Development of hydrometallurgical processes for zinc recovery from steelmaking waste

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BILBOKO INGENIARITZA GOI ESKOLA TEKNIKOA

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DEVELOPMENT OF HYDROMETALLURGICAL PROCESSES FOR ZINC RECOVERY FROM STEELMAKING WASTE

A dissertation submitted to the University of the Basque Country in partial fulfillment of the requirements for the degree of

Ph.D. in Chemical Engineering

by

Mr. Néstor Antuñano Martín

Thesis Advisor: **Prof. Pedro Luis Arias Ergueta**

Bilbao, 2015

“Ninguna cantidad de experimentación puede probar definitivamente que tengo razón, pero un solo experimento puede probar que estoy equivocado” **Albert Einstein**

AGRADECIMIENTOS

Una vez terminada esta tesis me viene a la mente el recuerdo de toda la gente que ha colaborado en su realización y a la que no puedo más que mostrar mi agradecimiento en este apartado. Finaliza aquí esta travesía que surgió hace cuatro año entre discusiones científicas con el Prof. Pedro Luis Arias Ergueta, quien ha dirigido y guiado esta aventura. Sin su opinión, consejo y conocimiento de la tecnología no habría sido posible completar esta investigación, gracias por liderar este proyecto. No puedo dejar de agradecer al Prof. José Francisco Cambra que me haya dejado ser su compañero de viaje por los numerosos escenarios en los que se ha desarrollado este periplo. Ha sido un verdadero placer formar parte de vuestro equipo, sois un ejemplo de lo que se disfruta trabajando cuando crees en lo que haces, ya que es la única forma de conseguir resultados. Por supuesto, agradecer el apoyo económico, logístico y moral que me ha proporcionado el Departamento de Ingeniería Química y del Medio Ambiente de la Escuela Técnica Superior de Ingeniería de Bilbao, así como el Departamento de Educación, Política Lingüística y Cultura del Gobierno Vasco.

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No puedo terminar este escrito sin agradecer a mis padres Marisa y José Miguel que me hayan permitido firmar esta tesis doctoral que es suya, puesto que todo lo que soy se lo debo a ellos. Yo solamente he seguido el camino que vuestro ejemplo me ha ido marcando, gracias. Por último, agradecer a Iraia que haya sido el apoyo que ha mantenido intacta la ilusión y el tesón con el que se ha realizado este trabajo. Porque estando a tu lado has hecho siempre que los malos momentos sean regulares y los buenos, geniales. Nire ametsak eta esperantza ilunaldietan pizten dituzuna zara.

Eskerrik asko denoi / Gracias a todos / Mercy beaucoup a tous / Thank you everyone

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SUMMARY

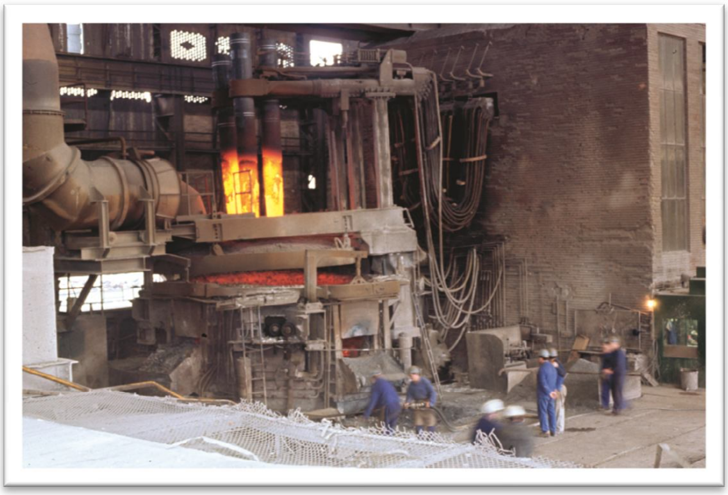
The recycling of steel scrap is an integral part of modern steelmaking, as it reduces the need for iron ore extraction. Approximately 1.200 million tons of steel are necessary every year, 40 % of the processed steel is obtained from recycled waste-feed in electric arc furnace (EAF) (World Steel Association, 2010). The steelmaking industry that uses electric arc furnaces generates dust (EAFD) as its main residue, which must be treated to recycle some heavy metals for economic reasons and to prevent negative environmental impacts. In this secondary fusion of steel around 15 kg of EAFD per ton of steel are generated (Dutra, A. J. B., 2006). This waste is formed basically by different metallic oxides with heterogeneous composition and size. Waelz process is the most common technology for this purpose, generating concentrates of Zn and Pb oxides (called Waelz oxides). At kiln operating temperatures of approx. 1.200 °C EAFD plus a reduction precursor such a coke force the reduction and transformation into a the gas-phase of all volatile elements, mainly zinc. Air is countercurrently fed to the kiln in order to oxidize the volatilized metals to form the so-called Waelz oxide, which is rich in zinc oxide. In a conventional plant, an industrial Waelz furnace can treat 160.000 tons of EAFD/year, obtaining 50.000 tons of Waelz oxide/year (Befesa Zinc Aser, 2010). The aim of this research is to facilitate expanding the market of the Waelz oxide, upgrading it to interesting products by sustainable processes. Thus these improvements in the Waelz oxide derived quality must increase the quantity of recycled zinc in the world.

As the main component of Waelz oxides is zinc nowadays and the production of metallic zinc and of high purity zinc oxide covers approximately 96 % of the zinc market. Therefore, the goal of this thesis is an in-depth study of new hydrometallurgical processes in order to achieve the production of these zinc products from Waelz oxide:

- To prepare an acceptable feed for the electrolysis metallic zinc production from Waelz oxide, one of the main problems to be solved is fluorine

removal. A new hydrometallurgical methodology has been designed by selective precipitation of fluorine in order to comply with the requirements of the electrolytic process of metallic zinc production. Further stages of this new process allow a significant increase in the zinc content as compared to the initial one of the Waelz oxide and waste treatments to recuperate valuable compounds or to avoid pollutants emissions.

