zn removal.

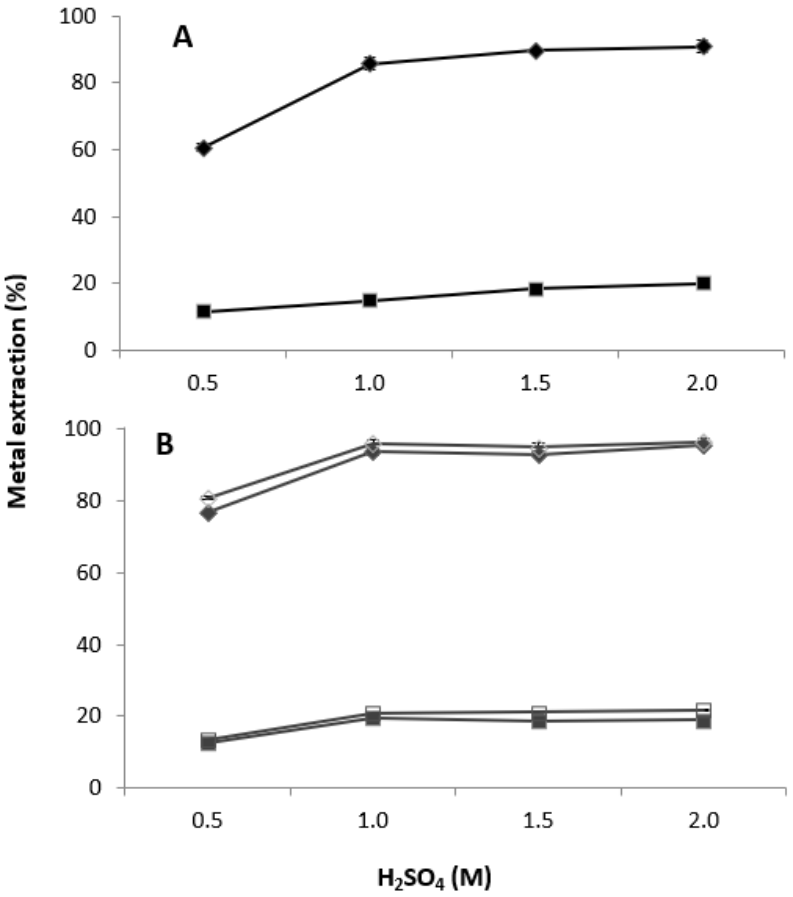


Fig. 3.2. *Influence of the H_2SO_4 concentration on the Zn (◆) and Mn (■) extraction from the washed spent alkaline batteries residue with a L/S ratio of 10 using conventional (3 h, 80 °C, 200 RPM)* ***(A)*** *or microwave-assisted (30 and 60 s: full and empty symbols, respectively) leaching* ***(B)****. Each point represents the average of at least three replicates with respective standard deviations (vertical error bars). Where no error bars are shown, standard deviations are within the points.*

Even though a smaller [Zn]/[Mn] ratio was obtained using microwave-assisted leaching, this approach appears to be more promising than the conventional method because better Zn leaching was obtained using the same concentration of leaching agent in much less time in the former approach, resulting in lower reagent and energy consumption.

The ultrasound-assisted method was used as a rapid sample pre-treatment technique to determine the possibility of simultaneously obtaining high extraction efficiency and improved selective leaching of Zn. Since the acid leaching extraction results obtained

using conventional and microwave approaches demonstrated that 0.5 M H_2SO_4 was not sufficient to leach Zn in high efficiency, we studied the effect of time on the ultrasound-assisted leaching of Zn and Mn at two different concentrations of H_2SO_4 (1 and 1.5 M) while maintaining the pulse and wave amplitude at 0.1 p and 20 %, respectively.

At 1 M H_2SO_4, the Zn leaching improved until 2 min, reaching 92 % (Fig. 3.3); longer assays did not result in higher Zn extraction. At 1.5 M H_2SO_4, Zn extraction increased in the longer assays, and 100 % of Zn was leached in 6 min. At both H_2SO_4 concentrations, Mn extraction increased with the leaching time and was slightly higher in the assays performed with 1.5 M H_2SO_4. Overall, the increase in leaching time resulted in a loss of selectivity.

Assays lasting 2 min and using 1 M H_2SO_4 were the best ultrasound-assisted leaching conditions, with which a high Zn extraction of 92 % was achieved in a short period of time, together with the highest Zn selectivity ([Zn]/[Mn] ratio of 5.1).

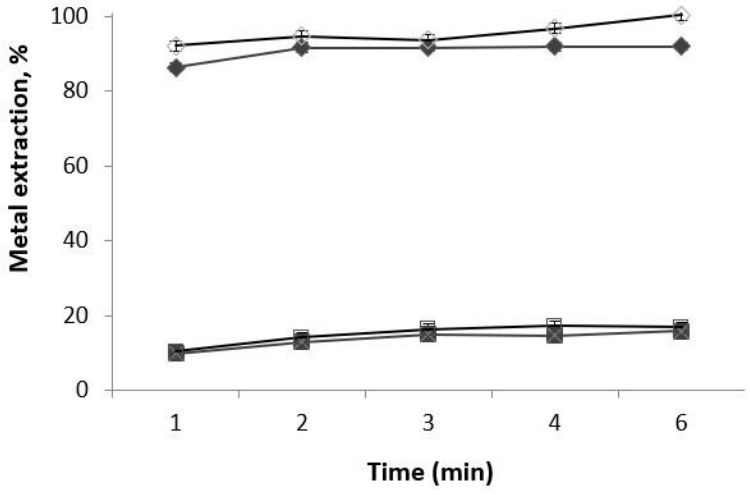


Fig. 3.3. *Influence of time on the ultrasound-assisted leaching of Zn (◆) and Mn (■) from the washed spent alkaline batteries residue with a L/S ratio of 10 using H_2SO_4 1 (full symbols) and 1.5 M (empty symbols). Pulse 0.1 p and 20 % amplitude. Each point represents the average of at least three replicates with respective standard deviations (vertical error bars). Where no error bars are shown, standard deviations are within the points.*

3.3.2.1. Comparative analysis of the three acid leaching strategies

Among the three approaches tested, the conventional method was the least efficient. Additional time and a higher acid concentration (2 M H_2SO_4) were needed to obtain the same results.

On the other hand, microwave- and ultrasound-assisted acid leaching resulted in high Zn removal (94 and 92 %, respectively) from the spent washed alkaline battery residue using a lower acid concentration (1 M H_2SO_4) and shorter leaching duration. However, ultrasound-assisted leaching proved to be superior over the microwave-assisted method since it produced a Zn solution with better selectivity ([Zn]/[Mn] ratio of 5.1 using ultrasound *versus* 3.5 using microwaves), which translates to a high-pure Zn solution.

Moreover, the overall ultrasound-assisted leaching method for Zn was faster than the microwave method [2 min for the ultrasound process *versus* 20.5 min (1 cycle of 30 s plus 20 min for sample cooling) for the microwave process].

The improved performance of the microwave technology compared to the conventional method is mainly due to the volumetric (direct conversion of electromagnetic energy into thermal energy instead of the conductive or convective energy transfer from the surface to the interior of the material or solution in the conventional process), controllable and selective (selective heating of solid particles over solutions, which results in a higher temperature of the reaction interface than the bulk solution; the temperature gradient generated between the two phases increases the reaction rate) heating by the microwave radiation, which results in higher temperature (which can be higher than 100 °C after 30 s of heating) and pressure inside the PTFE vessel. These conditions permit the rapid extraction of Zn using reduced reagent concentrations and a shorter processing time, which was not possible in the thermostatic bath.

On the other hand, in ultrasound-assisted leaching, extreme conditions of pressure and temperature (potentially reaching approximately 100 MPa and 5000 K, respectively) (Brunelli and Dabalà, 2015; Luque de Castro et al., 2011) are caused by cavitation (a consequence of the expansion and compression cycles created by the ultrasound waves, leading to the formation and implosion of small vacuum bubbles); the collapse of the

cavitation bubbles provokes the movement of high-speed micro-jets towards the solid surface (Brunelli and Dabalà, 2015; Luque de Castro et al., 2011) which results in the erosion and cracking of the solid surface and enhanced penetration of the liquid.

These facts explain the faster and more efficient dissolution of Zn compared to that observed in the conventional experiments. Comparison of the diffractograms of the washed residue and the residue that remained after microwave-assisted acid leaching [since similar removal of Zn was achieved using microwave and ultrasound-assisted leaching (94 and 92 %, respectively), this residue was selected as representative of both methods] revealed that the peaks related to ZnO and $ZnMn_2O_4$ were completely absent in the XRD pattern of the residue after acid leaching.

The differences between the XRD patterns of the washed residue and the residue that remained after microwave-assisted acid leaching suggest that these two chemical species were completely removed during the acid leaching, which is in good agreement with the high Zn leaching yield obtained (approximately 94 %) (Fig. 3.2 B).

Additionally, comparison of the XRD patterns of the washed residue and the residue that remained after microwave-assisted acid leaching indicates that Mn_3O_4 was also completely removed during acid leaching, and a new species, identified as MnO_2, was present in the XRD pattern of the residue after acid leaching (Fig. 3.1, grey line). The formation of this species agrees well with the chemical dissolution mechanisms described previously [chapter 2 (section 2.4), Eqs. (2.6) and (2.7)] and explains why a significant amount of Mn remained insoluble.

In Table 3.4, the metal compositions of the solutions obtained using the optimized ultrasound- and microwave-assisted conditions for acid leaching are shown. The leaching selectivity for Zn over Mn, expressed as the [Zn]/[Mn] ratio, is also given.

Both methods can recover high amount of Zn (final Zn concentration of ≥18.7 g/L) which achieved the purity of the final solution of Zn (83.3 and 77.7 % for ultrasound and microwave-assisted leaching, respectively) (Table 3.4).

Table 3.4. *Metals concentrations and Zn leaching selectivity (expressed as [Zn]/[Mn] ratio) of the leaching solutions obtained using optimum ultrasound- and microwave-assisted strategies for acid leaching conditions. The concentrations values presented are the average of at least three replicates determinations.*

	Acid leaching	
	Microwave (1 cycle of 30 s, 800 W, 2.45 GHz)	**Ultrasound (2 min, 0.1 p and 20 %)**
Zn (g/L)	19.2	18.7
Mn (g/L)	5.5	3.7
Fe (mg/L)	24	51
Ni (mg/L)	0.6	2
Cd (mg/L)	0.3	1
[Zn]/[Mn]	3.5	5.1
Zn purity (%)	77.7	83.3

3.3.3. Metal characterization of the residue obtained after the first leaching

The residue obtained from the ultrasound-assisted acid leaching (1 M H_2SO_4, L/S ratio of 10, 2 min, 0.1 p and 20 % wave amplitude) was used for further processing. The XRD analysis of this residue is shown in Fig. 3.1, which evidences that the residue in mainly constituted by Mn plus C.

In addition to this analysis, the metal quantification of the main metals present in the residue was obtained by total acid reductive digestion. The metal composition of this residue is provided in Table 3.5. Besides C, the residue contains Mn, which is the main metal present with approximately 90 % of the total metallic content, followed by Zn (9.2 %) and Fe (0.9 %). Minor amounts of Cd and Ni were also detected.

Table 3.5. *Metal composition of the residue after the first leaching. The data represent the mean and standard deviations of three replicates.*

Element	Mn	Zn	Fe	Ni	Cd
mg/g	338.8 ± 3.7	34.8 ± 0.99	3.5 ± 0.27	0.052 ± 0.001	0.008 ± 0.001

3.3.3.1. Reductive acid leaching

The XRD analysis of the waste after the first acid leaching (Mn-rich residue) evidenced that Mn in the residue was present as MnO_2. Therefore, a reductive acid leaching process is needed in order to solubilize Mn(IV) to Mn(II). For this purpose, several reductants have been described in the literature, like H_2O_2 (Buzatu et al., 2014; El Hazek et al., 2006), corncob (Tian et al., 2010), and different carbohydrates (Beolchini et al., 2001; Furlani et al., 2009; Pagnanelli et al., 2004; Trifoni et al., 2000) including glucose. Among them, glucose seems to be a good option considering its availability, price and reductive power.

The leaching process using glucose, as reducing agent, has the following global reaction (Veglio' and Toro, 1994):

$$C_6H_{12}O_6\,(aq) + 12MnO_2(s) + 24H^+(aq) \rightarrow 6CO_2\,(g) + 12\,Mn^{2+}(aq) + 18H_2O\,(l) \qquad (3.2)$$

where H^+ is supplied by H_2SO_4.

Comparatively to H_2O_2, glucose is a stronger reductant, as it can be anticipated by the redox potentials (Bleam, 2011):

$$E^o_{(MnO_2)/(Mn^{2+})} = 1.224\ V; \quad E^o_{(CO_2)/(C_6H_{12}O_6)} = 0.404\ V; \quad \Delta E^o_{cell} = 0.820\ V \qquad (3.3)$$

$$E^o_{(MnO_2)/(Mn^{2+})} = 1.224\ V; \quad E^o_{(O_2)/(H_2O_2)} = 0.695\ V; \quad \Delta E^o_{cell} = 0.529\ V \qquad (3.4)$$

Moreover, glucose is safer to use, as H_2O_2 carries safety concerns as well specialized material due to its high reactivity. Based on all these facts and considering that glucose is also economically more attractive, in this work, glucose was chosen as reductant.

Firstly, metal extraction was conducted using conventional leaching. The results are provided in Table 3.6.

Table 3.6. *Metal recovery yields from conventional leaching method using different L/S ratios with 1.5 M H_2SO_4 and 20 g/L glucose, at 70 °C for 4 h. Data represent the mean and standard deviations of three replicates.*

	Leaching yield (%)	
L/S ratio	**Mn**	**Zn**
10	92 ± 0.3	98.5 ± 0.6
20	95 ± 0.4	100.0 ± 0.4

For both metals, an increase of the L/S ratio resulted in a slight increase of the leaching yield. For the ratio of 20, total extraction of Zn was achieved (Table 3.6). However, this did not happen for Mn, for which a maximum recovery yield of 95 % was obtained even with the increase of the L/S ratio. When the L/S ratio was increased from 10 to 20 (a two-fold increase in the use of reagents (Table 3. 6) this only resulted in a very slight (3 %) improvement of the leaching of Mn.

Leaching yields of Zn were consistently higher than those of Mn. These leaching yields are in agreement with results described by other authors with alkaline battery residues in similar conditions (Chen et al., 2017; Furlani et al., 2009). However, since the leaching procedure required 4 h, which results in a high energy consumption, other leaching alternatives were considered.

Subsequently, ultrasound-assisted leaching was evaluated. Under these conditions, the extraction yields were: 9.3 and 41.8 % for Mn and 41.0 and 78.8 % for Zn, after 2 and 14 min, respectively (Table 3.7).

Table 3.7. *Metal recovery yield from ultrasound-assisted leaching at different times and with 1.5 M H_2SO_4 and 20 g/L glucose, L/S ratio of 20. Data represent the mean and standard deviations of three replicates.*

	Leaching yield (%)	
Time (min)	**Mn**	**Zn**
2	9.3 ± 0.1	41.0 ± 0.9
14	41.8 ± 0.1	78.8 ± 0.4

Comparatively, these results were worse than those obtained with the conventional method (Table 3. 6). This was somewhat unexpected, as the application of ultrasound-assisted methods have resulted in higher extraction yields of other complex matrices. For example, Li et al. (2008) have optimized an ultrasound-assisted extraction procedure of Mn from Mn rich slag, and concluded that it was superior to the conventional extraction. However, in their work, more than twice as much time (35 min) was required for the leaching procedure, and the extractant medium was concentrated H_2SO_4 with a small quantity of HCl and citric acid (2 g/L). These stronger conditions may be the cause of the increased Mn leaching yield.

Another reason may also be the type and the lower concentration of Mn present in the slag. Additionally, the cavitation generated by the ultrasound may produce H_2O_2 and ozone (O_3), which may impair the extraction of Mn by oxidising Mn^{2+} back into MnO_2 (Frolova and Shapa, 2011; Okitsu et al., 2009).

In a third attempt, microwave-assisted leaching was tested. To determine the suitability and best conditions for microwave-assisted leaching, different test conditions were used (Table 3. 8).

Table 3.8. *Mn and Zn extraction from the residue using microwave-assisted leaching method. Values represent the average of three replicates with standard deviations.*

Condition					Metal recovered (%)	
Test	**L/S ratio**	**H_2SO_4 (M)**	**Glucose (g/L)**	**Time (s)**	**Mn**	**Zn**
A)	20	1.5	20	60	99.8 ± 0.4	96.7 ± 0.2
B)	10	1.5	20	60	94.0 ± 0.2	93.5 ± 0.2
C)	5	1.5	20	60	66.9 ± 0.8	88.6 ± 0.4
D)	10	1.5	20	90	100.0 ± 0.5	100.0 ± 0.2
E)	10	1.0	20	90	88.5 ± 0.7	89.5 ± 0.4
F)	10	1.5	15	90	98.0 ± 0.07	100 ± 0.09

By using similar experimental conditions (L/S ratio of 20, test A, Table 3.8) as those used in conventional method, an almost total leaching of both metals (99.8 and 96.7% of Mn and Zn, respectively) was achieved from the residue with one 60s microwave cycle.

Similar leaching yields were achieved when conventional leaching was used, but a much longer leaching time (4 h) was necessary. The high pressure resulting from the production of carbon dioxide (CO_2) and the high temperature generated inside the unit pumps may be the reason for the effectiveness of the microwave methodology. Since almost all metals were extracted under these conditions, the possibility of reducing the amounts of reagents involved was evaluated.

In tests B and C (Table 3.8), the L/S ratios were decreased from 20 to 10 and 5, respectively, resulting in a two- and four-fold reduction of reagents used. Extraction results show that for test B, Mn extraction decreased by 6 % while Zn extraction did not decrease considerably. An even larger decrease was observed at a L/S of 5; under these conditions, only 66.9 and 88.6 % of Mn and Zn, respectively, were leached from the solid residue. This result is not in line with our objectives.