- The other part of this work deals with the development of a regeneration process of Waelz oxide leaching liquors used in a new hydrometallurgical process for this bulk oxide purification treatment producing high purity zinc oxide. In this process, Waelz oxides are dissolved using leaching solutions consisting of ammonium carbonate and ammonia aqueous solutions (Meseguer, V. et al., 1996). After oxidation and cementation stages to remove Fe, Cu and other impurities, a zinc carbonate precipitate is recovered by gas-liquid absorption of carbon dioxide (CO_2) coming from the Waelz furnace flue gas or the zinc carbonate calcination (Núñez, J., 2005). After the design of these hydrometallurgical processes in order to produce high purity zinc oxide, the missing stage to end with a feasible commercial ZnO production process is an effective and environmentally benign is a liquor regeneration stage able to minimize the environmental impact of future industrial plants and the reduction of their production costs. This has been fulfilled through the absorption of CO_2 and NH_3 generated in the hydrometallurgical process. CO_2 capture and NH_3 recuperation lead to significant environmental and economic improvements, but these processes are complex physicochemical stages demanding careful controls of temperature and pH. A key step to design such regeneration processes has been the modeling of the gas-liquid CO_2 and NH_3 interchanges, which are coupled with several reactions in the aqueous solution. A mathematical model, taking into account mass transfer and the whole reaction system has been therefore developed. Finally, CO_2 absorption experiments were also carried out at a bench-scale stirred tank reactor and these experimental results have enabled model tuning and validation.



Horno de Arco Eléctrico – Altos Hornos de Vizcaya (by Miguel Ángel Martínez Vitores)

Planta Waelz – BEFESA ZINC ASER (by BEFESA)

CHAPTER 1

1. INTRODUCTION

On a planetary scale, high-consuming life-style is becoming a huge problem in modern times. Sooner or later, at the current rate of consumption, the reserves of certain resources will be exhausted. The exhaustion of these natural reserves is in large part due to the use of raw materials instead of developing sustainable waste management strategies.

Natural resource and energy conservation is achieved by managing materials more efficiently. Choose from the efforts and resources below to learn how to conserve resources at home and at work. Recycling turns materials that would otherwise become waste into valuable resources. Collecting used bottles, cans, and newspapers and taking them to the curb or to a collection facility is just the first in a series of steps that generates a host of financial, environmental, and social returns. Some of these benefits accrue locally as well as globally.

In that sense, the best way of managing generated waste is not to produce it in the first place. After that, waste should be reduced, reused, recycled and recovered value wherever possible. The aim of this “waste hierarchy” is to extract the maximum practical benefits from products and to generate the minimum amount of waste. In this thesis, the management of metallurgical waste will be studied.

In 2004, the metallurgical industry supposed the 49 % of global value added in manufacturing industry, which corresponded to 11% of global GDP (Gross Domestic Product). Worldwide, 70 million people are employed in the metalworking industry (World Trade Organization, 2005 annual report). In industrialized countries, this represented about to 47 % of total employment in the manufacturing sector (World Trade Organization, 2005 annual report). Despite being vital for the economy, several environmental problems like depletion of non-renewable mineral resources and waste and pollution proliferation are generated.

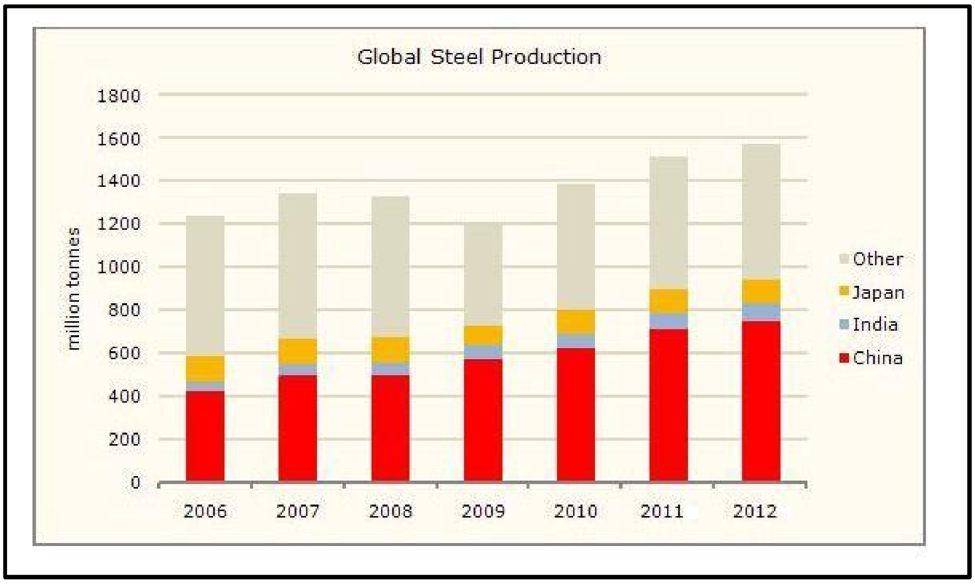


Figure 1.1: Global steel production (by World Trade Organization)

In the Basque Country, steelmaking is the main metallurgical industry. It produces 14 millions of tons per year, which means approximately 70 % of the Spanish steel production. (Registro estatal de Emisiones y Fuentes contaminantes, 2008). This implies a generation of 42.000 tons of waste per year.

There are five important steelmaking industrial holdings working at the present time in this region: Arcelor-Mittal (Sestao, Olabarria and Zumarraga), Gerdau-Sidenor (Basauri), Gallardo-Azpeitia (Azpeitia), ADA-Añón (Bayonne) and Nervacero-Celsa Group (Portugalete). All of them are electric steelmaking industrial facilities, obtaining different kinds of steels using galvanized scrap as one of feeds of the smelting process.

1.1 THE PROBLEMS WITH THE WASTE OF METALLURGICAL INDUSTRIES

The metallurgical industry generates high amounts of solid waste in order to produce and process the target metals. These solid residues are generated throughout main separation operations as toasting, melting, leaching and metal purifying.

These byproducts are categorized as dangerous and hazardous industrial waste (Boreiko, 1991). The main problem of these waste products lies in its disposal due to the high concentration of heavy metals as cadmium, lead, chromium, mercury and zinc. As they tend to bio-accumulate these metals may become extremely toxics even at low concentrations. For zinc a severe toxicity is considered when a dose between 225 and 450 mg/day exists (World Health Organization, 2011).

Accordingly, the metallurgic waste should be treated and if/when this is possible, they should be recycled to increase the added-value if the metals contained in those waste.

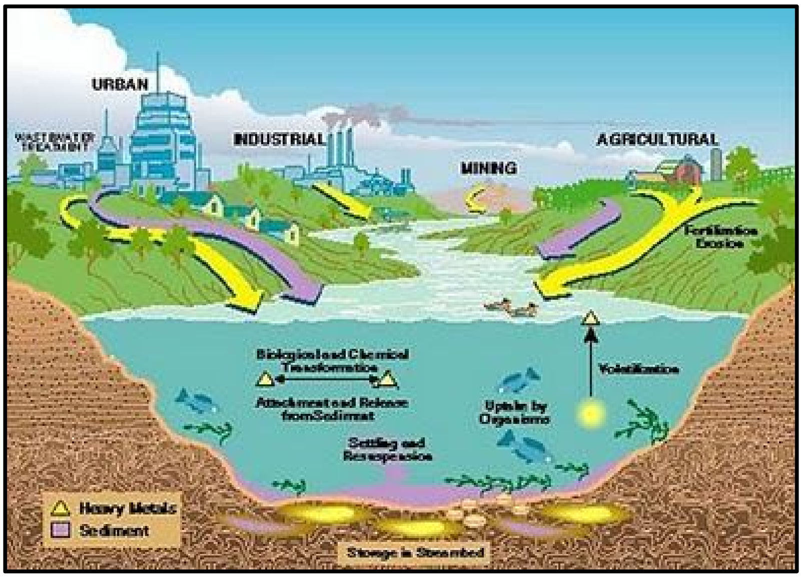


Figure 1.2: Life cycle of heavy metals (from US Geological Survery Circular 1133)

For that purpose, quantification of the solid waste generation per produced steel tone has to be deeply studied. Characterization of these residues will allow to design and put in place the proper treatment processes for their recover.

1.2. ELECTRIC ARC FURNACE STEELMAKING (EAF)

Approximately 1.200 million tons of steel are necessary every year. 40 % of the processed steel is obtained from recycled waste-feed, i.e. scrap smelted in electric arc furnaces (www.worldsteel.com, 2006). This fabrication process generates a solid waste called electric arc furnace dust (EAFD), which contains a considerable concentration of zinc, ranging from 22 % to 28 % (Nuñez et al., 1993). The percentage of zinc is so high because galvanized steel scrap is used as feeding of the melting process. EAFD residues appear mainly during the filtration to clean the flue gas from steel melting and refining operations.

The electric arc furnace steelmaking facility is an industrial installation designed to obtain different kinds of steels from scrap instead of using mineral ore.

The electric arc furnace is a cylindrical vessel with three electrodes of graphite. These electrodes are connected to a three-phase electric current provided. The furnace uses to be able with oxygen lances. The electric arc furnace operates as a batch melting process producing batches of molten steel.

Once a molten pool of steel is generated in the furnace, oxygen can be lanced directly into the bath. This oxygen will react with several components in the bath including aluminium, silicon, manganese, phosphorus, carbon and iron. All of these reactions are exothermic and supply additional energy to aid in the melting of the scrap. The metallic oxides formed during the process will end up in the slag.

The reaction of oxygen with carbon (supplied by the electrodes mentioned before) in the bath produces carbon monoxide (CO), which either burns within the furnace if sufficient oxygen is available, and/or is exhausted through the direct evacuation system where it is burned and conveyed to the pollution control system.

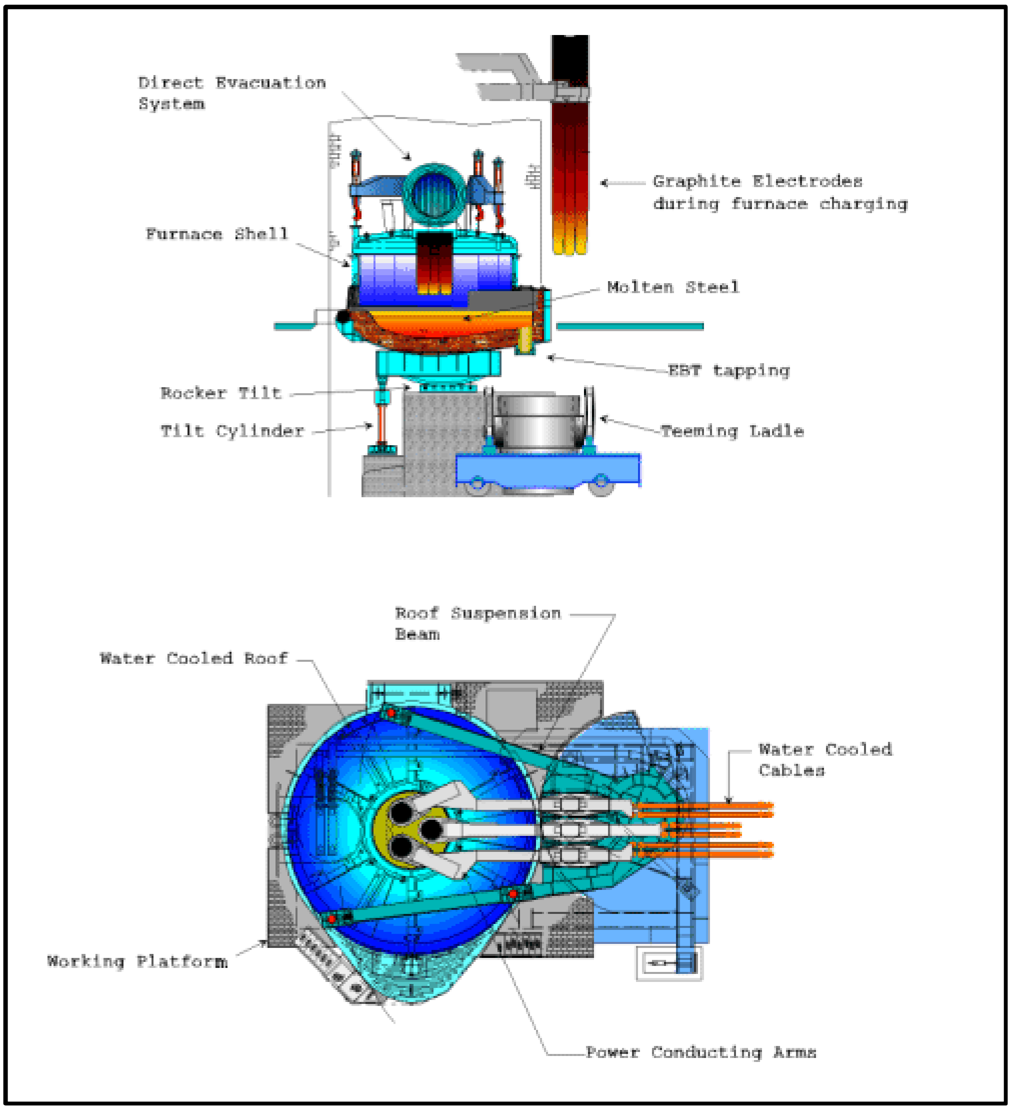


Figure 1.3: Electric arc furnace (EAF) (by Jeremy A. T. Jones, Nupro Corporation)

During the melting and blowing operations solid particulates are formed. These solids are recovered using bag-filters or an electrostatic precipitator installation. In most cases, this residue is also identified as electric arc furnace dust (EAFD).