However, the results obtained with a L/S ratio of 10 were satisfactory, as the decrease in the leaching efficiency was low, while a two-fold decrease of the amount of reagent used was attained (test B, Table 3.8). This test has also the advantage of producing a leachate containing metals at higher concentrations for further processing, with the potential to produce high-concentration final products.

With an optimal L/S set, the optimization of other settings was evaluated (tests D, E and F, Table 3.8). The increase of microwave cycle from 60 to 90 s (test D, Table 3.8) resulted in an extraction yield of 100% for both Mn and Zn alike. Given the total leaching of both metals with this test, this microwave time cycle was adopted for the last tests (E and F, Table 3.8).

Leaching experiments with a reduced concentration of H_2SO_4 resulted in 88.5 and 89.5 % of Mn and Zn, respectively, being recovered from the residue (test E, Table 3.8). This reduction is most likely linked to the decrease of $[H^+]$, which is responsible for aiding in the reduction of MnO_2 and the dissolution of Zn oxides, as it was discussed above.

On the other hand, reducing the amount of glucose from 20 to 15 g/L (test F, Table 3.8), resulted only in a slight decrease of the Mn leaching, with no effect on the leaching of Zn. Considering that under these conditions, there is a significant reduction (25 %) of the amount of glucose used during leaching, compared to the conditions used in test D, without compromising significantly (only 2 %) the leaching of Mn, these experimental conditions were assumed as the best ones and adopted in the subsequent work.

The use of microwave leaching brings the advantage of reduced time and amount of reagent (glucose) consumed together with an increasing of the efficiency of the leaching procedure. This is easily observed by comparing the results obtained with conventional and microwave-assisted leaching. Furthermore, the comparison with other works is also elucidative: for example, Fattahi et al. (2016) have performed a reductive leaching procedure on a Zn plant residue to recover Mn and Co (Fattahi et al., 2016). A recovery of 90 % of Mn was attained at 85 °C using a long leaching time (60 min), whereas in our case a slightly better recovery of Mn (98 %) was attained in a short period of time (within a 90 s microwave cycle) (test F Table 3.8).

In a similar work, Safarzadeh et al. (2011) have attained a total leaching of Mn from Zn plant residues with the aid of phenol as reducing agent (Safarzadeh et al., 2011). Again, such recovery rate was only achieved at 85 °C over 30 min.

The residue left over from reductive microwave-assisted leaching was analysed by XRD (Fig. 3.4). The analysis revealed that the main component in the residue is C, with no other substantial peaks for other species.

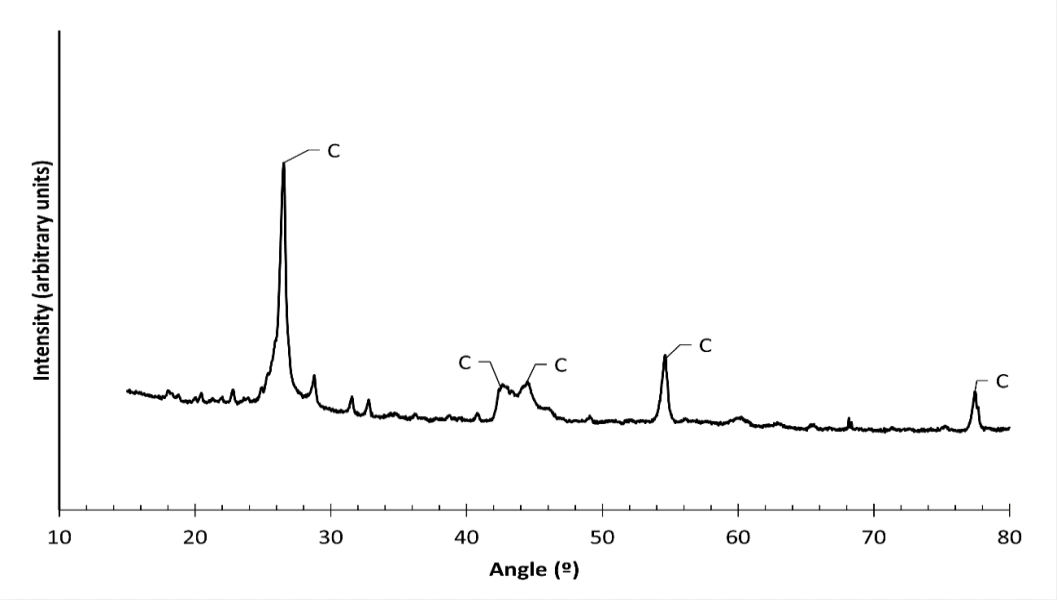


Fig. 3.4. *XRD spectrum of the residue resulting from the microwave-assisted reductive leaching, with indication of the main identification peaks.*

The total digestion of the remaining residue confirms that most of the metals were leached, as very low quantities were found: Mn: 3.87 mg/g; Zn: 0.15 mg/g; Fe: 0.036 mg/g. Considering its composition and the fact that it is already ground, this residue may be suitable for the lubrification industry or manganese dioxide graphite composite electrodes (Langley, C. E. et al., 2007).

Comparative analysis of the reductive acid leaching strategies

The final metal concentrations obtained using each leaching strategy under optimized leaching conditions are described in Table 3.9. Contrary to ultrasound-assisted leaching,

which was inefficient (Table 3.9) and, thus produced a final solution containing a lower amount of Mn, both conventional and microwave-assisted leaching indicated similar efficiencies on the extraction of Mn and Zn.

Table 3.9. *Metal concentrations of the solutions obtained after leaching the Mn-rich residue using optimal conditions of each leaching strategy. Data represent the mean and standard deviations of three replicates*.

	Metal concentration (g /L)	
Leaching strategy	**Mn**	**Zn**
Conventional	16.6 ± 0.1	1.65 ± 0.01
Ultrasound assisted	7.30 ± 0.03	1.30 ±0.01
Microwave assisted	33.2 ± 0.1	3.48 0.05

However, the microwave-assisted leaching generated the liquor with the highest Mn concentration, which was double than the one achieved using the conventional method as a consequence of the highest metal extraction yields obtained when a lower L/S ratio was used. Moreover, when we compare the corresponding experimental tests, it is clear that microwave-assisted leaching presents advantages since smaller amounts of glucose and leaching solution (lower L/S ratio) were used in a much faster time for recycling the same amount of residue.

These achievements, together with the fact that a more concentrated metals liquor solution was attained, clearly suggest that microwave-assisted appears to be the most suitable method to leach Mn (and also Zn) from the residue.

3.3.4. Metals purification

Even though a fairly concentrated Mn solution was achieved (33.2 g/L) using the microwave-assisted leaching process (Table 3.9), the solution still contains an

appreciable contamination of Zn and Fe (9.4 and 1 %, respectively). So, to produce a high-purity Mn product, a further purification of Mn from this solution was imperative.

Precipitation can be used effectively to remove Fe from the solution, as it is predicted from the chemical speciation simulations, since it precipitates readily at low pH (pH≈2.5-3.5) with a minimum loss of both Mn and Zn (Fig. 3.5).

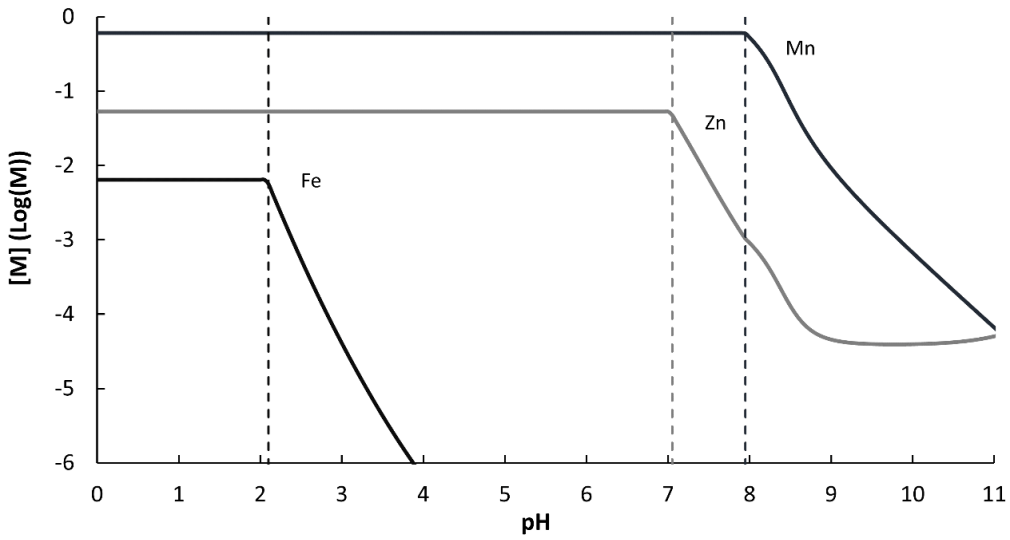


Fig. 3.5. *Log [Free metal] versus pH. Initial concentrations (M): [Fe]= 6.41 x 10^{-3}; [Zn]=5.32 x 10^{-2}; [Mn]=6.04 x 10^{-1}.*

However, in the same speciation diagram, it is possible to see that alkaline precipitation is not a feasible strategy for recovering pure Mn, as at the pH where Mn precipitates there are still appreciable quantities (10^{-3} M) of Zn in solution, which would constitute a contaminant in the final product. On the other hand, sulphide precipitation strategy is not an option for recovering Mn due to the restrictive pollution control and management requirements; moreover, MnS is not a convenient product for the Mn industry as it needs to be converted (Zhang and Cheng, 2007).

So, in this work, the ability of oxidative precipitation or solvent extraction for recovering Mn with high yield and purity was evaluated. These two strategies were first preceded by the quantitative removal of Fe by precipitation, as a rust-brown gelatinous solid

indicative of the formation of iron (III) hydroxide [Fe $(OH)_3$] after increasing the pH of the leached solution up to ≈ 3.3. The solution was allowed to settle overnight and then was filtered. Under these conditions, 97.2 % of the total amount of Fe initially present in the leachate solution was removed (Table 3.10).

In a first attempt, it would be expected that Fe should be present in solution as Fe(II), due to the reduction of Fe(III) to Fe(II) by the glucose that remained in the leachate solution, as it is suggested by the ΔE° value (Bleam, 2011; Haynes et al., 2016) :

$$E^{o}_{(Fe^{3+})/(Fe^{2+})} = 0.771\ V;\ \ E^{o}_{(CO_2)/(C_6H_{12}O_6)} = 0.404\ V;\ \ \Delta E^{o}_{cell} = 0.367\ V \qquad (3.5)$$

However, this did not occur since almost all Fe (97.2 %) (Table 3.10) precipitated in the form of $Fe(OH)_3$. This fact was probably due to the complexation of Fe(III) by glucose and/or the unfavourable kinetics of Fe(III) reduction (Geetha et al., 1995) :

$$E^{o}_{(Fe^{3+}-D-glucose)/(Fe^{2+}-D-glucose)} = -0.378\ V;\quad E^{o}{}_{(CO_2)/(C_6H_{12}O_6)} = 0.404\ V;\quad \Delta E^{o}_{cell} = -0.782\ V \qquad (3.6)$$

Table 3.10. *Metal concentrations of the original solution (after reductive leaching) and solutions obtained after each purification strategy. Unless for Fe, data represent the mean and standard deviations of three replicates.*

Purification strategy	Metal concentration (g/L)		
	Mn	**Zn**	**Fe**
Initial solution	33.2 ± 0.1	3.48 ± 0.05	0.358 ± 0.003
Solution after Fe precipitation	32.7 ± 0.6	3.43 ± 0.06	9.7×10^{-3}
1) Mn oxidation with persulphate			
Aqueous phase from oxidation	$2.3 \times 10^{-3} \pm 1 \times 10^{-4}$	3.30 ± 0.05	1.2×10^{-3}
Purity		99.9%	
2) Solvent extraction with Cyanex			
Aqueous phase	32.6 ± 0.3	0.031 ± 0.001	2.5×10^{-3}
Purity	99.9%		
Stripped from Organic phase	0.52 ± 0.02	35.2 ± 0.2	0.06
Purity		98.4%	

3.3.4.1. Selective precipitation of manganese with peroxydisulphate

In this work, $Na_2S_2O_8$ was chosen to oxidize Mn(II). Even though a higher pH favours the oxidation of Mn(II) to Mn(IV), a careful choice of the pH value for performing this oxidation should be made to avoid (i) acid catalysed decomposition of $S_2O_8^{2-}$ (Kolthoff and Miller, 1951) and (ii) precipitation of $Zn(OH)_2$ (Fig. 3.5). Considering all these facts and the 1:1 stoichiometry of the oxidation reaction (Eq. 3.7), in a first attempt, a $S_2O_8^{2-}$: Mn ratio 1 was evaluated after raising the pH to 5.

$$MnSO_{4(aq)} + Na_2S_2O_{8(aq)} + 2H_2O_{(l)} \rightarrow MnO_{2(s)} + Na_2SO_{4(aq)} + 2H_2SO_{4(aq)} \qquad (3.7)$$

Under these conditions, the oxidation was inefficient and only 56 % of Mn precipitated after 3h of reaction (Table 3.11). To further increase the precipitation yield, two higher $S_2O_8^{2-}$: Mn ratios (1.5 and 2) were evaluated. An increase of the precipitation yield was observed with both ratios: 83 and 99.4 % for ratios 1.5 and 2.0, respectively (Table 3.11).

Joo et al. (2013) have obtained similar recovery rates of Mn using a $S_2O_8^{2-}$:Mn ratio of 1. The reason why a higher $S_2O_8^{2-}$: Mn ratio was required in our experiments can probably be attributed to the excess of glucose not consumed during leaching; due to the reductive power of glucose and other possible derivatives present in the leached solution, a higher amount of $S_2O_8^{2-}$ was needed to neutralize their reductive power.

Table 3.11. *Precipitation of Mn from leachate solution as function of peroxydisulfate-Mn ratio ($S_2O_8^{2-}$: Mn), at pH = 4.8, 90 °C, 3 h, 150 RPM. Data represent the mean and standard deviations of three replicates.*

$S_2O_8^{2-}$: Mn Ratio	**Mn precipitation (%)**
1.0	55.5 ± 0.2
1.5	82.8 ± 0.4
2.0	99.4 ± 0.6

The XRD analysis of the solid recovered from the ratio of $S_2O_8^{2-}$: Mn 2 experiment shows that MnO_2 is solely present (Fig. 3.6). Additionally, metal quantification performed after reductive acid digestion of this precipitate confirmed its high (99.7 %) purity, with Zn and Fe as the main impurities (0.25 and 0.07 %, respectively) present in the solid. On the other hand, almost all (94.8 %) Zn was recovered as a Zn solution with high purity (99.9 %) (Aqueous phase from oxidation, in Table 3.10).

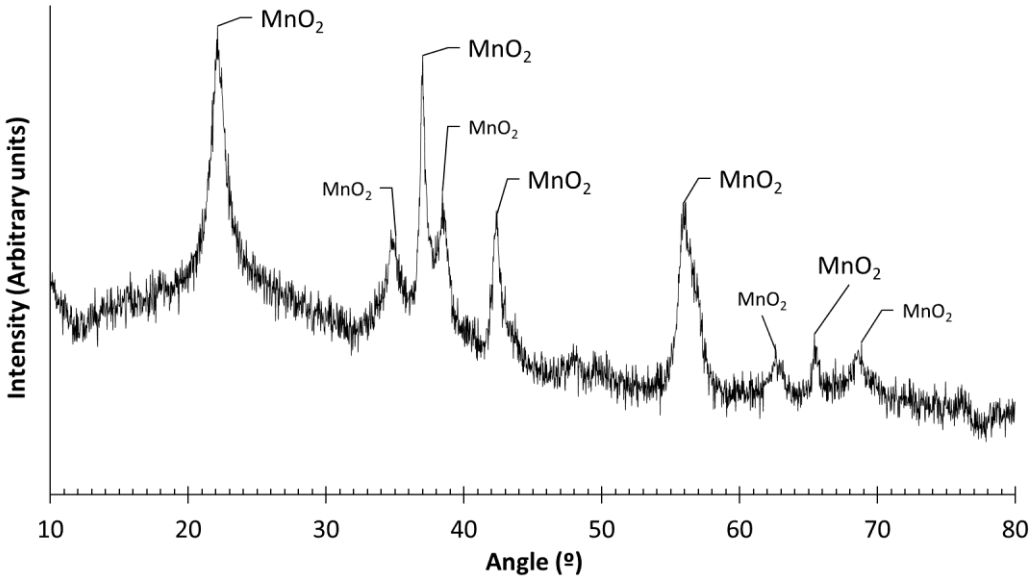


Fig. 3.6. *XRD spectrum of the precipitate resulting from oxidative precipitation, with the main peaks identified.*

3.3.4.2. Manganese recovery using solvent extraction

In this work, the ability of Cyanex 302 for the simultaneous Mn purification plus Zn concentration and purification from our leached solution using a single stage extraction was evaluated. The main results obtained after this extractive procedure are presented in Table 3.10. We can see that more than 99 % of Zn was removed from the aqueous solution and transferred, via complexation with Cyanex 302, to the organic (kerosene) phase. Only a minor amount of Mn was co-extracted together with Zn from the leached solution to the organic phase. This strategy allowed the recycling of the major amount of Mn as a Mn solution with a concentration of 32.6 g/L and a purity of 99.9 %. The remaining impurities were mostly due to Zn, accounting for almost 0.10 %, while Fe was negligible. On the other hand, by using H_2SO_4, as the stripping agent, from the organic phase, the Zn was totally recovered into an aqueous solution, as $ZnSO_4$, with a concentration of 35.2 g/L and a purity of 98.4 %. Our results are in agreement with those found by Biswas et al. (2016), where Zn and Mn were extracted from Zn-C battery residue.

3.3.4.3. Comparative analysis of the metal purification strategies

Even though both purification processes were demonstrated to be able to recover Mn with high efficiency ($\geq$ 98.2 %) (Table 3.10), the purity of the Mn solution obtained by solvent extraction (99.90 %) was slightly higher than the purity of MnO_2 (99.7 %) achieved by persulphate precipitation.