In the secondary fusion of steel approximately 15 kg of EAFD per ton of obtained steel are generated (Dutra, 2006). This waste is formed basically by different metallic oxides with heterogeneous composition and size. The type of the steel produced in the tap will set the composition of the electric arc furnace dusts.

In Table 1.1, an appropriate composition of these dusts:

Table 1.1: EAFD composition by Befesa Zinc Aser process (Erandio, Spain) (2007)

Element	% Weigh	Element	% Weigh
Zn	23 - 26	S_{total}	0,5 - 1,0
Pb	3 - 5	F	0,15 - 0,3
Cd	0,03 - 0,10	Cl	2,4
Cr	0,1 - 0,3	Ni	0,01 - 0,1
Cu	0,4 - 0,5	C_{total}	0,5 - 1,5
Sn	0,01 - 0,1	FeO	27 - 32
As	0,04 - 0,08	MnO	2,5 - 3,5
BaO	0,01	Na_2O	0,5 - 1,0
Al_2O_3	0,7 - 0,9	K_2O	1 - 2
SiO_2	3,5 - 4,5	MgO	1,5 - 2,5
CaO	6 - 7	H_2O	0 - 14

The zinc concentration in the dust depends on the kind of scrap it is processed in the electric arc furnace. However, in the last few years this value tends to increase because steelmaking factories are using more galvanized scrap every year (de Goicoechea y

Gandiaga, 1999). The main problem of this waste product lies in its disposal. EAFD has to be treated in order to solve this problem.

1.3. ALTERNATIVE TREATMENTS FOR ELECTRIC ARC FURNACE DUST

According to EPA (*Environmental Protection Agency*) and OECD (Organisation for Economy Co-operation and Development) Waelz Process is the best option for EAFD recycling. Nevertheless, there are also a number of alternatives divided in two main groups:

1.3.1. PYROMETALLURGICAL TREATMENTS

Pyrometallurgy is that branch of extractive metallurgy which deals with extraction of metal from their ores or raw materials by thermal methods (Habashi, 1986). The pyrometallurgical via needs a high initial investment and it must treat great quantity of raw material to make it viable on an industrial scale. At the present time, the treatments of EAFD are carried out through pyrometallurgical process.

1.3.1.1. Plasma Technology

The EAFD are introduced into a furnace provided with two electrodes, with the vessel operating between 3.000 ºC and 4.000 ºC (Copsey, 1990).

In this process, zinc, lead and all EAFD’s volatile components are reduced, passing to the flue gas and they are finally recovered in the gas clean-up system.

In the melting phase, the chromium, the nickel and the molybdenum appear as ferritic alloys; these products are used in the stainless steel obtaining process.

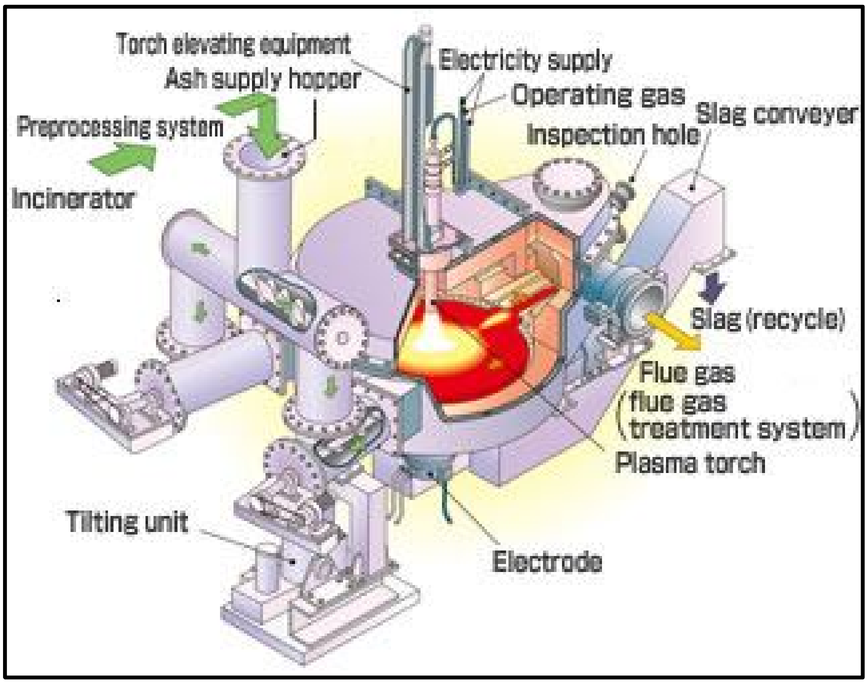


Figure 1.4: Plasma furnace (by Kawasaki Heavy Industries, Ltd)

Besides, some of the best known Plasma Technology patents are: Tetronic (Chapman et al., 1989), Scandust (Johansson et al., 1990), Tibur, Mintek, Davy Mc Kee (Steel Times, 1989).

1.3.1.2. Electric Arc Furnace Technology

In this case, the installation comprises a continuous vessel heated with electrodes. This furnace only can treat dust with a zinc concentration higher than 15 % (Aune et al., 1990).

1.3.1.3. The Basic Oxygen Process

This furnace recovers Zn, Pb, Ag, Au and Cu which are present in the fed. Inside the vessel, the charge is melted and gasified with oxygen lances that are inserted in the broth from the top of the furnace.

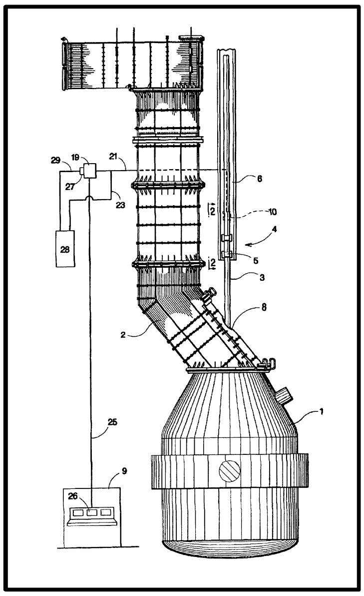


Figure 1.5: Basic Oxygen Furnace (by Thomas P. Swift)

To the best of author’s knowledge, there are mainly two Basic Oxygen process patents: Sirosmelt Process (Ausmelt Company) and Isasmel Process (Australian Mount Isa Mining Ltd.).

1.3.1.4. Flame Reactor Process

This process is designed in two stages. The first one is carried out in a vertical tubular vessel, where feed enters through the top and the fuel is fed axially. In this stage, metal reduction reactions are produced downwards. The final stage is a horizontal vessel, where the reduced metals in gas phase are separated from the ferritic slag. The metals are collected in the flue gas depuration system.

1.3.1.5. Waelz Process

This process is thoroughly described in chapter 1.4, because its product (Waelz oxide) is the basics of this research.

1.3.2. HYDROMETALLURGICAL TREATMENTS

Even if there are a lot of studies published about hydrometallurgical treatments, pyrometallurgical treatments are the most used technologies at industrial level. Hydrometallurgical treatments are able to dissolve the zinc contained in the EAFD as ZnO. However, their major problem is their inability to recover the zinc from ferrites. Moreover, the hydrometallurgical via always needs a zinc concentration upper than 35 % in the EAFD to be a viable alternative. Table 1.1 shows that this could suppose a limiting factor.

Currently, two main processes exist: acid leaching with sulphuric acid or with hydrochloric acid. In any case, to the best knowledge of the authors, none of them is being applied in the industry (Nuñez et al., 1993).

1.4. WAELZ PROCESS

Zinc containing materials (specially EAFD) are the feed supplied to the Waelz Process. The rotational movement developed inside the furnace (Figure 1.6) forces the operator to control the composition of the introduced raw material. Accordingly, it may well require the addition of some additives as lime and sand in order to customize the physicochemical characteristics of the load. The fine material must also be pelletized to avoid the load being swept away by the flue gas.

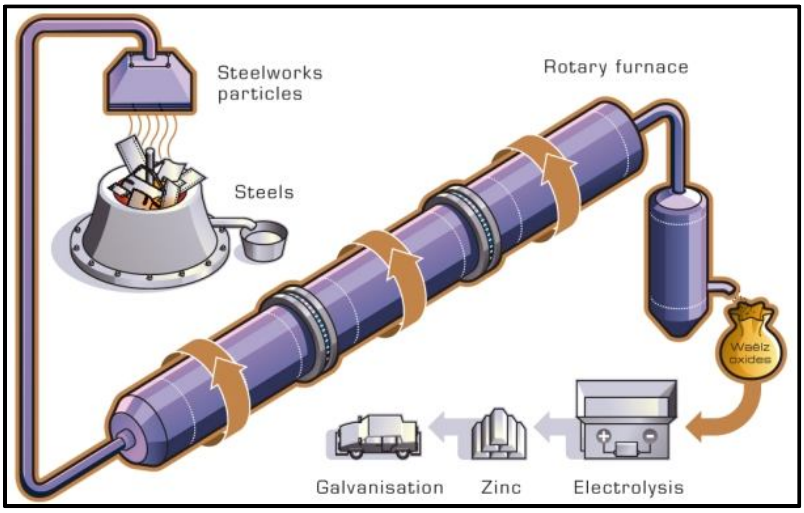


Figure 1.6: Scheme of the Waelz Process (by Recytech S.A)

Breeze coke makes up 25-40 % of Waelz Process supply. This material is going to generate reducing conditions throughout the furnace (de Goicoechea y Gandiaga, N. 1996). The rotational movement of the furnace and the slope of the designed vessel (2 %) make the raw material advance within the installation. Raw material load into the furnace must be controlled during the entire duration of operation: its physical and chemical uniformity should prevent from final product's segregation. Material residence time inside the furnace is around five hours.

The furnace is split up into two zones (Figure 6):

- Load zone: harsh reducing conditions are established; charcoal and zinc containing materials are supplied.
- Free zone: weak reducing and oxidizing conditions are found; this atmosphere favours the gaseous zinc transformation in ZnO particles.

The temperature inside the equipment is adjusted by means of the air introduced in the furnace. Temperature can reach 1.250 ºC due to carbon monoxide (CO) and metallic zinc reaction in the free zone (de Goicoechea y Gandiaga, 1996). Zinc steams and CO gas flow are employed in order to separate the two zones of the furnace (Figure 6). Both flows come from the inlet zone with a defined pressure and the combustion occurs over the surface of the load.

These reactions occur because the furnace operates with an excess of breeze coke, the most of it is recovered from the process.

This process is the combination of the following main reactions which are represented in the Figure 1.7:

$C + \frac{1}{2} O_2 \rightarrow CO + 110.4\ KJ\ mol^{-1}$ (Initial reaction) Eq. 1

$ZnO + CO \rightarrow Zn + CO_2 + 186.0\ KJ\ mol^{-1}$ Eq. 2

$C + CO_2 \rightarrow 2\ CO – 172{,}2\ KJ\ mol^{-1}$ (Boudouard's reaction) Eq. 3

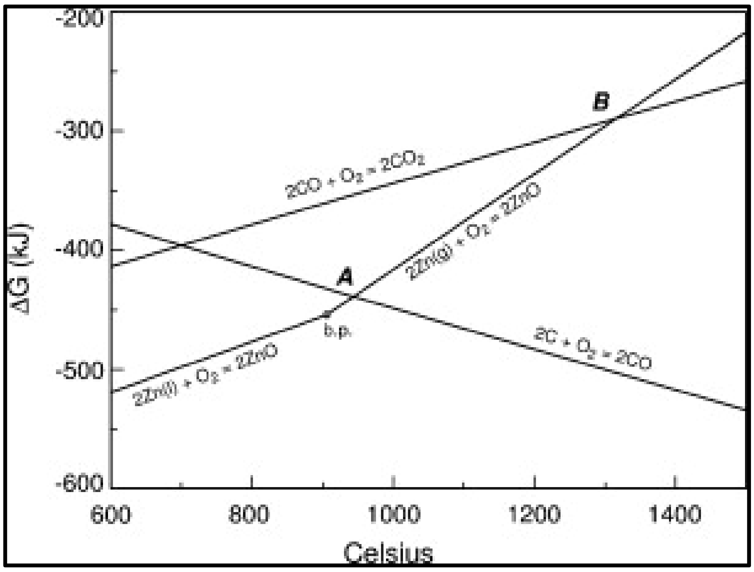


Figure 1.7: Ellinghan diagram for Waelz Process

During Waelz Process, the lead (Pb) contained in the EAFD is volatilized significantly as lead (II) sulphide (PbS). With the exception of the lead (II) chloride ($PbCl_2$) compound, PbS shows the highest vapour pressure (130 Pa) amongst of lead compounds.