Contrary to the latter process where a direct production of chemical manganese dioxide (CMD) occurs even though with a lower purity, in the first purification strategy, Mn should be precipitated from solution and processed into CMD, which represents an additional cost to the process. On the other hand, the use of this solution, which has a significant concentration of Mn (approximately 33 g/L), for the preparation of EMD is an appealing option. As for side products, both methods produce high purity Zn solutions (Table 3.10) adding value to both methods. Both purification strategies fulfil the principles of a circular economy since both metals (Mn and Zn) were almost totally recovered with high purity which allows their effective reuse.

3.4. Proposal of a closed-loop process to recycle spent alkaline batteries

Fig. 3.7. summarizes the simple nearly zero-waste hydrometallurgical strategy described above for the entire work for recycling all various raw materials (metals plus C) from spent alkaline batteries. The application of ultrasound-assisted method using 1 M H_2SO_4, L/S ratio of 10 for 2 min allowed a more selective leaching of Zn than other studied conditions (92 % Zn, 13 % Mn leached, respectively).

After the first leaching of the spent alkaline battery using H_2SO_4, it is necessary to recover all main constituents (Mn plus Zn and C) from a rich Mn residue. Microwave-assisted leaching was revealed to be the fastest (one cycle of 90 s) and most efficient (≥98 % of Mn and Zn leached), using lower amounts of chemicals, and was used to produce leachate for subsequent purification experiments.

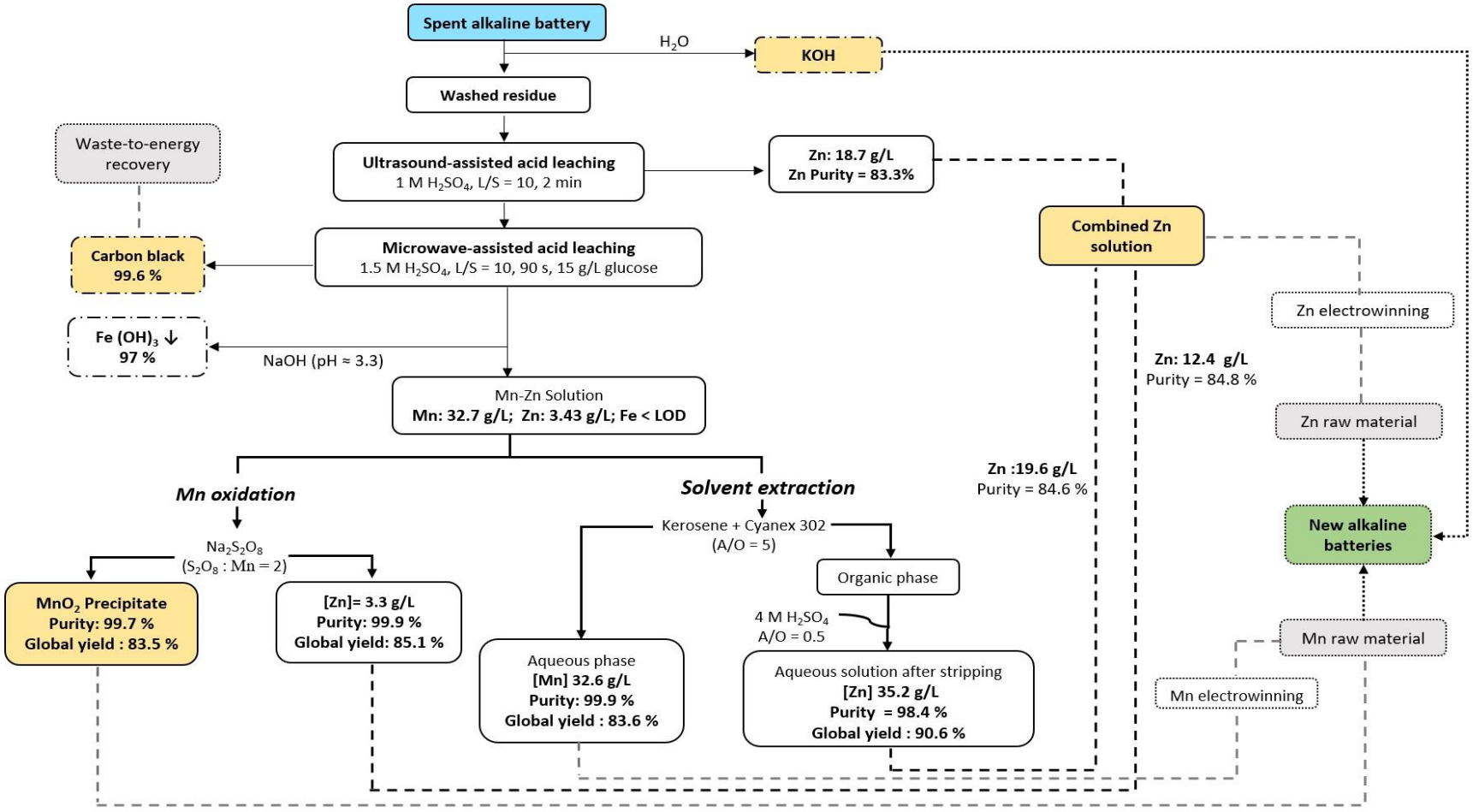


Fig. 3.7*. Overview of the hydrometallurgical process developed. Blue box shows initial residue, yellow boxes represent the products obtained in this study and grey boxes represent final raw materials resultant from the implementation of this hydrometallurgical process. Green box represents the start of a new product based on the combination of all raw materials. Discontinued lines represent processes not performed in this study.*

From this point on, two options to recover Mn were explored after two initial sequential solid-liquid separation steps for recovering C and Fe (at about pH 3.3). The first option consisted on using $Na_2S_2O_8$ at pH= 4.8, followed by Mn precipitation, as MnO_2. The second purification strategy was performed by solvent extraction using Cyanex 302 as extractant. In both situations, high purity Mn products and Zn solutions were produced. From the first purification strategy, an end CMD product with a purity of 99.7 % was achieved while a higher purity (99.9 %) and concentrated (approximately 30 g/L) Mn solution resulted from the implementation of the second purification strategy. In addition, from comparing material safety data sheet of battery industries with high purity MnO_2 resulted from the precipitation method, it can be concluded that the final MnO_2 solid product achieved in this work can be used as raw material for new battery production (Duracell, 2016; Toshiba, 2018).

3.5. Conclusions

In this study, all main raw materials (Zn, Mn and C) present in spent alkaline batteries were recovered with high yield and purity.

After a first selective acid ultrassound-assisted leaching, most of Zn was recovered, which when combined with the additional Zn recovered after a subsequent two-step leaching plus purification applied to the remaining Mn enriched residue resulted in a Zn solution with a purity of about 85% suitable for electrowinning. Considering the Mn purification strategies (oxidative precipitation of Mn with persulfate or solvent extraction with Cyanex 302 as the extractant) implemented in this work, high ($\geq$ 99.7 %) purified Mn products were achieved in both cases, which enable their use as Mn raw materials for producing new alkaline batteries. Moreover, the final residue, which contains 99.6 % C black, can also be used for combustion.

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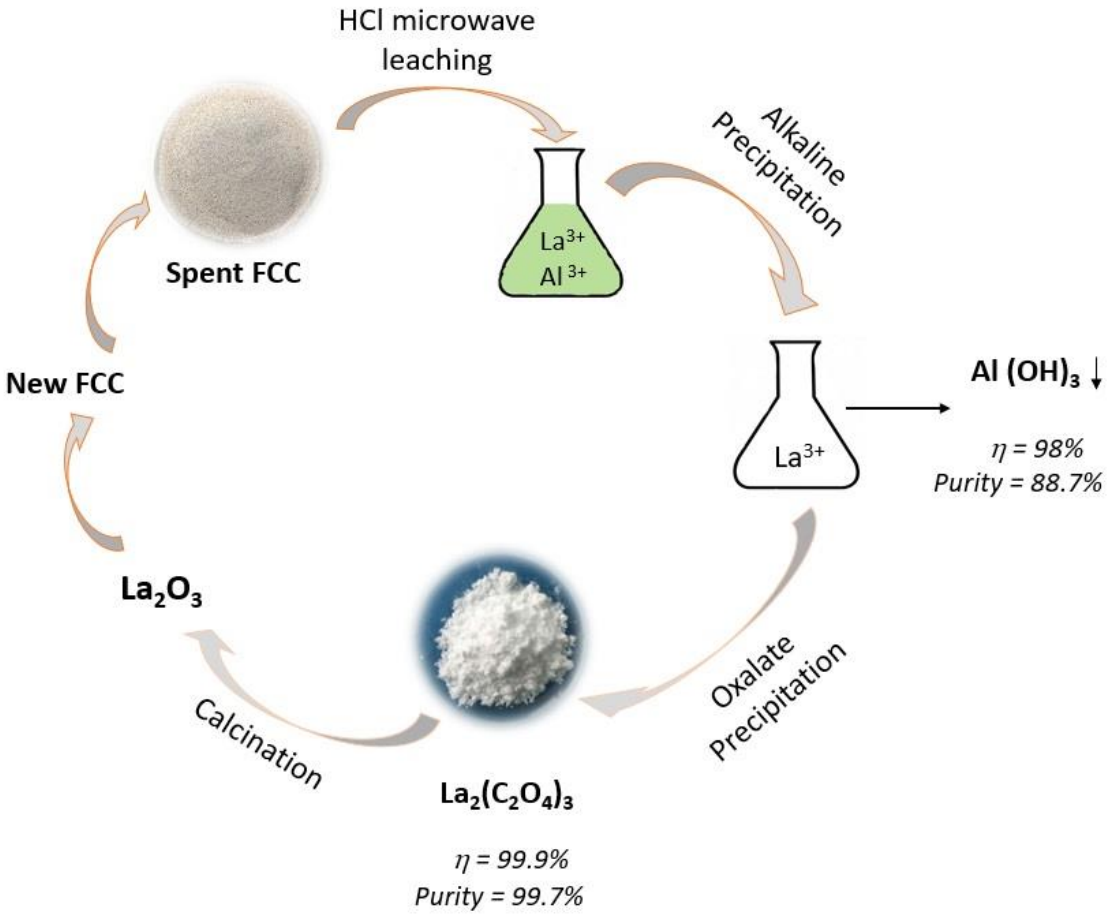
Chapter 4

Recovery of lanthanum (and aluminum) from spent fluid cracking catalysts



Abstract

Spent fluid cracking catalyst (FCC) is an abundant waste material derived from oil refining processes and notably characterized by its content in rare earth metals, such as cerium (Ce) and lanthanum (La). In this work, it was our aim to develop a simple but effective workflow, based on a single assisted-acid leaching followed by two consecutive precipitation steps, for recovering La and Al with high purity from the FCCs. Firstly, three (conventional, ultrasound- and microwave-assisted) leaching strategies were tested using two acids (H_2SO_4, and HCl). Microwave-assisted leaching revealed to be the most efficient [(99.4 ± 0.9) % of La dissolution] and faster (1 cycle of 90 s) strategy using a low concentration of acid (1 M HCl). Subsequently, a sequential selective alkaline and oxalate precipitation steps produced high quality aluminium hydroxide (88.7 % of purity) by increasing the pH up to 6 and a high pure (99.7 %) salt of lanthanum oxalate (which can be, later, calcinated into a reusable lanthanum oxide) using a reduced oxalate concentration, respectively. The proposed process is independent of the initial Al concentration present in the hydrochloric acid FCCs leachates and universal (for [La] > 0.04 M, complete La precipitation regardless of its initial concentration will be ensured using a molar [oxalate]/[La] ratio of 2.5). Moreover, it is significantly simpler and faster than existing methods and minimizes the consume of energy and reagents to a bare minimum, with accompanying cost reduction and environmental benefits.

4.1. Introduction

Fluid cracking catalysts (FCCs) are used in the oil industry to breakdown, i.e., to crack large molecules into smaller hydrocarbons of interest, such as gasoline and other products. Since 2014, the world supply accounted for 840 thousand metric tons of FCC (Ferella et al., 2016) with an estimated annual increase of 5 %. As a result of this annual production, about 80 thousand tons of waste slag in China (Wang et al., 2017a) were produced while the use of FCC resulted in an estimated 20 thousand tons of spent FCCs worldwide (Zhao et al., 2017).

In terms of metals composition of the fresh FCCs, the following average values can be considered: 141 g/kg of Al, 260 g/kg of Si, 2.7 g/kg of La and 3.4 g/kg of Ce, among other minor components, such as V (< 33 mg/kg) and Ni; 31 mg/kg (Ferella et al., 2016). Spent FCC, by comparison with fresh FCC, has increased Ni (3930 mg/kg) and V (1455 mg/kg) content (Ferella et al., 2016) as a result of the impurities accumulated during the catalytic reactions.

Spent FCC is mostly reused as a cement additive or as catalyst in other reactions while the recovery of the REEs contained within is less frequent (Ferella et al., 2016). It is estimated that 17800 tons of La_2O_3 were used for FCC production in 2008 alone, which represents 46 % of its worldwide use (Akah, 2017). Considering the large volume of FCC waste generated on a yearly basis as well as its content in REEs, which are critical raw materials of strategic importance for the EU (EU Commission, 2017), recycling this material may be a relevant secondary source of La and Ce and will certainly contribute to a more circular economy.

The recycling of REEs from FCCs requires a leaching step, where metals are transferred into the liquid phase and a subsequent step (or series of steps) to recover them as purified solid rare earth compounds.

For leaching REEs from FCCs, mineral acids such as HNO_3, H_2SO_4, or HCl are usually used. However, because these acids are non-selective, besides the extraction of the intended metals (i.e, La and/or Ce), other metals, such as Fe and Al, are also extracted. The Al, in particular, due to the presence of aluminosilicates in the spent FCC waste, is leached in quantities that are far superior to that of the rare metals and is the most limiting factor for the final purification of these

metals. The current acid leaching practices applied for extracting REEs from FCCs required significant processing time (Innocenzi et al., 2015; Nguyen et al., 2018; Sishi et al., 2017; Wang et al., 2017b, 2017a; Zhao et al., 2017) and concentrated acids (Innocenzi et al., 2015; Nguyen et al., 2018; Wang et al., 2017b; Zhao et al., 2017), which resulted in a high consumption of energy and reagents. Considering these drawbacks, in this work, our first aim was to improve the efficiency of the acid leaching process in order to simultaneously reduce the consumption of chemicals and leaching time (and, thus, energy).

Purification strategies for recovering REEs from FCCs acid leachates, described in the literature up to now, present significant limitations, which unable their implementation at an industrial scale. One of the most used method for purification of rare earth metals is solvent extraction. However, the efficiency of solvent extraction is severely limited due to the acidic character of the extracting agents that compromises the extraction yield. Alternatively, saponified solvent extraction was proposed in the context of spent FCC (Zhao et al., 2017) but this technique produces contaminated wastewaters (Chang et al., 2010). Additionally, high concentrated acid solutions are needed for stripping REEs from the organic phase (Innocenzi et al., 2015) which increases the cost of the overall process. Other alternative purification strategies were also evaluated. They were based on the selective precipitation of rare earths as double sulfates (Innocenzi et al., 2015; Wang et al., 2017a) or the combination of different techniques [solvent extraction followed by oxalate precipitation (Innocenzi et al., 2015) or previous selective alkaline leaching of Al followed by an acid leaching of rare earths from the remaining residue and subsequent recovery of REEs by oxalate precipitation (Wang et al., 2017b). However, rare earth compounds of high purity were only recovered when multiple purification steps (Innocenzi et al., 2015; Wang et al., 2017b) were used with the consequent high consume of energy and reagents. Moreover, the use of a single precipitation step did not originate rare earth compounds of high purity (Innocenzi et al., 2015). In this work, it was our aim to develop a simple but effective flowsheet for recovering La (and also Al) with high purity based on a reduced number of separation processes, ideally, precipitation steps, which are the most convenient to be implemented at industrial scale.

Therefore, in order to prosecute the aims mentioned above, the potential beneficial influence of using auxiliary energy sources, such as ultrasound or microwave irradiation, for improving the leaching efficiency of REEs from FCCs was evaluated for the first time. Subsequently, a simple, universal and efficient sequential selective separation process, in which Al goes through an initial alkaline precipitation without rare metal co-precipitation followed by a high yield oxalate precipitation of rare metals with high purity and minimal reagent use, was developed.

4.2. Materials and Methods

4.2.1. Reagents and analytical techniques used

The stock solutions of HCl (Sigma-Aldrich, 37 %), H_2SO_4 (Chemlab, 96 %), HNO_3 (Chemlab, 65 %), NaOH (Eka, p.a) and oxalic acid ($C_2H_2O_4$, Sigma-Aldrich, ≥ 99.0 %) were of analytical grade and used without purification.

The La and Ce determinations were performed by inductive coupled plasma-atomic mass spectroscopy (ICP-MS) using the iCAPTM Q (Thermo Fisher Scientific, Bremen, Germany) instrument equipped with a MicroMistTM nebulizer, a Peltier-cooled baffled cyclonic spray chamber, a standard quartz torch and a two-cone interface design (sample and skimmer cones). High-purity (99.9997 %) argon (Gasin II,) was used as the nebulizer and plasma gas. The ICP-MS analysis was conducted under the following conditions: radio-Frequency (RF) power, 1550 W; argon flow rate, 14 L/min; auxiliary argon flow rate, 0.8 L/min; nebulizer flow rate, 0.98 L/min. AAS-FA using an Analytik Jena novAA 350 (Jena, Germany) spectrophotometer was used for the determination of all other metals, with air-acetylene flame for Fe, Ni and nitrogen protoxide-acetylene flame for Al, V and Ti. Finally, quantification of Na was performed by atomic emission spectroscopy (AES) with a Perkin Elmer AAnalyst 400 spectrometer (Norwalk, CT, USA).

4.2.2. Characterization of FCC

The spent FCC catalyst used for this study was supplied by a Portuguese refinery and has been used directly without any further treatments. The metal content of the spent FCC was characterized by total acid digestion with aqua regia. Namely, 2 g of FCC was mixed with 15 mL of HCl (37 %) and 5 mL of HNO_3 (65 %) for a L/S ratio of 10 and boiled for 4 h.

The particle size distribution of the original spent FCC was determined in aqueous medium by laser dispersion using a Coulter LS230 equipment. 90 % of particles were below 184 µm with an average particle diameter of 120 µm.