Zn, PbS and CO vapours generated in the load zone are subsequently burnt with excess air in the free zone of the furnace. This process produces the following main reactions:

$CO + ½\, O_2 \rightarrow CO_2 + 282{,}6\ KJ\ mol^{-1}$ Eq. 4

$Zn + ½\, O_2 \rightarrow ZnO + 469{,}2\ KJ\ mol^{-1}$ Eq. 5

$PbS + 2\, O_2 \rightarrow PbSO_4$ Eq. 6

Roasted zinc ores (from EAFD) hold several impurities and other zinc derived by-products such as ferrites, silicates, sulphides and sulphates. Since zinc is less noble than iron, zinc ferrite ($ZnFe_2O_4$) will react below 900 ºC according to the reaction:

$ZnFe_2O_4 + 3\, CO \rightarrow ZnO + 2\, Fe + 3\, CO_2$ Eq. 7

Released zinc oxide (ZnO) and $ZnFe_2O_4$ are not particularly damaging in the carbothermic production of zinc.

Since silica is more stable than zinc oxide, zinc silicate will be reduced by the following reaction:

$Zn_2SiO_4 + 2\, CO \rightarrow 2\, Zn\ (g) + SiO_2 + 2\, CO_2$ Eq. 8

Bag filters or electrostatic precipitators located after the furnace are the responsible for cleaning produced furnace gas. This gas contains the finely divided zinc fume. Oxidation heat radiates back to the inlet load and helps to provide the necessary heat for the reduction process (Rosenqvist, 2004).

Waelz oxide is collected with a redler and transported afterwards to the hot briquetting plant or to other treatment plants by means of pneumatic system.

1.5. WAELZ OXIDE

Waelz oxide is the product of the Waelz process. This solid is a mix of zinc and lead oxides with several impurities. The characterization of the Waelz oxide used as raw material in this study is shown in Table 1.2.

Table 1.2. Composition of Waelz oxide supplied by Befesa S.A.

Element	% Weigh	Element	% Weigh
Zn	55 - 58	S_{total}	0,7 - 1,0
Pb	7 - 10	F	0,15 - 0,18
Cd	0,3 - 0,5	Cl	4,5 – 6,5
Cr	0,1 - 0,3	Ni	0,03 – 0,12
Cu	0,2 - 0,6	C_{total}	1,0 – 2,0
Sn	0,1 - 0,2	FeO	5 - 7
Al_2O_3	0,1 - 0,4	MnO	0,4 – 0,7
SiO_2	0,5 - 1,5	Na_2O	1,1 – 1,5
CaO	0,3 – 1,0	K_2O	1,5 - 2
MgO	1,5 - 2,5	Hg (ppm)	3 - 30

Waelz oxide is a solid compound with a powdery appearance; it has a grey color and its particle size is d_{50} = 5 µm.

Figure 1.8: Waelz Oxide.

The objective of this thesis is the processing of this material in order to obtain secondary added-value products.

1.6. THE WAELZ OXIDE SITUATION INSIDE THE ZINC MARKET

Zinc is a natural component of the earth's crust and an inherent part of our environment. Zinc is present not only in rock and soil, but also in air, water and the biosphere.

Zinc is a metallic chemical element. It is a bluish-white, lustrous, diamagnetic metal, though most common commercial grade of the metal have an uniformly dull finish. It has a hexagonal crystalline structure.

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper with an annual production of about 12 million tonnes. China is the largest producer country in the world, followed by Peru and Australia (Tolcin, 2011). About 70 % of the world's zinc originates from mining, while the remaining 30 % comes from secondary zinc recycling. The level of recycling is increasing each year, in step with progress in the technology of zinc production and zinc recycling. Today, over 80 % of the zinc available for recycling is indeed recycled (International Zinc Association, 2008).

The most commonly found zinc mineral is *sphalerite* (ZnS), also known as *zinc blende*, which is found in almost all mined zinc deposits. The mineral crystallizes from the hydrothermal solution as pure zinc sulphide. 80 % of zinc mines are underground, 8 % are of the open pit type and the remainder is a combination of both. However, in terms of production volume, open pit mines account for as much as 15 %, underground mines produce 64 % and 21 % of mine production comes from the combined underground and open pit mining (International Zinc Association, 2008). Rarely is the ore, as mined, rich enough to be used directly by smelters; it needs to be concentrated. Zinc ores uses to contain 5 – 15 % zinc.

Over 12 million tons of zinc are produced annually worldwide, 90 % of this quantity are different types of metallic zinc and the rest (10 %) is consumed in compounds such as zinc oxide and zinc sulphate (International Lead and Zinc Study Group, 2011). These first-use suppliers then convert zinc into in a broad range of products (Figure 9). Main application areas include: construction, transport, consumer goods and electrical appliances and general engineering.

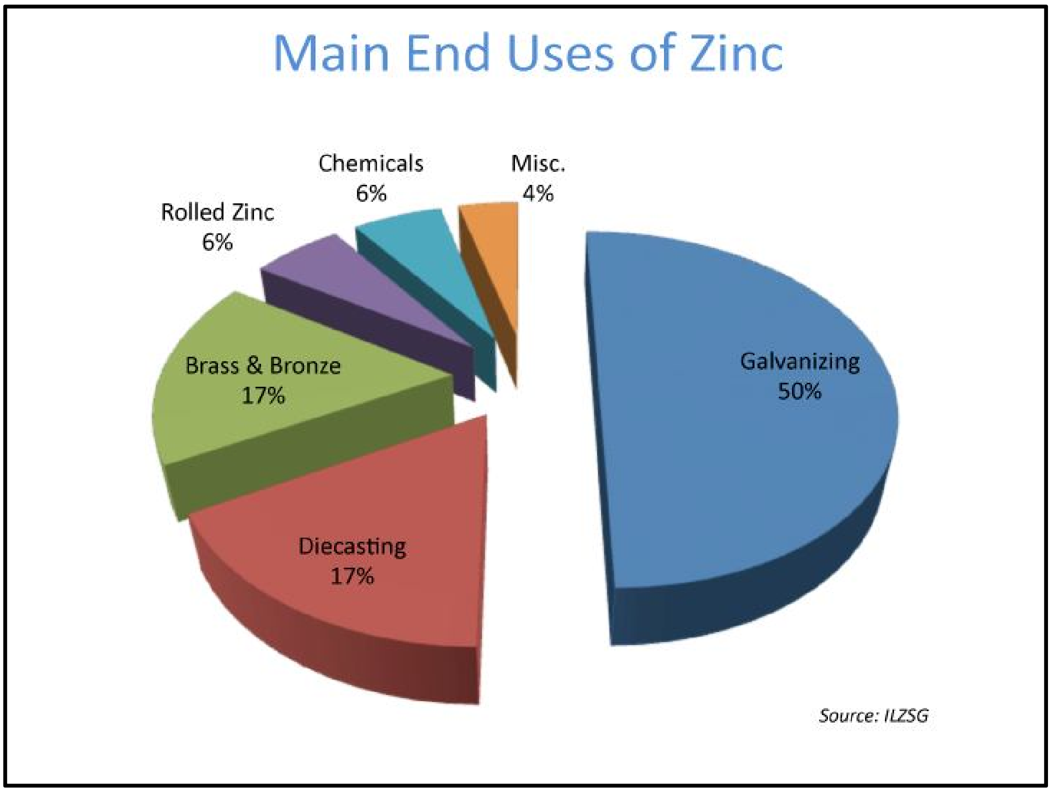


Figure 1.9: Graphical scheme of main end uses of zinc (by ILZSG)

1.6.1. THE PRODUCTION PROCESSES AND MARKETS OF DIFFERENT ZINC PRODUCTS

In this section the different zinc products will be studied. The production processes and the possibility of using Waelz oxide as raw material to obtain these products is also discussed.