4.2.3. Leaching tests

Three different leaching strategies (conventional, ultrasound and microwave-assisted leaching) were performed with H_2SO_4 and HCl to compare the leaching efficiencies. The conventional leaching experiments were carried out using falcon tubes with conical bottoms, immersed in a shaking water bath with temperature control (60°C) (OLS200, Grant) and stirring of 150 RPM. The effects of the following variables on the La and Al dissolution were studied: acid concentrations (0.5, 1 and 1.5 M for H_2SO_4 and 1, 2 and 3 M for HCl, respectively) and time (1 and 3 h). Note that these concentrations of acids were chosen to have similar concentrations of H^+ (0.5 M H_2SO_4 approximately equal to 1 M HCl in terms of H^+).

For ultrasound-assisted leaching, tests were accomplished using a Bandelin Sonoplus HD 2200 (power of 200 W and output frequency of 20 kHz ± 500 Hz) with a titanium microtip of 3 mm (Berlin, Germany). The ultrasonic parameters were maintained constant in pulse (0.1s) and wave amplitude (20 %) and the variation of acid [H_2SO_4 (0.5, 1 and 1.5 M) or HCl (1, 2 and 3 M)] concentration and time (20, 30 and 60 min) were studied.

Microwave-assisted leaching assays were performed inside a PTFE bomb including 23 mL container and using a domestic microwave oven (800 W, 2.45 GHz) using varying the concentration of H_2SO_4 (0.5, 1 and 1.5 M) and the time (1 cycle of 30 or 60 s) or varying the

concentration of HCl (1 and 2 M) and the time (for 1 M HCl: 1 cycle of 30, 60 and 90 s; for 2 M HCl: 1 cycle of 30 and 60 s). After each leaching cycle, samples were allowed to cool during 20 min at room temperature to decrease the excessive pressure and temperature generated during the microwave heating.

For all leaching conditions, the L/S ratio of 5 was used. In order to assure reproducibility, all experiments were repeated in triplicate.

4.2.4. Selective precipitation

To predict the most appropriate experimental conditions to recover Al and La selectively using alkaline and oxalate precipitation, respectively, chemical speciation calculations were carried out using the software MINTEQ ver. 3.1 (Gustafsson, 2013). Metal speciation analysis with MINTEQ generates chemical equilibrium concentrations of all species being considered in the model by the program reactions, based on component stability constants (Martell et al., 2004) and total molar metal concentrations.

Leached solution resultant from optimized microwave-assisted leaching (1 M HCl, L/S ratio of 5, 1 cycle of 90 s) was used for the sequential selective precipitation of Al and La. For this purpose, the pH of each leachate was increased using pellets of NaOH (to avoid the increase of the total volume) in order to precipitate Al. Several final pH values (between 5 and 6.5) were tested. After precipitation, samples were filtered (Ø = 0.45 µm) and the concentration of metals (Al, La, Fe, and V) in the filtrates as well as in the initial leachate were measured as described in subsection 4.2.1. In the next step, oxalic acid was used to selectively precipitate La from the solution as lanthanum oxalate [$La_2(C_2O_4)_3$]. Based on the previous chemical simulations, a concentration of 0.1 M oxalic acid was applied at pH 6. The solution was settled overnight and then filtrated. The concentration of metals was measured in the filtrate as described in subsection 4.2.1.

To quantify the Al and La precipitation yields, as well as the purity of the solids recovered, the solids were re-dissolved using concentrated HCl and the amount of Al, La and other metals (Fe, V and Na) was determined as described in subsection 4.2.1.

XRD data for the solid recovered from the oxalate precipitation was collected at ambient temperature on an Empyrean diffractometer (Cu K_α 1,2 X-radiation, λ1 = 1.54060 Å; λ2 = 1.54443 Å), under operating configuration of 45 kV, 40 mA with a step size [2Θ°] of 0.026° and a scan step time of 96.39 s.

4.2.5. Statistical analysis

All experiments were conducted in triplicate and data are presented as mean ± standard deviation.

To test the best performing conditions, statistical analysis was performed when relevant. Statistical analyses were done using Stastistica 8.0 software (StatSoft, Inc., Tulsa, USA). Shapiro-Wilk test was used to test for normal distribution. Since all samples were normally distributed, ANOVA and t-test were used. Pos hoc Tukey was performed when ANOVA test gave statistically significant results to pinpoint which parameters were different. Significant level of $p < 0.05$ was used.

4.3. Results and discussion

4.3.1. Metal characterization of the residue

In this study, the original spent FCC was used. The metal chemical composition of the spent FCC, determined by total acid digestion with aqua regia, is presented in Table 4.1. Al was the metal present at the highest concentration, (135±2) mg/g and the REE content was mainly consisted by La [28.1±2 (mg/g)]. Other major metal constituents were V, (3.7±0.2) mg/g, and Fe, (2.5±0.1) mg/g while titanium (Ti) [0.30±0.04 (mg/g)] and Ce [$5.7x10^{-2}$±$5x10^{-3}$ (mg/g)] were present as minor amounts. The levels of other metals (Ni, Cu, Zn, Mn and Pb) were lower than 0.1 % and are not listed in Table 4.1.

Table 4.1. *Element content of the spent FCC catalyst determined by total acid digestion.*

Element	Al	La	V	Fe	Ti	Ce
Content (mg/g)	135±2	28±2	3.7±0.2	2.5±0.1	0.30±0.04	$5.7x10^{-2}$±$5x10^{-3}$

4.3.2. Leaching tests

Literature describes the recovery of REEs from spent FCC and FC slag using different mineral acids, such as HCl (Wang et al., 2017a, 2017b; Zhao et al., 2017), H_2SO_4 (Innocenzi et al., 2015) or HNO_3 (Nguyen et al., 2018). However, even though high leaching yields were achieved, namely when HCl was used, very concentrated acid solutions and long periods of time were used (Wang et al., 2017b, 2017a; Zhang et al., 2016). Considering that the leaching efficiency can be optimized using auxiliary energy sources, such as ultrasound (Güngör and Elik, 2007; Li et al., 2014; Pinto and Soares, 2012; Sadeghi et al., 2017) or microwave irradiation (Pinto and Soares, 2012; Sadeghi et al., 2019, 2017) and in order to minimize the consumption of acid and enabling the efficient extraction of La and Al from FCC in a short period of time, the performance efficiency of H_2SO_4 and HCl for extracting La from the FCC using these two leaching strategies was evaluated, for the first time, and compared with the conventional process. The variables, reaction time, type of acid and H^+ concentration were varied while the L/S ratio was kept constant at 5. Table 4.2 summarizes the results obtained of the leaching efficiency of La and Al for all three leaching strategies with both acids.

For conventional method using H_2SO_4, the La extraction yields were $\leq$ 56 % whatever the concentration of acid and duration of leaching time (Table 4.2.A). Statistical analysis evidence that the application of 1 M H_2SO_4 for 1 h correspond to the best La leaching conditions (55.7±0.1) in terms of time and concentration of acid. A slight increase of the performance of the La leaching was observed when ultrasound-assisted leaching was applied, namely for both 1 and 1.5 M concentrations of H_2SO_4 during 1 h, where leaching yields of about (70±1) % were achieved. Again, statistical analysis demonstrated that the application of 1 M H_2SO_4 for 1 h corresponded

to the best La leaching compromise where a La extraction of (69.8±0.8) % was achieved. Even though, ultrasound-assisted leaching allowed a slight increase of the La extraction yield (about 16 %) comparatively to the conventional method, the best leaching performance was achieved when microwave-assisted strategy was implemented. Under these conditions, when 1 M H_2SO_4 was used, the leaching yield was of the same order of magnitude (about 73 %) to the achieved with ultrasound-assisted method (69.8 %) but was obtained fastly (0.017 *versus* 1 h). Statistical analysis also confirms that this extraction yield was equivalent to the one achieved when 1.5 M H_2SO_4 was used for both leaching times (0.008 and 0.017 h), which evidences that no further increase of the acid is needed. However, the leaching of Al was much higher (about 48%) than the one achieved by ultrasound-assisted method (about 23%) (Table 4.2.B), which may pose problems in subsequent separation process, with no significant improvement of La extraction.

Contrarily to what happened with H_2SO_4, statistical analysis indicated that for HCl using conventional or ultrasound-assisted leaching, there was always an increase of the La extraction with time and concentration of H^+ (Table 4.2.A). At 3 M HCl for 1 h, the La ultrasound-assisted extraction reached (97.1±0.3) %, an improvement of 27 % comparatively to the conventional treatment for similar leaching conditions. Comparing the performance of conventional and ultrasound-assisted leaching under similar experimental conditions (the same leaching time, 1h, and the same concentration of H^+), statistical analysis evidences that the ultrasound-assisted leaching process proved to be more efficient in dissolving La. However, this leaching strategy still required long leaching time and high HCl concentration. Therefore, microwave-assisted leaching was executed in order to evaluate if La extraction efficiency could be improved. Taking into account that high La leaching yields were observed when ultrasound-assisted leaching for 1 and 2 M HCl concentrations was performed (Table 4.2.A), the efficiency of microwave-assisted for leaching La using these two acid concentrations for microwave heating cycles of 8×10^{-3} and 0.017 h was evaluated. A total extraction of [(99 $\pm$ 2) %] La was achieved when 2 M HCl was used for 0.017 h.

Table 4.2. *La extraction efficiency for each leaching strategy and type of acid* ***(A)****, Al extraction efficiency for each leaching strategy and Type of acid* ***(B)****.*

(A)		**La leaching (%)**					
		H_2SO_4 (M)			**HCl (M)**		
Strategy	**Time (h)**	**0.5**	**1**	**1.5**	**1**	**2**	**3**
Conventional	1	38.4±0.3	55.7±0.1	55.5± 0.9	46.3±0.4	59.5±0.7	69.8±0.6
	3	42.9±0.6	54±3	55±2	56.6±0.5	70.8±0.9	83.3±0.6
Ultrasound	0.33	48.8±0.5	51.6±0.4	53.4±0.5	50.0±0.5	60.1±0.6	70.4±0.6
	0.5	54.4±0.4	60.9±0.7	63.0±0.5	63.7±0.4	75.8±0.5	83.9±0.4
	1	63.3±0.3	69.8±0.8	70.1±0.6	77.0±0.6	87±2	97.1±0.3
Microwave	0.008	54.1± 0.5	60.9±0.5	74.7±0.7	82.6±1.3	92.9±0.6	-
	0.017	60.9±0.7	72.6±0.6	75.4±1.0	88.1± 0.8	99±2	-
	0.025	-	-	-	99.4±0.9	-	-

(B)		Al leaching (%)					
		H_2SO_4 (M)			HCl (M)		
Strategy	**Time (h)**	**0.5**	**1**	**1.5**	**1**	**2**	**3**
Conventional	1	10.2± 0.5	14± 1	15.8± 0.6	12.7± 0.2	20.4± 0.4	30 ± 1
	3	14.2± 0.6	20.5± 0.3	24.3± 0.9	19.6± 0.2	31.7± 0.8	42.1± 0.6
Ultrasound	0.33	8.6± 0.6	9.7± 0.5	12.3± 0.6	6.9± 0.2	10.1± 0.3	12.1± 0.4
	0.5	10.5± 0.3	12.7	14.4± 0.4	10.6± 0.1	14.6± 0.5	17.8± 0.3
	1	18.7± 0.4	22.8± 0.3	23.2± 0.7	17.5± 0.3	22.3± 0.3	25.8± 0.2
Microwave	0.008	18.9± 0.3	23.1 ± 0.3	25.9± 0.4	21.2 ± 0.5	27.5 ± 0.5	-
	0.017	20.1± 0.5	48.1 ± 0.9	69.4± 0.7	32 ± 2	48 ± 2	-
	0.025	-	-	-	34.1 ± 0.3	-	-

Additionally, considering that Al is the main metal component of the FCC, which is also extractable by these two acids, its extraction behavior was also evaluated (Table 4.2.B).

For conventional leaching, as it is presented in Table 4.2.B, the Al extraction increased significantly with time and H_2SO_4 concentration. The best conditions for leaching La using H_2SO_4 are 1 M and 1 h. Under these conditions, the maximum amount of La was extracted (55.6 %) minimizing the amount of Al leached (Table 4.2).

Similarly, for HCl acid leaching, for the experimental conditions tested herein that enabled the highest La extraction was 3 M of HCl and 3 h, the highest acid concentration and highest time, respectively. However, this also means a high Al extraction (42.1 %) (Table 4.2.B).

The Al co-extraction using ultrasound-assisted strategy followed the same trend as La extraction throughout time, with a maximum result of (22.8±1) % and (23.2±2) % for 1 and 1.5 M of H_2SO_4 at 1 h, respectively. Therefore, the most favorable conditions for extracting La using ultrasound treatment corresponded to 1 M H_2SO_4 for 1 h, which corresponded to an improvement of 13.9 % of the La extraction efficiency over conventional treatment.

For HCl, throughout the time of ultrasound-assisted leaching, even though it apparently seems that more Al extraction variations occurred between the different HCl concentrations when compared with H_2SO_4, similar Al extractions efficiencies than the ones observed with H_2SO_4 were observed; for the best condition (3 M HCl for 1 h), a maximum extraction value of (25.8±0.8) % was achieved.

For microwave-assisted leaching, 1M H_2SO_4 for 30 and 60 s resulted to the extraction of Al 23.1 and 48.1 %, respectively. In terms of using HCl for microwave-assisted leaching, as it is shown in Table 4.2.B, although 2 M HCl resulted in a higher La efficiency, Al extraction was also very high (48$\underline{+}$2) %. So, it is clear that these experimental conditions for leaching La are not the preferable ones because a high concentration of Al may pose more problems in the subsequent separation process. It is also important to note that for 1 M HCl for 0.017 h, less Al co-extraction (32±2) % was achieved when compared to the one recorded with 2 M HCl for 0.017 h. Based on these facts and since statistical results demonstrated that the La extraction efficiency increased in a gradient of time when microwave-assisted leaching was used, we decided to increase the leaching time

to 0.025 h and keeping the lower concentration of HCl (1 M). Under these conditions, (99.4±0.9) % of La was leached. This result was statistically better than the ones obtained for 8 x 10^{-3} ($p < 0.05$) and 0.017 ($p = 0.08$) h for the same acid concentration but statistically similar to the ones obtained to 2 M HCl for 0.017 h.

4.3.2.1. Comparative analysis between the three leaching strategies and with the literature

For H_2SO_4, even though, ultrasound-assisted leaching allowed reducing the leaching time (1 h) with a concomitant slight increase of the La extraction yield (about 14 %; 1 M H_2SO_4) comparatively to conventional method (3 h), the best leaching performance was achieved when microwave-assisted strategy was implemented. Under these conditions, the leaching yield was of the same magnitude (72.6 %) to ultrasound-assisted method (69.8 %) but was obtained much fastly (0.017 *versus* 1 h). On the other hand, for HCl, an improvement of the La extraction was obtained when equivalent H^+ concentration (2 M) was used under conventional (about 15%) or ultrasound-assisted leaching (about 17 %) relatively to H_2SO_4. For ultrasound-assisted leaching, this achievement was reached using an equivalent leaching time than the one used for H_2SO_4 but, in the case of conventional method, a longer leaching time (3 h) was needed. Comparatively to these later conditions, microwave-assisted strategy allowed extracting totally La from the spent FCC catalyst using half of the amount of H^+ (1 M) in a very shorter period of time (0.025 h), which is an important advantage in terms of saving reagents, time and energy.

A comparative analysis of the results obtained in this work with others described in the literature also corroborate the significant advantages of using microwave-assisted leaching comparatively to the conventional method. In fact, even though comparable extraction yields of REEs were reported when conventional method was employed in a similar way as in this work, more concentrated acid solutions were needed combined with a longer period of leaching time (Wang et al., 2017b) and high temperature (Innocenzi et al., 2015; Zhao et al., 2017). For example, Innocenzi et al. (2015) reported an extraction yield of 89 % of La from FCC. However, these

authors have used 2 M H_2SO_4 for 3 h at 80 °C, which is not a substantial higher yield compared to the best conditions (microwave) achieved in this study (73 %) where half amount of acid (1 M H_2SO_4) was used during a very short period of time (0.017 h). Moreover, in another work, even though high REEs extraction yields ($\geq$ 82 % for La and Ce) were achieved when leaching had been performed at low temperature (20 °C), a very concentrated acid solution (9 M HCl) was used (Wang et al., 2017a).

In conclusion, the results obtained with HCl were statistically better than those achieved with H_2SO_4 whatever the leaching strategy and experimental conditions (time and amount of acid) used. Moreover, the extraction of La from FCC using H_2SO_4 was $\leq$ 75 % for all conditions tested while La was totally leached using less amount of H^+ when microwave-assisted leaching using 1 M HCl for 0.025 h was implemented.

This significant improvement of the leaching performance when microwave-assisted leaching was used comparatively to conventional or ultrasound-assisted leaching is a consequence of the high temperature and pressure inside the PTFE vessel, which is possible to be reached due to the inherent characteristics (volumetric, controllable and selective heating) of the microwave radiation (Sadeghi et al., 2019). The lower La extraction efficiency achieved with H_2SO_4 can be a consequence of the lower coordination effect of SO_4^{2-} ion compared to Cl^- (Zhao et al., 2017). Additionally, insolubilization of La may also occur after being solubilized, likely as a double sulfate formation due to the presence of alkali electrolytes to form sparingly soluble $NaLa(SO_4)_2$ or $KLa(SO_4)_2$ or even as $La_2(SO_4)_3$ (although this precipitate is more soluble) (Porvali et al., 2018).

4.3.3. Selective recovery of leached metals

Considering the high La extraction yield (99.4 %) achieved using 1 M HCl in a shorter period of time (0.025 h), subsequent recovery of La and Al was performed using the leachate prepared under these experimental conditions. Under these conditions, the leached solution was mainly constituted by Al (8650 mg/L), La (5590 mg/L), Fe (201 mg/L) and V (275 mg/L) at pH 2.7. In this work, a sequential selective alkaline and oxalate precipitation for recovering Al and La, respectively, from the pregnant solution was considered. In order to design the feasibility of the

process as well as the best conditions that allow recovering Al and La from the solution with greater efficiency and purity along with minimizing the consume of reagents, various chemical speciation simulations were performed. In a first attempt, the influence of the pH on the selective precipitation of Al *versus* La was evaluated (Fig. 4.1.A). The simulations predicted that it is possible to separate Al from the solution, by precipitation, as aluminum hydroxide, whilst maintaining all La in the solution. Fig. 4.1.A clearly evidences that Al should precipitate completely in the pH range between 5 and 9 while La only starts to precipitate at pH 7. These facts open the possibility of separating Al from the solution, by precipitation in the pH range between 5 and 7, as aluminum hydroxide, whilst maintaining all La in the solution.

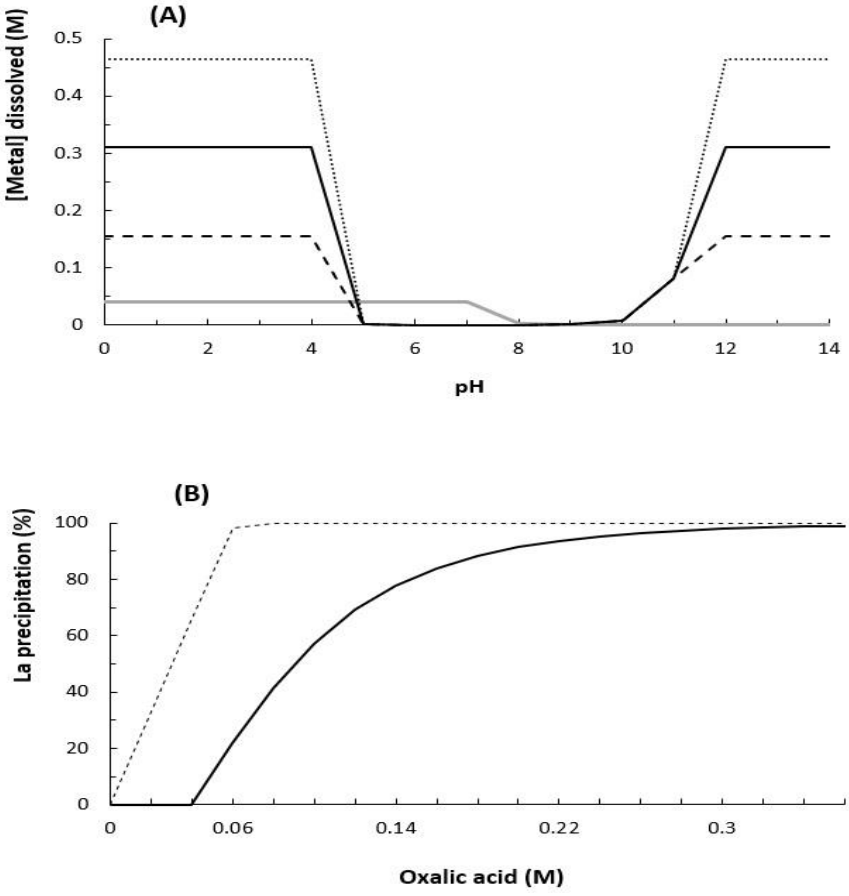


Fig. 4.1. *Influence of the pH on the amount of La (grey line; initial concentration: 0.04 M)) and Al [initial concentrations: 0.16 M (dashed line); 0.31 M (black line); 0.47 M (dotted line)] soluble* ***(A)****. Variation of the amount of La precipitated at pH 2.7 (black line) and pH 6 (dashed line) with increasing oxalic acid concentration; for both pH values, the initial concentration of La is 0.04 M* ***(B)****.*

Moreover, Fig. 4.1.A also indicates that this separation method is robust to changes of the initial Al concentration: independently of the initial Al concentration, the final concentration of soluble Al in the leachate will be minimal and of the same order of magnitude. As a result, the subsequent negative effect of the amount of Al on the consume of oxalate for La precipitation is minimized, which is not the case when the selective La oxalate precipitation is conducted at lower pH values (Innocenzi et al., 2015).

On the other hand, further chemical simulations (Fig. 4.1.B). also indicated that the selective precipitation of La, as $[La_2(C_2O_4)_3]$, under the initial conditions of the leachate (8650 mg/L of Al and 5590 mg/L of La at pH 2.7) would require a quantity of more than 31.7 g/L (0.36 M) of oxalic acid to precipitate 99 % of La if Al was not previously removed by precipitation. This is because, at pH 2.7, most of the added oxalic acid would be diverted to complex with Al present in solution (about 81 %) while only about 19 % would be used to precipitate La (data not shown). Thus, at pH 2.7, a huge expense of oxalic acid would occur. On the other hand, chemical simulations (Fig. 4.1.B) also predicted that the oxalic acid amount would decrease about four times (7.2 g/L, which corresponds to 0.08 M) if the pH was previously increased up to 6; at this pH, chemical simulations predict a very low amount of Al ($1.4x10^{-3}$ M) (data not shown) compared with the quantity of La to be precipitated (0.04 M) and, thus, a small quantity of oxalic acid would be consumed by complexation with Al.

Taking into account all these aspects, as a first attempt, the effect of the increase of pH of the initial leachate in the pH range between 5 and 6.5, in the absence of oxalic acid, on the precipitation of Al and possible co-precipitation of La was investigated (Table 4.3).

Table 4.3. *Metals (Al and Fe) content that remained in leached solution after raising the pH, as well as removed (or lost, in the case of La) from the leachate during the process. The purity of La in the remained leached solution, after precipitation, is also indicated.*

	[M] remained in solution (ppm)		**Metal precipitated (%)**			
pH	**Al**	**Fe**	**Al**	**Fe**	**La lost (%)**	**La purity in the leached solution (%)**
5	890±60	16±2	89.6	91.8	1.0	86.0
5.5	464±47	0.95±0.01	94.6	99.5	2.5	92.2
6	172±52	0.88±0.05	98.0	99.6	2.8	96.9
6.5	0.4±0.1	0.25±0.01	100	100	43.3	99.9

As it can be seen in Table 4.3, at pH 5, about 90 % of Al precipitation already occurred without almost no co-precipitation of La (only 1 %). For higher pH values (up to 6), the results presented in the table evidence that the increase of pH still allows the precipitation of Al without significant co-precipitation of La. In fact, the increase of the pH up to 6 resulted in the precipitation of about 98 % of the total amount of Al initially present in the leachate with insignificant co-precipitation of La (less than 3 %). Tests performed at pH values higher than 6 demonstrated an unacceptable loss of La by precipitation (>40 %) (Table 4.3). Additionally, a similar trend was found for Fe; although a significant portion of Fe (about 92 %) was precipitated at pH 5, the increase of the pH, particularly in the range between 5.5 and 6, resulted in almost total removal of this metal from solution. Vanadium was also found as one of the impurities present in the leachate. However, its concentration reduced from an initial value of 275 mg/L, before the precipitation step with NaOH, to a concentration $\leq$4.7 mg/L in all the pH range tested, which corresponds to a minor amount.

Based on these results, the best conditions for removing Al and Fe from the leachate corresponds to pH 6; under these experimental conditions, insignificant (2.8 %) amounts of La were lost due to co-precipitation with Al and a leached solution of La with high (97 %) purity was achieved.

Therefore, subsequently, the recovery of La, as $La_2(C_2O_4)_3$, from the previous pre-purified leached solution containing La was evaluated using a concentration of 0.1 M (9 g/L) of oxalate. This procedure allowed the total recovery of La (99.9 %), as a solid, and simultaneously improved the purity of the solid of La (99.7 %) relatively to the pre-purified La solution due to the fact that Al remained in solution complexed with oxalate. Further chemical simulations (data not shown) also predicted that for FCCs leachates containing $\geq$0.04 M of La, a complete La precipitation regardless of its initial concentration will be ensured using a molar [oxalate]/[La] ratio of 2.5 at pH 6.

Additionally, the XRD analysis of the solid recovered from the oxalate precipitation experiment evidences that all the peaks could be indexed to lanthanum oxalate hydrate ($C_6H_{20}La_2O_{22}$) with a monoclinic crystal structure. Taking a closer look at the pattern of the solid indicates that no other phases or components are found in the product. The calculated lattice constants were a= 11.370 Å, b=9.608 Å and c= 10.490 Å, which are in agreement with ICDD file no. 01-075-7132 (Fig. 4.2).

A comparative analysis of the workflow developed in this study with other simple flowsheets described in the literature evidence that the final recovered REEs product obtained in our work presented much higher purity (99.7 %) relatively to the one (about 11 % of Al was present as contaminant) described by Innocenzi et al. (2015). On the other hand, other works (Innocenzi et al., 2015; Wang et al., 2017b, 2017a) described the achievement of recovered REEs products with a purity grade more comparable (80-98.7 %) to the one obtained herein. However, in these cases, the flowsheets were more complex (various and, in some cases, more complex separative operations, such as solvent extraction, were involved) and/or a high consumption of reagents (for instance higher acid concentration at higher L/S ratio) were needed (Innocenzi et al., 2015; Wang et al., 2017b).

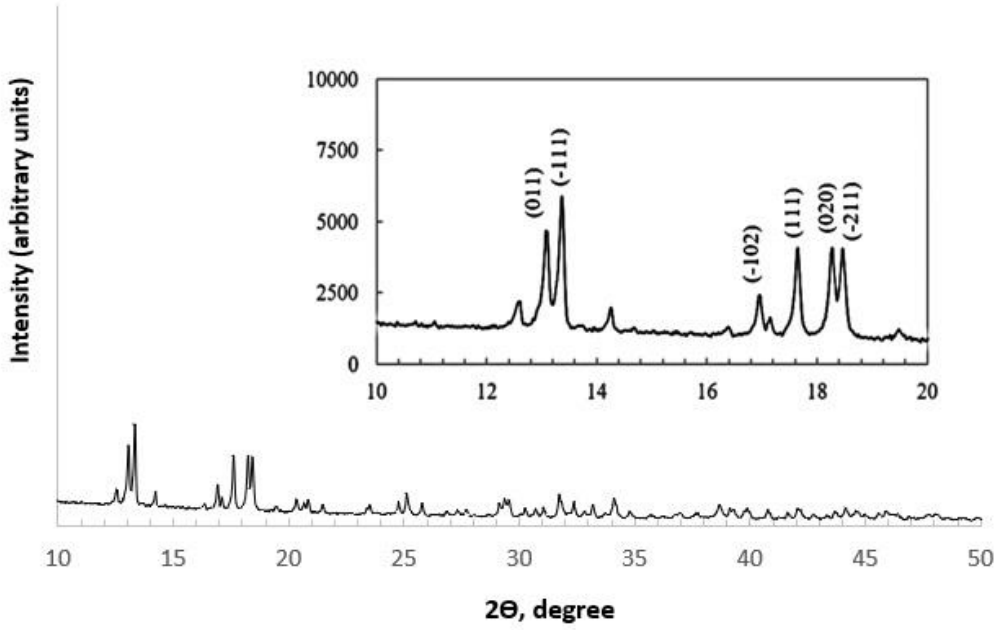


Fig. 4.2. *XRD pattern (Cu Kα radiation) of the solid recovered from the oxalate precipitation experiment. All peaks match $C_6H_{20}La_2O_{22}$ reference peaks. The insert shows the intensity of three times higher than the initial pattern.*

4.4. Proposal of a closed-loop process to recycle spent FCC catalyst

The flow sheet of whole process presented in Fig.4.3, consisted of simple and feasible techniques. The process begins with the microwave-assisted leaching of spent FCC using L/S ratio of 5 and 1 M of HCl for 90 s. This leaching strategy was capable of extracting 99.4 % of La and 34.1 % of Al. The solid from the leaching has been suggested that it can be incorporated into new zeolite production (Wang et al., 2017b). Subsequently, the main metals (Al and La) present in the leachate were sequentially recovered by selective precipitation. Firstly, almost all (98 %) Al was recovered by alkaline precipitation after raising the pH up to 6 with NaOH; under these conditions, a solid of $Al(OH)_3$ of high purity in Al (88.7 %), which can be used for Al-Fe alloys production, was obtained. Further precipitation of La with oxalate resulted in the total recovery

of La, as a solid of $La_2(C_2O_4)_3$, with high purity (99.7 %), which can be calcinated to produce La_2O_3, a form that can be directly reused in the industry.

The effluent generated during this process is mainly constituted by oxalate, which is biodegradable, and minor amounts of Al; depending on the regional industrial discharge rules, it can be directed to a wastewater treatment facility.

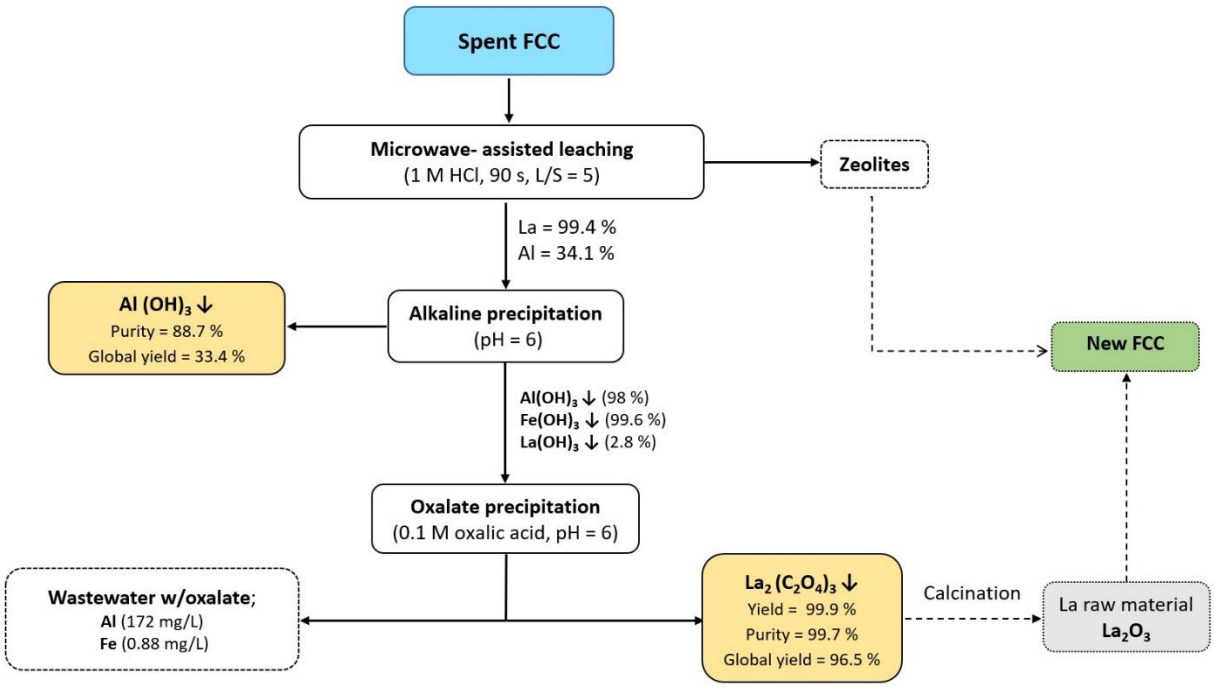


Fig. 4.3. *Proposed process flowsheet for total recovery of all resources and metals from spent FCC (Blue box represents an initial residue; yellow boxes show final products obtained in this study, grey box illustrates final raw material resultant from the implementation of this hydrometallurgical process, green box indicates the start of a new product and dashed lines represent final products not tested within this study).*

4.5. Conclusions

In this study, a new, simple and effective workflow for recovering La (plus Al) from spent FCCs was developed. The process is based on a single and fast (90 s) microwave-assisted leaching using a reduced amount of acid (1 M HCl), which allowed extracting all La from the residue. Subsequently, almost all (> 98%) Al and La extracted were recovered, as high purified grade products of $Al(OH)_3$ and $La_2(C_2O_4)_3$, respectively, using two step-wise selective [alkaline (pH 6) followed by oxalate] precipitation steps.

Comparatively to other workflows described in the literature, the process developed herein is capable of recovering Al and La salts with high purity and yield using reduced amount of reagents, being much faster, simpler and cost effective, with the consequent saving of energy, reagents and human resources, which is ideal for industrial application. Moreover, the process constitutes a nearly closed process (almost no tertiary effluents are produced) and, particularly, the precipitation step of Al is flexible to modifications of the initial concentration present in the hydrochloric acid FCC leachate without compromising the quality of the final metal products recovered. In conclusion, the closing of the loop of FCC´s production system, as it is proposed in this novel FCC´s recycling strategy, will contribute for reducing the mining worldwide and the amount of spent FCCs landfilled each year, and, thus, to improve the environmental quality and ecological and human health envisaging a more circular economy and a sustainable environment.