1.6.1.1. Metallic Zinc

Nowadays, iron and steel galvanizing suppose the biggest use of zinc. Other uses of zinc include: die casting, sheet metal applications and brass alloy applications. Zinc is coated onto steel by either dipping the steel object into molten zinc or through electroplating. Iron or steel coated with zinc is called galvanized iron or steel. Once iron or steel is galvanized, the zinc at the surface reacts with oxygen to form zinc oxide which then reacts with carbon dioxide and water to ultimately form zinc carbonate. A film of oxide, hydroxide and carbonate effectively prevents further oxidation of the zinc and iron and gives the aged product a grey and slightly powdery look. However, if a scratch exposes some iron and zinc the special electrochemical properties of zinc allow the zinc closest to the iron to take up the oxygen and protect the iron with the resultant oxides and carbonates (Geological Society of Australia, 2011).

Brass is a widely used alloy which contains zinc. Here, copper is alloyed with anywhere from 3 % to 45 % zinc, depending upon the type of brass. Brass is generally more ductile and stronger than copper and has superior corrosion resistance. These properties make it useful in communication equipment, hardware, musical instruments, and water valves (American Zinc Association, 2009).

Alloys of primarily zinc with small amounts of copper, aluminium, and magnesium are useful in die casting as well as spin casting, especially in the automotive, electrical, and hardware industries. These alloys are marketed under the name Zamak (Lehto, 1968).

At the present time, two different ways are being used to produce metallic zinc: Imperial Smelting Furnace (ISF) and electrolytic process.

- **Imperial Smelting process (IS):** Currently about 8 – 10 % of the primary zinc of the world production are through the Imperial Smelting Process. The process co-produces lead bullion in addition to zinc metal using a mix of lead and zinc concentrates or complex lead-zinc concentrates as raw material. The Imperial Smelting Process is similar to blast furnace processes except that it is operated with hot top whereby preventing reoxidation of zinc vapours.

  The burden, zinc sinter and coke, is preheated to about 500 °C before it is charged into furnace through a double bell-and-hopper lock. Preheated air is introduced at the nozzles and reacts with coke to give CO and a temperature above 1300 °C. Rising through the shaft CO reacts with ZnO and with other oxides like PbO to give a top gas mixture with 5 % Zn, 10 % CO_2, and about 20 % CO, the remainder being nitrogen.

The hot gas mixture is withdrawn at 1.000 ºC and shock cooled to about 550 ºC in a condenser where the gas is met by a shower of liquid lead, which causes the zinc to condense and dissolve in the lead without appreciable reoxidation. Zinc is dissolved in the lead up to a concentration of about 2,5 % (w). This melt is withdrawn and is cooled to about 440 ºC in the lead cooling launders (Rosenqvist, 2004). The zinc phase is withdrawn for further processing, whereas the lead phase is returned to the condenser. Thus, the zinc content of the lead phase changes only by about 0,25 %, and about 400 tonnes of lead need to be circulated between the condenser and the cooling launders for every ton of zinc produced (Rosenqvist, 2004).

The IS process is an energy-intensive process and consequently, became very expensive following the rise of energy prices. Today, Imperial Smelting furnaces are only in operation in China, India, Japan and Poland.

Waelz oxide is a fully valid option to be used as raw material in this process. It must just be briquetted to improve the mechanical properties of the Waelz oxide. Therefore, there is a big market for the secondary zinc obtained from EAFD by means of the Waelz process.

- **Electrolytic process:** Refining zinc by distillation is a heat-consuming process. It may be economic in localities with cheap fuel and with demand for high-purity zinc. On the whole, however, the market for high-purity zinc is covered by the electrolytic process. Today, over 90 % zinc is produced hydrometallurgically in electrolytic plants (International Zinc Association, 2011).

The zinc industrial hydrometallurgical processes usually consist of the following steps:

- Leaching of the ore or of an intermediate metallurgical product with acid, caustic, or a complex-forming solvent, often combined with oxidation.
- Purification of the solution by precipitation of insoluble compounds, cementation of unwanted metals, or by solvent extraction.
- Precipitation of wanted product, either as an insoluble compound or as a metal, either by chemical or electrochemical methods.

Electrowinning processing leaches zinc from the ore concentrate by sulphuric acid (Gupta, 1990):

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \qquad \text{Eq. 9}$$

The obtained purified solution passes an electrolytic process where the purified solution is electrolyzed between lead alloy anodes and aluminium cathodes. An electrical current is circulated through the electrolyte by applying an electrical difference of 3,3 – 3,5 volts between the anode and cathode causing the zinc to deposit on the aluminium cathodes in high purity (Porter, 1991).

$$2\ ZnSO_4 + 2\ H_2O \rightarrow 2\ Zn + 2\ H_2SO_4 + O_2 \qquad \text{Eq. 10}$$

The deposited zinc is stripped off, dried, melted and cast into ingots. The zinc ingots may have different grades: High Grade (HG) 99,95 % and Special High Grade (SHG) 99,99 % of zinc (London Metal Exchange, 2011).

Nowadays, there are not industrial facilities able to work with Waelz oxide as a raw material: several impurities must be compulsory removed before electrolysis stage. Besides, halogen content in the product may also significantly reduce the value of the products (Guozhu et al., 1999).

In conventional electrolytic methods using previous hydrometallurgical processes, halogen (such as chlorine and fluorine) concentration should be less than 100 ppm (de Goicoechea y Gandiaga et al., 1999). A high concentration of fluorine is particularly harmful to the process compared with other impurities such as copper, nickel and cobalt (Garcia-Carcedo et al., 1999).