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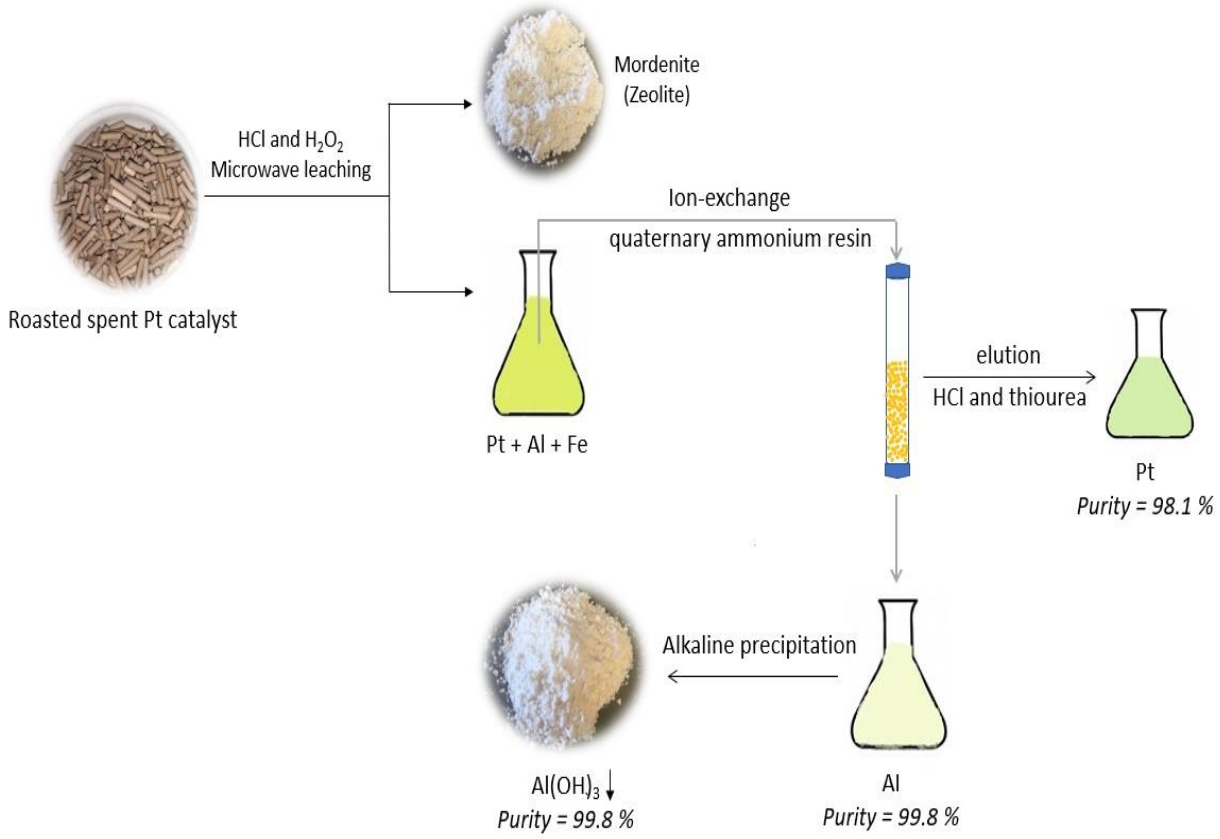
Chapter 5

Recovery of platinum and aluminum from spent reforming petroleum catalyst



Abstract

Pt is one of the most precious metals on Earth with a variety of unique industrial applications, particularly in catalytic reactions. Its recovery after use is therefore essential. This work aims to recover Pt efficiently from a spent petrochemical Pt catalyst using a more economical and environmentall sustainable process. To that end, the effectiveness of a two-steps workflow [microwave-assisted leaching using a mixture of HCl and H_2O_2 followed by an ion-exchange purification] was developed and optimized. It was found that roasted powder size catalyst required less time but higher reagent quantities for complete leaching (single 45 s cycle with 30 % HCl and 3 % H_2O_2) when compared to roasted original size catalyst (2 cycles of 60 s with 25 % HCl and 2 % H_2O_2). Furthermore, the strong anionic exchange resin used for subsequent separation of Pt from Al and Fe, was capable of effective separation of the metals: Pt in the eluate presented a purity of 98.1 % while Al, in the raffinate, presented a purity of 99.8 %. These results evidence the high selectivity of the resin for Pt. In summation, it can be concluded that the overall process is a potentially good addition to a more circular economy as it manages to recover high quality Pt for recycling in new catalyst production as well as other by-products, whilst minimizing leaching time and environmental impacts.

5.1. Introduction

Platinum group metals or PGMs – which includes Pt, Pd, Rh, Ru, Ir, and osmium (Os) – are precious metals that share similar characteristics. These metals are often used in catalytic reactions in industrial settings, jewelery and biomedical applications among other aspects (Safarzadeh et al., 2018). In 2013, 73 % of the world's production of Pt and Pd was originated in South Africa. However, the supply from this country is expected to be partly suppressed due to the absence of new mining projects and closure of existing ones as well as the decreasing ore head grades and labor efficiency (Safarzadeh et al., 2018).

Furthermore, there is a high depletion rate of high-grade PGMs resources due to increasing demands leading to decreasing PGMs concentration in the remaining naturally occurring ore (Jha et al., 2013). Therefore, secondary sources are necessary to meet demands as well as to minimize environmental impacts of the mining process.

These secondary sources often reportedly have a content of PGM a thousand times higher than that of Pt primary ores, further proof of the untapped potential of these sources (Sun and Lee, 2013). To recover this precious metal from spent catalyst, a combination of pyro and hydrometallurgical processes are often applied. The process is optionally initiated with roasting of the catalyst at high temperatures as a form of pre-treatment, which eliminates existing organic compounds (Jha et al., 2013). This is followed by a leaching step, which might be performed with a strong acid, such as HCl, combined with an oxidant (Sun and Lee, 2013) or with cyanide (Shams et al., 2004). However, the existing leaching methods have a variety of shortcomings. For instance, the use of dangerous compounds, such as cyanide with its potentially toxic fumes (Shams et al., 2004) or the use of extreme concentrations of acid (Sasaki and Maeda 2014; Suoranta et al., 2015) as well as very long leaching time and high L/S ratios (Zanjani and Baghalha, 2009) leads to an overall highly inefficient, energy and cost intensive process. Therefore, the optimization of reagent use and leaching time is of paramount importance. To that end, the use of microwave, as an auxiliary energy source has shown advantages over conventional process for other wastes (Pinto and Soares, 2012; Sadeghi et al., 2019, 2017; Suoranta et al., 2015) but not

yet extensively tested for Pt recovery from spent reforming catalyst. Since among the various leaching agents available, HCl is the only cost-effective media able to dissolve PGMs (Bernardis et al., 2005; Hubicki et al., 2008) and the chloride chemistry of PGMs is well understood, in this study, our first aim was to evaluate the potentialities of microwave-assisted HCl leaching under oxidative conditions (H_2O_2 was chosen as oxidant) to improve the overall efficiency (mainly by reducing the amount of reagents needed and the leaching time) of this process. A positive outcome of this step will contribute to improve the HCl leaching kinetics as well as to reduce environmental hazardous and increase safety.

After leaching, metal purification is required to separate Pt from the other metals, mainly Al, also extracted during the leaching. For this purpose, there are several options already studied in the literature, such as ion exchange (Shams et al., 2004), precipitation (Jha et al., 2013) and solvent extraction (Sun and Lee, 2013). Several solvent extractants have been studied in the literature to separate Pt from other metals from the leached solution, such as hydroxyoximes, dialkyl sulphides and sulphoxides, quaternary ammonium salts, etc. However, these strategies have several drawbacks, such as the high cost of solvents and the use of complex and difficult equipment to operate, which often present problems with reagent losses (Nikoloski and Ang, 2014). On the other hand, ion exchange technique has been recognized as a powerful purification method and provides the possibility of enriching final PGMs concentration after elution if the resin has high affinity (Shen et al., 2010). Ion exchange resins are reported to have high capacity and selectivity for PGM as well as being constituted by particles with high mechanical strength and toughness (Hubicki et al., 2007) but the use of strongly oxidizing reagents can cause severe damage of the resin (Nikoloski et al., 2015), which may unable multiple cycles of loading and elution. Another limitation of these ion exchangers is related with its low elution capacity, which often leads to the need of its calcination (Marinho et al., 2011) to recover most of the adsorbed metals, greatly shortening the life span of the resins. Therefore, in this work, it was our ultimate goal to integrate all aspects mentioned above to create a simple yet cost effective and complete Pt recovery process from spent catalysts, capable of contributing to a more circular economy, mainly based on two sequential steps: firstly, a microwave-assisted leaching step, which simultaneously allows extracting all Pt from the spent catalyst minimizing the consume of

extractants and leaching time (and, consequently, energy), followed by a selective ion-exchange step, where the use of a quaternary ammonium resin permitted to obtain a highly purified Pt eluate.

5.2. Material and Methods

5.2.1. Reagents and analytical techniques used

The stock solutions of HCl (Sigma-Aldrich, 37 %), (HNO_3 (Chemlab, 65 %), H_2O_2 (Chemlab, 30 %), NaOH (Eka, p.a), thiourea (CH_4N_2S, Alfa Aesar, 99 %), platinum(IV) chloride ($PtCl_4$, Acros organics, 99 %), aluminum chloride ($AlCl_3$, Acros organics, 99 %, anhydrous, granules) and iron(III) chloride hexahydrate ($FeCl_3.6H_2O$, Sigma-Aldrich, 97 %) were of analytical grade and used without further purification.

The AAS-FA using an Analytik Jena novAA 350 (Jena, Germany) spectrophotometer was applied for the determination of all metals, with air-acetylene flame for Fe, Pt, Ni, Cu, and Zn and nitrogen protoxide-acetylene flame for Al, V, Sn, and Ti. Before any measurement, solutions were filtered using cellulose nitrate (CN) membrane filter with pore size of 0.45 µm. XRF was conducted for semi-quantitative chemical analysis using a WD-FRX Axiosmax 4kW equipment with Rhodium ampoule and Omnian software from Panalytical for characterization of rosted powder of spent Pt catalyst in oxides form. XRD was carried out to determine the structure of the final residue after leaching process at ambient temperature on an Empyrean diffractometer (Cu Kα1,2 X-radiation, λ1 = 1.54060 Å; λ2 = 1.54443 Å), under operating configuration of 45 kV, 40 mA with a step size [2Θ°] of 0.026° and a scan step time of 96.3 s.

5.2.2. Catalyst pretreatment and characterization

Spent Pt catalyst with commercial name of Z771A was used in this study. This catalyst has cylinder shape with average particle lengths of (6± 3) mm (n=300) measured by paquimeter. Part of the spent Pt catalyst was manually ground by porcelain ball mill to reduce the size of its particles and create a powder. The particle size distribution of this powder was measured in aqueous medium by laser dispersion using a Coulter LS230 equipment. 90 % of particle were below 331.5 µm with an average particle diameter of 141.9 µm.

Both original and catalyst in powder form were roasted in a muffle as a pretreatment: temperature was raised gradually by 50 °C and then remained at 700 °C for 90 min. The roasted spent catalyst was cooled down in the muffle and was kept in a desiccator before experiments. The loss of mass during this process was roughly 1.6 %.

For characterization, the roasted catalyst (original and powder) was analyzed by acid total digestion with aqua-regia (HCl: HNO_3 ratio of 3:1). This digestion process was performed on a heater for at least 4 h by boiling the solution at approximately 100 °C. Metal concentration in the final solution was controlled by AAS-FA after filtration. Simultaneously, an XRF of the roasted powder catalyst was also performed to compare with acid digestion and vice-versa.

5.2.3. Leaching tests

Leaching tests were performed using either conventional or microwave-assisted methods on both roasted of the original and the powder form of the catalyst. The initial conventional leaching tests were performed with two different concentrations of HCl (10 and 30 %) and H_2O_2 (1 and 3 %) using a shaking thermostatic bath with a L/S ratio of 20, at 70 °C for 2 h and 180 RPM. Final concentrations of Pt, Fe and Al were measured by AAS-FA and its leaching efficiency calculated. The studies of microwave-assisted leaching were performed inside a PTFE bomb including a 23 mL container and using a domestic microwave oven (900 W, 2.45 GHz). After each test, a 30 min cooling time was necessary to avoid excessive pressure and temperature generated during the microwave heating. The efficiency of the microwave-assisted leaching was evaluated initially for

the powder form, testing different combination of time (30, 45 and 60 s) number of cycles (1 and 2 cycles), HCl concentration (25 and 30 %), H_2O_2 concentration (2 and 3 %) and microwave power (540, 630, 720 and 810 W). A L/S ratio of 20 was used for all leaching tests. Subsequent leaching tests were performed with the original catalyst using a fixed microwave power (810 W) whilst changing HCl (20, 25 and 30 %) and H_2O_2 (2 and 3 %) concentrations as well as time (45 and 60 s) and number of cycles (1 and 2 cycles). For all experiments, the L/S was kept constant at 20, unless otherwise indicated.

5.2.4 Metal purification

A chromatographic glass column with adjusting top screw (d= 10 mm, h= 100 mm) was used to study ion exchange. A rigorous amount (1.2 g) of a quaternary ammonium resin (resin B) was transferred to the column with water in order to simultaneously wash the resin and remove the air pockets from the bed column by attaching the water line at the bottom of the column.

Initial tests were performed using model synthetic solutions prepared in 25 % HCl and 2 % H_2O_2 and containing approximately the same amount of metal composition present in the optimized leachate resultant from microwave-assisted leaching of the catalyst. The resin was washed with 100 mL deionized water between adsorption and elution. After elution, resin was washed and reused for another experiment. For adsorption experiments, a flow rate of 0.25 mL/min was used provided by a peristaltic pump MS-Reglo (Ismatec, Switzerland). Samples of the outlet solution were collected at different intervals for 20 min followed by the determination of metal concentrations by AAS-FA. Elution of the adsorbed metals was subsequently performed with fixed concentration (2 M) of HCl and varied concentration (0.5 and 1 M) of thiourea and flow rates (0.5 and 1 mL/min). The eluates were collected during the experiment for defined period of time (3-6 min depending on the flow rate) and analyzed by AAS-FA.

All tests herein described were performed at room temperature and for each experiment, at least two independent assays were done.

At a final phase, the real leached solution was tested for both the adsorption and elution steps, using the best performing conditions previously obtained for the model synthetic solutions. Adsorption was performed for 660 min. Then, elution of metals adsorbed in the resin was done using 2 M HCl and 1 M thiourea for 60 min. Flow rates of 0.25 and 0.5 mL/min were used for adsorption and elution, respectively.

For each metal, relatively to Pt, the separation number (SN) was calculated according to Eq. 5.1:

$$\text{Separation number} = \frac{[\text{Pt}]_{\text{eluate}} \,/\, [\text{Metal}]_{\text{eluate}}}{[\text{Pt}]_{\text{feed}} \,/\, [\text{Metal}]_{\text{feed}}} \qquad (5.1)$$

5.3. Results and discussion

5.3.1. Catalyst characterization

The metal(loid) composition of the spent Pt catalyst was determined by XRF analysis and total acid digestion with aqua regia (Table 5.1). Unless SiO_2, which is not solubilized with aqua regia, Table 5.1 evidences that the composition of the main components present in the spent catalyst determined by both methods are in good agreement. Results shown in Table 5.1 also confirm that the composition determined corresponds to a typical spent Pt catalyst: a dominance of Al due to the presence of the aluminosilicates of the catalyst as well as a relatively high content of Pt, a vital metal for the catalyst reaction, and impurities in the form of iron oxides.

Table 5.1. *Composition of spent Pt catalyst, expressed in percentage of metal(loid)s oxides, determined by XRF analysis and acid digestion using aqua regia.*

Method	Al_2O_3	SiO_2	PtO_2	Fe_2O_3	Other metals
XRF	71	27	0.43	0.11	≤ 1.2
Aqua regia digestion	71	-	0.40	0.11	≤ 1.5

5.3.2. Leaching tests

Literature describes a wide variety of leaching agents using mineral acids, such as HCl, H_2SO_4, HNO_3 or bases, NaOH for recovering PGMs from spent catalyst (Kasuya et al., 2016; Matjie et al., 2005; Shams and Goodarzi, 2006; Sun and Lee, 2013). However, as it would be expected, NaOH was found that has no effect on Pt dissolution. The most common way for complete extraction of Pt is the addition of different possible oxidizers, such as H_2O_2, HNO_3 and chlorine with acids such as HCl as a complexing agent (Baghalha et al., 2009; Sun and Lee, 2013). Considering that several studies, where diferent metals were extracted from various secondary sources, demonstrated that microwave-assisted heating, as an auxiliary energy source, was an efficient method for recovering metals from different types of residues with significant reduction in time and reagent use (Jafarifar et al., 2005; Pinto and Soares, 2012; Sadeghi et al., 2019, 2017; Suoranta et al., 2015) comparatively to the traditional conventional process. In this study, the efficacy of microwave-assisted leaching of Pt from the spent Pt catalyst was evaluated.

Leaching tests were performed for both the original spent catalyst as well as its powder form using both conventional and microwave-assisted techniques. For both leaching techniques, a combination of HCl and H_2O_2 was used. The presence of chloride ions, from HCl, leads to increase Pt dissolution by changing the oxidation potential and creating stable chloro-complexes in high acid concentration solutions (oxidation potential without and with chloride present: Eqs. 5.2 and 5.3, respectively) (Sun and Lee, 2013):

$$Pt\,(s) \leftrightarrow\ Pt^{4+}(aq) + \ 4e^{-} \qquad E°= -\ 1.150\ V \qquad (5.2)$$

$$Pt\,(s) + 6\ Cl^{-}(aq) \leftrightarrow\ PtCl_6{}^{2-}(aq) + \ 4e^{-} \qquad E°= -\ 0.774\ V \qquad (5.3)$$

The addition of H_2O_2 serves as an oxidant to further increase the leaching efficiency, leading to a complete reaction as follows (Eq. 5.4) (Sun and Lee, 2013):

$$Pt\,(s) + 2\ H_2O_2(aq) + 6\ HCl\ (aq) \leftrightarrow\ 2H^{+} + PtCl_6{}^{2-}(aq) + \ 4H_2O \qquad \Delta E°= 1.002\ V \qquad (5.4)$$

Extraction of Al from alumina catalyst support by acid attack occurs as it is presented in Eq. 5.5 (Steinlechner and Antrekowitsch, 2015):

$$Al_2O_3\ (s) + 6H^{+}\ (aq) \leftrightarrow\ 2Al^{3+}(aq) + 3H_2O\ (l) \qquad (5.5)$$

5.3.2.1. Conventional leaching

Tests using conventional leaching were performed in two sets of conditions: (i) 10 % HCl + 1 % H_2O_2 and (ii) 30 % HCl + 3 % H_2O_2 with a L/S ratio of 20 (Table 5.2). Metal extraction results followed a predictable pattern: higher HCl and H_2O_2 as well as lower particle size (i.e, powder spent Pt catalyst) resulted in higher leaching efficiency for every tested metal. However, the difference is not always constant when comparing particle size; iron leaching increase for powder when compared to original but for condition (ii) (30 % HCl + 3 % H_2O_2) this increase was lower than for the other metals. This might be an indicator that 52.5 % of Fe leaching might be close to the highest possible Fe leaching efficiency under conventional conditions.

Similarly, when comparing the differences between the various concentrations of reactants, it can be seen that the increase due to higher concentrations is two times larger for Pt (approximately 20 % more *vs* 8-9 % for Al, Fe) when compared to the other metals. This also seems to indicate slightly higher selectivity of the leaching process for Pt at higher concentrations.

Table 5.2. *Influence of different HCl and H_2O_2 concentrations on the metal extraction yield (expressed in %) from original and powder spent Pt catalyst at L/S ratio of 20 with conventional leaching conditions.*

	10 % HCl; 1 % H_2O_2 (v/v)		**30 % HCl; 3 % H_2O_2 (v/v)**	
Metal	**Original**	**Powder**	**Original**	**Powder**
Pt	30.2±0.7	34.6±0.4	50.4±0.6	56.9±0.1
Al	24.9±0.7	29.6±0.5	33.1±0.6	37.8±0.4
Fe	41.0±0.6	45.7±0.5	50.1±0.3	52.5±0.9

Overall, a maximum leaching efficiency of 56.9 % for Pt, 37.8 % for Al and 52.5 % for Fe was obtained during 2 h of conventional leaching, which, in the case of Pt, is quite a limited efficiency considering the economic value of Pt. The lower leaching efficiency of Pt in our work compared to the results reported by Sun and Lee (2013), where complete dissolution of Pt was achieved (10 % HCl + 1 % H_2O_2, 70 °C, L/S ratio of 20, 300 RPM for 2h) can be explained by the higher metals content in our spent catalyst (0.34 % *vs.* 0.09 % of Pt and 37.6 % *vs.* 10.2 % of Al, respectively).

5.3.2.2. Microwave-assisted leaching

Initially, microwave-assisted leaching was performed on powder spent Pt catalyst, testing the effect of microwave power potential settings, leaching time, number of cycles and concentration of HCl and H_2O_2 (Table 5.3). Using the highest amount of HCl and H_2O_2 tested in conventional treatment [condition (ii)], where the highest extraction of Pt was achieved, the initial conditions were chosen to be 540 W and 2 cycles of 60 s in the microwave oven. Under these conditions, the Pt leaching efficiency was about 29 % higher comparatively to the best conventional leaching condition tested (Table 5.2). This result clearly demonstrates how microwave-assisted leaching can outperform conventional leaching even with a significant reduction of leaching time. Despite the high Pt extraction efficiency achieved (about 86 %), a significant portion of Pt still remains in the catalyst; so, the next step was to study the influence of microwave power on the Pt leaching efficiency maintaining constant all other experimental conditions.

Table 5.3. *Influence of microwave power potential set (and spent of energy), number of cycles, leaching time and concentration of reagents on the metals leaching efficiency from powder spent Pt catalyst at L/S ratio of 20.*

		Microwave Conditions			Metal leaching efficiency (%)		
Set up	**Reagents (v/v)**	**Power (W)**	**No. of cycles and Time**	**Spent Energy (kJ)**	**Pt**	**Al**	**Fe**
A	30 % HCl, 3 % H_2O_2	540	2 cycles of 60 s	64.8	85.6±0.9	99.3±0.2	86.5±0.5
B	30 % HCl, 3 % H_2O_2	630	2 cycles of 60 s	75.6	92.8±0.02	100.0±0.4	94.4±0.02
C1	30 % HCl, 3 % H_2O_2	720	2 cycles of 60 s	86.4	100.0±0.3	98.9±0.5	99.7±0.1
C2	30 % HCl, 3 % H_2O_2	720	1 cycle of 60 s	43.2	96.4±0.6	95.7±0.8	96.2±0.3
D1	30 % HCl, 3 % H_2O_2	810	1 cycle of 60 s	48.6	100.0±0.5	100.0±0.3	99.4±0.3
D2	30 % HCl, 3 % H_2O_2	810	1 cycle of 45 s	36.5	100.0±0.3	100.1±0.9	100.0±0.5
D3	30 % HCl, 3 % H_2O_2	810	1 cycle of 30 s	24.3	65.6±0.8	63±2	70.1 ±0.8
D 4.1	25 % HCl, 3 % H_2O_2	810	1 cycle of 45 s	36.5	96.1±0.5	86.4±2.1	92.2±0.9
D 4.2	30 % HCl, 2 % H_2O_2	810	1 cycle of 45 s	36.5	86.4±0.9	79.6±2.2	83.8±1.3
D 5.1	25 % HCl, 3 % H_2O_2	810	1 cycle of 60 s	48.6	97.5±0.4	92.9±1.3	93.1±1.8
D 5.2	30 % HCl, 2 % H_2O_2	810	1 cycle of 60 s	48.6	95.8±1.2	88.2±1.9	94.8±1.1

The progressive increase of power from 540 to 720 W led to an increase of about 14 % of the Pt leaching efficiency, being Pt totally leached for the highest power. Since total Pt extraction was achieved for 720 W, a tentative to reduce the energy consumption was tried. When the leaching time was reduced for 1 cycle of 60 s (set up C2), which resulted in the consume of half amount of energy, only a small (4 %) decrease of the Pt leaching efficiency occurred. Considering the high value of Pt, the aim was to maintain the highest leaching efficiency possible (close to 100 %); so, the power was increased to 810 W, maintaining the same time (1 cycle of 60 s) (set up D1). This led again 100 % Pt leaching efficiency while still spending less energy than 2 cycles of 60 s at a lower power of 720 W (set up C1). In fact, the reduction in time is even larger considering the cooling time of 30 min required between cycles. To further reduce the consume of energy, two consecutive assays where the duration of leaching time was progressively decreased (15 s in each case; set ups D2 and D3) revealed that the high performance of the leaching process (100 % leaching efficiency of Pt for set up D2) still occurs when a duration cycle of 45 s was used but not when 30 s were used, where a significant reduction of Pt leaching efficiency (about 35 %) was observed. Further tentative to reduce progressively the quantities of each reagent (HCl or H_2O_2) were assayed (set ups D4.1, D4.2, D5.1 and D5.2). However, for all conditions tested, Pt leaching efficiency decreased even when the leaching time was increased (set ups D5.1 and D5.2).

Previously, it was found that the ideal conditions for leaching Pt totally from the powder catalyst were those corresponding to set up D2 (Table 5.3). Considering these good results, our next step was to evaluate the possibility of leaching Pt directly from the original roasted catalyst starting with similar conditions as those power value (810 W) whilst changing the time and number of cycles as well as the concentration of chemical reagents used (Table 5.4). The initial conditions mimic the best conditions obtained for powder form: 30 % HCl, 3 % H_2O_2, 1 cycle of 45 s (set up A). Compared to the results achieved with powder form, leaching efficiency was reduced by only 5-6 % for all three metals, which indicates that the milling process might not be cost-effective as it seems to present limited advantages. This is further backed up by the next test (set up B), in which the time was increased by only 15 s with a resulting leaching efficiency being the optimal value and equal to the value obtained for the same conditions in powder form.

Table 5.4. *Influence of concentration of reagents (HCl and H_2O_2) and leaching time (number of cycles and duration of each cycle) on the leaching efficiency of metals from original spent Pt catalyst at L/S ratio of 20 (unless set up G, where a L/S ratio of 15 was used) and with 810 W microwave power.*

		Microwave Conditions		Metal leaching efficiency (%)		
Set up	**Reagents (v/v)**	**Cycle and Time**	**Spent Energy (kJ)**	**Pt**	**Al**	**Fe**
A	30 % HCl, 3 % H_2O_2	1 cycle 45 s	36.5	94.8±0.1	96.4±0.2	94.5±0.04
B	30 % HCl, 3 % H_2O_2	1 cycle 60 s	48.6	100.0±0.2	100.0±0.7	100.0±0.2
C1	30 % HCl, 2 % H_2O_2	1 cycle 60 s	48.6	94.2±0.3	95.2±0.2	93.7±0.4
C2	30 % HCl, 2 % H_2O_2	2 cycles 45 s	72.9	100.0±0.6	100.0±0.1	100.0±0.1
C3	30 % HCl, 2 % H_2O_2	2 cycles 60 s	97.2	100.0±0.2	100.0±0.3	100.0±0.2
D1	25 % HCl, 2 % H_2O_2	2 cycles 45 s	72.9	96.2±1.0	97.3±0.1	92.7±0.3
D2	25 % HCl, 2 % H_2O_2	2 cycles 60 s	97.2	100.0±0.7	100.0±0.5	100.0±0.3
E	25 % HCl, 1 % H_2O_2	2 cycle 60 s	97.2	78.6±0.2	90.6±0.1	90.0±0.4
F	20 % HCl, 2 % H_2O_2	2 cycles 60 s	97.2	83.6±0.03	87.4±0.3	85.1±0.1
G	25 % HCl, 2 % H_2O_2	2 cycles 60 s	97.2	70.3±0.4	86.3±0.1	80±0.5

After that, the third test (set up C1) was meant to test if it was possible to reduce the quantity of spent reagents – by decreasing the H_2O_2 concentration from 3 to 2 %. This led to a decreased leaching efficiency around 94.2 % for Pt, similar to that obtained in set up A, which clearly evidences that there is potential to reduce reagents. Under the premise that the reduction of reagent use should be prioritized over the leaching time and, thus, spent energy savings, subsequently, the same concentration of reagents used in set up C1 was tested by increasing progressively the leaching time: (i) 2 cycles of 45 s (set C2) and (ii) 2 cycles of 60 s (set C3). Under both conditions, all metals were totally extracted. Subsequently and following the priority of reducing the quantities of reagents, two experiments, where the amount of HCl was decreased to 25% and the H_2O_2 concentration was maintained (25 % HCl, 2 % H_2O_2) were tested using two leaching times: (i) 2 cycles of 45 s (set D1) and (ii) 2 cycles of 60 s (set D2). Whereas the first set up condition lead to a small yet significant reduction in Pt efficiency (about 96 %), total Pt leaching was achieved when longer leaching time was used. Two additional tentative to reduce the amount of reagents were made, where the concentration of H_2O_2 and HCl were reduced in an independent way (set ups E and F, respectively), originated unsatisfactory Pt leaching yields.

Finally, considering that the best conditions to minimize reagent used whilst maintain performance was found to be 25 % HCl, 2 % H_2O_2 for 2 cycles of 60 s, this condition was tested with a lower L/S ratio of 15 (set up G). However, this led to a significant drop in Pt leaching efficiency (70.3 %) and, therefore, the original value obtained for L/S of 20 was deemed to be the ideal combinations of set parameters. Under this condition (set up D2), final concentration of metals in the leached liquor were 18.7 g/L Al, 170 mg/L Pt and 36.9 mg/L Fe (Table 5.5).

Table 5.5. *Metal concentrations and purity (Al and Pt) in the leachate obtained from the original spent (25 % HCl, 2 % H_2O_2, L/S ratio of 20 and two microwave cycles of 60 s at 810 W) and in the other various solutions obtained throughout the purification process.*

Solution	Pt (mg/L)	Al (g/L)	Fe (mg/L)	Metal purity (%)	
				Pt	Al
Leachate	170	18.7	36.9	0.90	98.9
Raffinate	8.9	17.7	29.0	-	99.8
Eluate	285	2.7×10^{-3}	2.6	98.1	-

The XRD analysis of the remaining residue after leaching (Fig. 5.1) proved a complete extraction of all metals from spent Pt catalyst since the residue consisted of only mordenite, a zeolite mineral with high ratio of silicon to aluminum atoms, which makes it more resistant to attack by acids than most other zeolites. All presented peaks in Fig. 5.1 match to mordenite reference peaks and agree with ICDD file 04-014-7674.

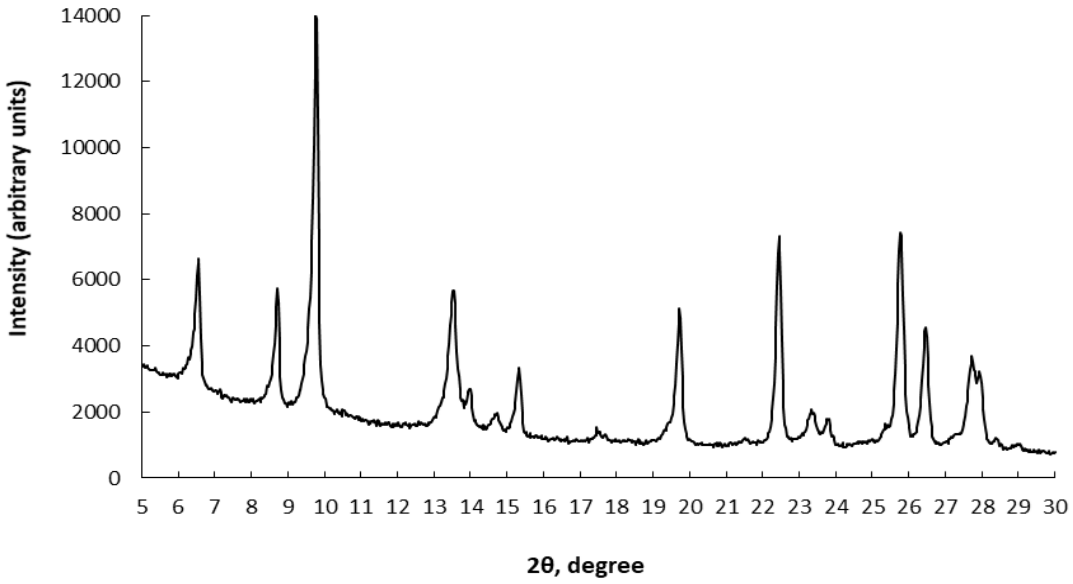


Fig. 5.1. *XRD pattern of the final residue that remained after microwave leaching of original spent Pt catalyst.*

5.4. Metals purification and recovery

In this work, a strongly basic anion-exchange resin (resin B) was selected for evaluating its potential to adsorb selectively Pt from the leachate and, thus, to simultaneously concentrate and purify it. Since under the chemical conditions used, the predominant complex ion of Pt(IV) species should be $PtCl_6^{2-}$ (Nikoloski and Ang, 2014) and the resin is positively charged, the adsorption of the Pt complexes onto the resin will occur by an ion-exchange interaction according to Eq. 5.6:

$$2 \vdash N^+R_3Cl^- + [PtCl_6]^{2-} \Leftrightarrow [\vdash N^+R_3]_2\,[PtCl_6] + 2\,Cl^- \qquad (5.6)$$

where the symbol ⊢ denotes the inert matrix (polymer structure) of the resin. Eq. 5.6 shows that anionic chloride complex of Pt, $[PtCl_6]^{2-}$, is highly polarized and has high affinity to positive charged functional groups of resins and, thus, shift the equilibrium to the right side. In addition, by the theory of hard and soft acids and bases (HSAB) of Pearson, more stable complexes will occur between metal ions and ligands with similar electronegative donor atoms and, thus, nitrogen and sulphur functional groups are suitable for precious metal ions selective adsorption. In Fujiwara et al. (2007), crosslinked chitosan resin was used to investigate the adsorption of Pt(IV), Pd(II) and Au(III) from aqueous solutions and it was also reported that nitrogen atoms are the main adsorption sites for Pt (IV), Pd(II) and Au(III). Another aspect studied by Fujiwara et al. (2007), was the influence of the pH values on the sorption capacity. Existence of more HCl, leading to lower pH values leads to the formation of more adsorbable species of Pt(IV), which are more available due to the higher chloride anions in the solution (Eq. 5.6) and lead to Pt separation from other metal ions.

In order to verify the suitability of the resin for retaining Pt and define the maximum period of time that the resin is effective to adsorb Pt (at least up to 90 % adsorption of Pt), column assays were performed using a model synthetic solution, prepared in 25 % HCl plus 2 % H_2O_2, which metals composition matched the leachate achieved under optimized conditions. A flow rate of 0.25 mL/min, which correspond to normalized flow rate of 0.21 mL/ (min. g) was used for all column assays and samples of the outlet (raffinate) were collected throughout time. Variation of

the ratio between metal concentration in the outlet (C_o) and inlet (C_i) with time can be visualized in Fig. 5.2.

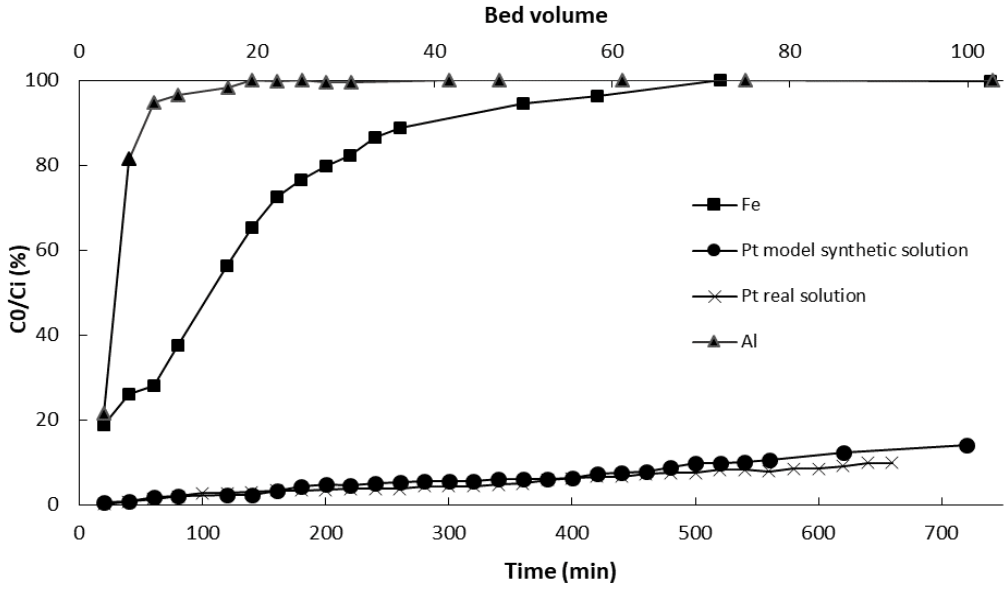


Fig. 5.2. *Metal concentration ratio in the outlet, C_o, and inlet, C_i, in the column over time and bed volume (BV) for Pt in both experiments (model synthetic solution and real solution) and Al and Fe in the case of the experiment performed with model synthetic solution. Flow rate: 0.25 mL/min.*

Fig. 5.2 evidences that the resin retained Pt efficiently for a long period of time. In fact, Pt was continuously being adsorbed and after 540 min [75 bed volume (BV)] still 90 % of total Pt is retained by the resin. Fe was retained efficiently in the first 60 min (8 BV); when C_o/C_i reached 30 %, the concentration of Fe in the outlet solution started to increase and, after 420 min (58 BV), all Fe was found in the raffinate. Also Fig. 5.2 clearly indicates that the resin has almost no affinity to Al and the concentration of Al in the outlet increased rapidly from the beginning of the experiment; C_o/C_i reached 1 after 80 min (11 BV). These results all together demonstrate the affinity of the resin for adsorbing Pt and suggest that the resin fulfills the requirement of Pt and (Al + Fe) separation.

These results are slightly inferior when compared to Sun and Lee (2011) (Fig. 9 in their study) in which the use of the same 25 % HCl (3 M) concentration lead to a more distinct separation of Fe

from Pt (although with increasing BV, i.e, with time, it also had almost complete retention of Fe as well). On the other hand, comparing with the same study, Al in this study took similar time to equilibrate with the effluent solution. Sun and Lee (2011) saw improvements in Fe and Pt separation while using lower HCl concentration but so lower concentration of HCl is not suitable for leaching Pt from spent catalyst.

In this work, in order to promote the elution of Pt adsorbed from the resin, a HCl solution containing thiourea was used. Several studies described that noble metals have difficulty to be desorbed from loaded resin due to the high retention between metal ions and resin functional groups (Alam et al., 1998; Kononova et al., 2009). Therefore, efficient elution of Pt from the loaded resin can only be achieved using eluent reagents that form stronger complexes with Pt than those formed between Pt and resin. Among the various eluents, thiourea shows high affinity to precious metals, such as Au, Ag and other PGMs by forming stable complexes due to the presence of amine and sulfur groups in its structure (Fujiwara et al., 2007; Neto et al., 2016; Nikoloski et al., 2015; Parodi et al., 2008). Therefore, to promote the elution of Pt adsorbed to the resin, a HCl solution containing thiourea was used. The elution reaction might be explained by Eq. 5.7:

$$[\vdash \mathrm{N^+R_3}]_2\,[\mathrm{PtCl_6}] + 2\,\mathrm{Tu} \iff [\mathrm{PtTu_2}]^{4+} + 2 \vdash \mathrm{N^+R_3Cl^-} + 4\,\mathrm{Cl^-} \qquad (5.7)$$

Based on the previous adsorption experiments (Fig. 5.2), an adsorption time of 540 min was defined. In order to evaluate the best conditions to obtain a concentrated purified Pt eluate solution using the lowest volume and concentration of reagents possible, continuous adsorption experiments were carried out over 540 min; subsequently, various elution tests were performed under different experimental conditions (concentration of reagents and flow rate of elution).

Initially, elution tests, conducted with 2M HCl + 0.5 M of thiourea using a flow rate of 1 mL/min (tested for 36 min, equivalent to 20 BV), leaded to a fast and concentrated recovery of Pt in the leachate as it can be seen in Fig. 5.3. A. Subsequently, another elution experiment, where the flow rate was reduced to half (0.5 mL/min) and maintaining the same concentration of reagents (tested during 72 min, equivalent to 20 BV) was done. Under these conditions, after 12 min, a

more concentrated Pt eluate was collected. This means that not only this condition enables more Pt to be recovered but also at a higher concentration. A final elution test was performed maintaining the same flow rate (0.5 mL/min) and concentration of 2 M HCl but doubling the thiourea concentration (1 M) (tested during 84 min, equivalent to 23.3 BV), which resulted in a more defined concentration peak eluate, which has advantages in which concerns the further recovery of the metal. This result closely resembles that of Fujiwara et al. (2007) with a similar type of resin, in which the Pt desorption with 2 M of HCl and 0.7 M of thiourea was the best case scenario.

Based on this test and looking for the Pt elution profile, expressed in cumulative concentration and yield (Fig. 5.3.B), it can be seen that, after 60 min, 95 % of Pt was already eluted and the Pt concentration in the eluate still remains relatively high (about 217 mg/L). As a result, 60 min was chosen as the ideal time to stop elution in order not to dilute Pt too much and facilitate its recovery at a later stage.

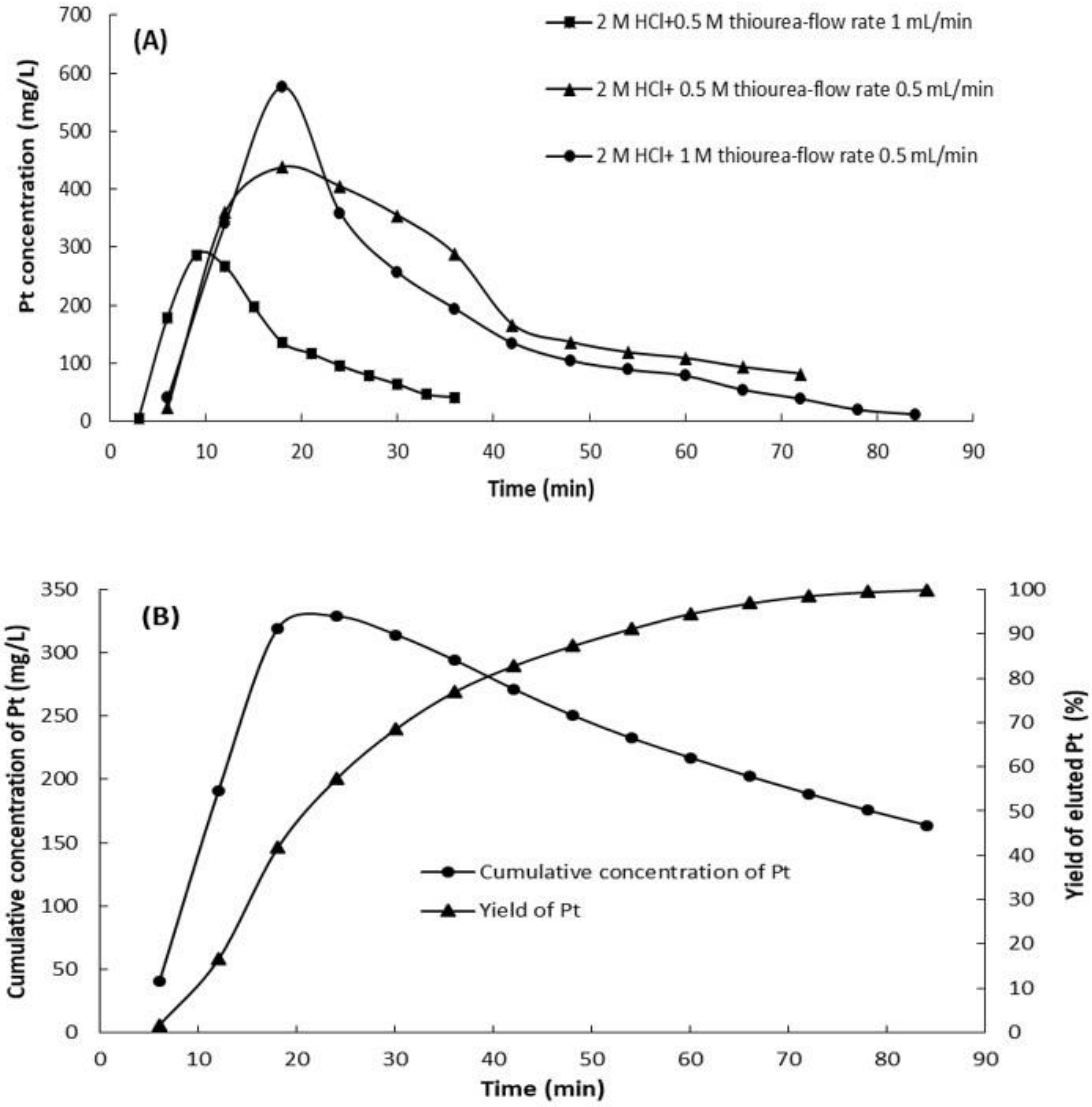


Fig. 5.3. *Elution profiles of Pt with a fixed 2 M HCl and different concentrations of thiourea and flow rates* ***(A)*** *Pt cumulative concentration and Pt yield recovery for elution with 2 M HCl plus 1 M of thiourea with a flow rate of 0.5 mL/min* ***(B).***

Taking into consideration all the information obtained from tests with model synthetic solution and in order to validate these results, a real leached solution achieved under optimized leaching conditions from the spent Pt catalyst, which composition was described above (Table 5.5), was passed through the column at 0.25 mL/min (Fig. 5.2). The results proved to be comparable better

than even with the model synthetic solution with Pt being retained at an acceptable level (i.e., over 90 %) during more time.

Additional experiments to purify Pt from the real leached solution were done using the experimental (adsorption and elution) conditions previously optimized. The metal composition of the eluate and raffinate are presented in Table 5.5. Even though Al was the major metal present in the leachate (18.7 g/L, which corresponded to 98.9 % of the total metal content), due to the high selectivity of the resin to Pt over Al (SN = 11605) (and also Fe but in a much less extent, SN = 24), a very high purified Pt eluate was obtained (Table 5.5). In fact, besides Pt, which hexachloro-platinate(IV) anionic complex, $[PtCl_6]^{2-}$, should be the predominant species present at the chloride concentration present in the leachate, the other two metals are present as positive chloride complexes ($FeCl^{2+}$ and $AlCl^{2+}$) or as aqua species ($Mn.n^{+}$). Due to this fact, they do not have tendency to be adsorbed by the resin. Simultaneously, the purity of Al, the main metal present in the raffinate, was slightly improved (from 98.9 to 99.8 %) (Table 5.5) mainly as consequence of the adsorption of Pt to the resin.

Under the oxidizing conditions tested, the lifetime of the resin tested in this work was of at least 5 adsorption-washing-elution-washing cycles. Similar behavior was found by Fujiwara et al. (2007) and Parodi et al. (2008). Although, chemical degradation and mechanical breakage can occur during adsorption and desorption process using acid treatments, which are deemed to shorten lifetime of the resin, this strategy still remains more favorable from an economic perspective. Additionally, results presented in Table 5.5. clearly indicate that ion exchange resin is a suitable method to separate and purify Pt with high purity grade (98.1 %) from the acid chloride leached liquor.

5.5. Proposal of a nearly closed-loop process to recycle spent catalyst

Based on the results obtained a flowsheet for a nearly closed-loop recycling process is herein proposed (Fig. 5.4). After an initial heat pre-treatment, a microwave-assisted leaching is

performed using 25 % HCl, 2 % H_2O_2 and 2 cycles of 60 s at 810 W. The metals in the resulting leached solution are then separated through ion exchange: the raffinate mostly contains Al, which can be precipitated and reused by simply increasing the pH with NaOH while the eluate, after treating the resin with 2 M HCl + 1 M thiourea, contains high concentration of Pt with a purity of 98.1 %, which can then be used to produce Pt for reuse on the production of new spent catalysts.

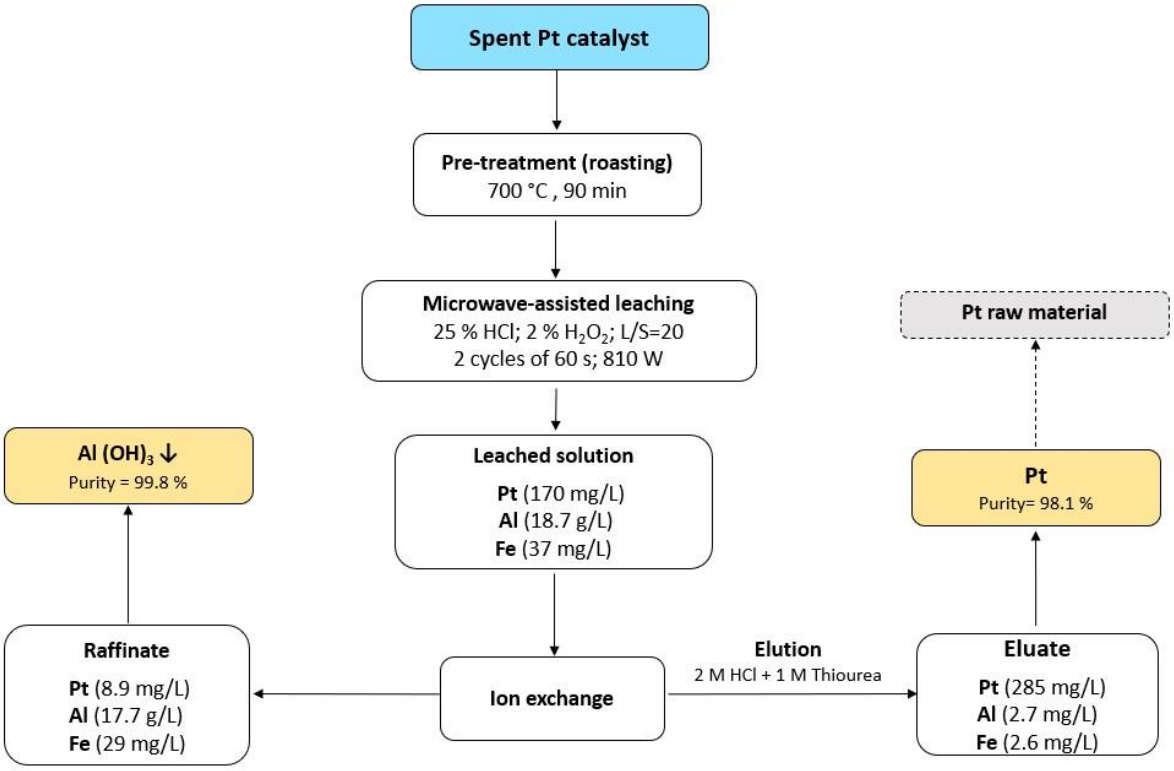


Fig. 5.4. *Overview of the process developed to recover Pt from the spent reforming catalyst (Blue box represents an intial residue, yellow boxes show final product resultant in this study, grey box illustrates possible final raw material resultant from this process and dashed line represents final products not tested within this study).*

5.6. Conclusions

In this work, a new, more economical and environmentally sustainable process was able to recover Pt from a spent petrochemical Pt catalyst with high efficiency through the use of a microwave-assisted leaching using a mixture of HCl and H_2O_2 followed by an ion-exchange purification.

While powder size catalyst required just a single 45 s cycle at 810 W along with 30 % HCl and 3 % H_2O_2 to achieve complete leaching of Pt, original sized spent Pt catalyst required 2 cycles of 60 s at the same power but with lower reagent amounts (25 % HCl and 2 % H_2O_2). Milling the spent catalyst only provided marginal improvements in efficiency. Therefore, it is unlikely to be an attractive option for future applications. Subsequently, ion exchange proved to be highly selective for Pt and enabled an easy and efficient separation of the metals present in the leachate into two highly purified metal solutions: Pt (98.1 %) in the eluate and Al (99.8 %) in the raffinate.

Among the conditions tested in this study, the finely tuned optimization of all leaching conditions (size of spent catalyst, HCl and H_2O_2 concentrations, time, microwave power) provide the most cost-efficient process possible and it can be highlighted as one of the main innovative aspects of this study. Similarly, the ion exchange purification step enables the reuse of the resin without calcination, unlike other similar studies, providing an innovative solution to the purification step. The overall process is capable of producing high quality Pt for recycling in new catalyst production as well as other by-products, whilst minimizing leaching time and environmental impacts, contributing to an overall more circular economy and also create a feasible industrial application opportunity.

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Chapter 6

Conclusions

Concluding remarks

This thesis focused on the recovery of metals from secondary sources, i.e., wastes, namely spent alkaline batteries, spent fluid cracking catalysts and petroleum reforming catalysts.

Due to the through state of the art performed, it was possible to identify the main recycling strategies currently being researched in the literature for each waste, which include all steps of the process, from leaching of metals to their separation afterwards. In order to compare data from the literature more correctly, it was necessary to lay extensive ground work of conversion and creation of novel parameters, such as molar quantity of leachant or reductant per weight of waste. These aspects may remain relevant in the future to compare novel works with existing ones and truly assess which is most efficient methods in terms of reagent used. This state of the art allowed the identification of research gaps that this thesis only partly explored, and therefore remains relevant for future work or for other researchers to get an overview of the theme as well point outdirections for novel research.

Recycling of spent alkaline batteries is the most common of the studied wastes. However, the novel proposed flowsheet presented in this thesis presents a new and unique perspective into the incorporation of the concepts of circular economy. By carefully manipulating the relative concentrations of Mn and Zn in the different stages, this study, unlike most other studies in the literature, enables the production of very high purity Zn and Mn solutions that can then be used to produce raw metals of sufficient quantity for some of the strictest of applications, such as battery production itself. It also provides a choice in terms of separation, i.e., either through precipitation or through solvent extraction, both technically feasible as proved within this thesis. The choice of one over the other may then be made based on economic or other parameters, giving more options for a potential application in the industry.

As for the recycling of spent cracking catalysts, the proposed flowsheet is significantly simpler than most reported in the literature as it does not involve complex saponified solvent extraction for the separation, but two simple precipitation steps. This part of the work highlights the importance of using chemical speciation models to streamline the process as it was the

exploration of this method that enable the selection and testing of such a simpler process. Not only that, but the chemical speciation models lead the way into a clear reduction of reagent used by separating the precipitation into two, more cost effective steps. Finally, the models also enable to provide indications of the robustness of the method to changes in initial metal concentrations, which is natural to occur in a real scenario with wastes of slightly different composition entering the recycling process. This aspect provides more guarantees of success for any potential industrial application of the developed flowsheet. Despite the fact that the flowsheet of FCC recycling is not completely closed, the wastewater generated is mainly constituted by easily biodegradable oxalate and, therefore, does not pose any environmental risks.

Finally, as for the recycling of reforming catalyst containing Pt, the developed flowsheet also provided important improvements over traditional methods. The leaching step was highly improved, which, in the case of a metal as valuable as Pt, any increase of the leaching yield is significant. Additionally, the ion exchange separation method proved to be less resource intensive as elution was possible with a combination of thiourea and HCl, while traditional methods often calcinate the resin, rendering it enable for reuse in another separation run.

Furthermore, an overall result that can always be seen in all the studies performed is the potential of auxiliary energy sources, in particular microwave, to greatly enhance leaching by reducing the time, reagent and likely energy required to perform similarly to other methods. Provided that certain conditions applied, it is likely that the use of microwaves is a powerful tool to enhance leaching of other metals in other wastes and future research should focus on that aspect.

Overall, this Thesis is a contribution to the development of novel recycling processes of metals from secondary sources with concepts of circular economy and environmental sustainability in the forefront but also contributing to its economic feasibility in the mid to long term.