1.6.1.2. Zinc Compounds

Several zinc compounds are used at the industrial level:

- **Zinc oxide:** it is the most widely used zinc compound and it is used in the vulcanization of rubber as a catalyst in its manufacture. It is also employed in ceramics, paints, animal feed and pharmaceuticals, and many other products and processes. A special grade of zinc oxide has long been used in photocopiers. The oxide is also used in varistors, providing protection against over-voltages. The ZnO market supposes 100.000 tonnes per year, by three main ways (Klingshirn, 2007):

    - French process (pyrometallurgycal method)
    - American process (pyrometallurgycal method)
    - Wet chemical process (hydrometallurgycal method)

- **Zinc chloride:** It is an odorless, white, crystalline (sand like) granule or powder. It can be produced in its solid anhydrous form or also in liquid form in any concentration up to 65%. It can also be shipped in different ways according to the general packing specs. The main uses for this product are the following: textile processing, metallurgical fluxes, and chemical synthesis.

- **Zinc sulfate:** It was historically known as "white vitriol". It is a colorless solid which is a common source of soluble zinc ions (Lide, 2006). The hydrates, especially the heptahydrate, are the primary forms used commercially. The main application is as a coagulant in the production of rayon. It is also a precursor to the pigment lithopone. Zinc sulphate is used to supply zinc in animal feeds, fertilizers and agricultural sprays. Zinc sulphate, like many zinc compounds, can be used to control moss growth on roofs. It is also used as in electrolytes for zinc plating, as a mordant in dyeing, as a preservative for skins and leather and in medicine as an astringent and emetic (Rohe, 2005).

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Almacén de sales amoniacales – Sefanitro (by CIHMA – Luis Cholla Alamaraz)

Muelle de carbón – Altos Hornos de Vizcaya (by Miguel Ángel Martínez Vitores)

CHAPTER 2

2. OBJECTIVES AND APPROACH OF THE DOCTORAL THESIS

The main objective of this thesis is to design and to develop different hydrometallurgical processes to upgrade Waelz oxide into commercial products or higher value-added intermediates. The aim of the research is to expand the market of the Waelz oxide looking for new opportunities for this product. These improvements in the Waelz oxide quality must increase the quantity of recycled zinc in the world.

This research includes the development of two processes to produce the most demanded zinc products from Waelz oxide:

- The first one deals with the production of high purity zinc oxide (commercial grade) from Waelz oxide using ammonium carbonate and ammonia aqueous solutions as leaching liquors.
- The second one has as objective the purification of Waelz oxide up to the required quality to be used as a direct feed for the electrolytic zinc production process (removal of chlorides and fluorides).

Along the development of both processes a special consideration will be dedicated to the assessment of the all generated residues in order to minimize environmental impacts and to improve their technoeconomic feasibility.

2.1. DEVELOPMENT OF A HIGH PURITY ZINC OXIDE PRODUCTION PROCESS, USING AMMONIUM CARBONATE AND AMMONIA SOLUTIONS AS LEACHING LIQUORS

The hydrometallurgical production process of zinc oxide from Waelz oxide using ammonium carbonate and ammonia solutions as a leaching liquor has been studied by different researchers (Nuñez, 2005 and Meseguer et al, 1996). A successful production yield can be taken as the main conclusion of these previous works. Nevertheless, the final industrial development must include the exhausted liquor recycling technology. Therefore, the aim of this work is to develop this liquor regeneration process in order to finish with a technoeconomically feasible process to convert Waelz oxide into commercial zinc oxide.

Table 2.1: Target zinc oxide composition and specifications

Parameter	Unit	Quantity
ZnO min.	%	98
PbO max.	%	0,04
CuO max.	%	0,0004
MnO max.	%	0,0001
Matter insoluble in HCl max.	%	0,0001
Lost on ignition max.	%	0,2
Matter insoluble in water max.	%	0,1
Size	µm	4 - 40

For this purpose the following tasks must be taken into consideration:

- The quantification of ammonia and carbonates losses along the hydrometallurgical processes in order to properly close the overall and stage mass balances of this process.
- The study of the gas-liquid absorption equilibria between water-ammonia, water-CO_2, ammonia-CO_2 and water-ammonia-CO_2.that are critically important to design all the stages related to the exhausted ammoniacal liquor regeneration and to avoid unacceptable pollutants emissions.

The design of the absorbers that are necessary to reformulate the new leaching liquor recovering most of the ammonia losses and minimizing the requirements of ammonia and ammonia carbonate fresh feeds.

2.2. DEVELOPMENT OF A WAELZ OXIDE PURIFICATION PROCESS TO USE IT AS THE MAIN SOURCE FOR THE ELECTROLYTIC ZINC PRODUCTION PROCESS

Nowadays, the only way to use Waelz oxide as a raw material to produce metallic zinc by electrolysis is feeding it to a previous roasting stage mixing it with other mineral raw materials. This roasting stage is required in order to eliminate the high concentrations of fluorides, chlorides, sodium and some other light metals that Waelz oxide contains.

As a result the process to be developed must fulfil the following objectives:

- To remove most of the Waelz oxide fluoride content to avoid serious cathode corrosion in the electrolysis stage.
- To eliminate most of the Waelz oxide chloride content which to prevent anode corrosion in the electrolysis stage.
- To separate from the Waelz oxide those metals present that cannot be removed before the electrolytic stage by cementation as nickel and chromium.
- To increase as much as possible the zinc content in the final product to raise its value.

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CHAPTER 3

3. HIGH PURITY ZINC OXIDE PRODUCTION USING AMMONIUM CARBONATE AND AMMONIA SOLUTIONS AS LEACHING LIQUORS

This part of the thesis, it was therefore an in-depth study about the production of high purity zinc oxide from Waelz Oxide, using ammonia solutions to dissolve the recovered metal, with careful consideration given to the possibility of the liquor regeneration.

3.1. INTRODUCTION

This work deals with the development of a regeneration process of leaching liquors, consisting in ammonium carbonate and ammonia aqueous solutions, which are used in a new hydrometallurgical process able to produce high purity zinc oxide from Waelz oxides. This process is used for the purification treatment of Waelz oxides by dissolving it in alkaline leaching solutions. After the oxidation and cementation stages to separate from the solution iron, cooper and other impurities, a zinc carbonate precipitate is recovered by acidification using gas-liquid absorption of CO_2 coming from the Waelz furnace flue gas or the zinc carbonate calcination. This step is accompanied by NH_3 desorption from the leaching solution, which must therefore be regenerated. CO_2 capture and ammonia recuperation lead to significant environmental and economic improvements.

3.2. EXPERIMENTAL

All experiments were conducted with Waelz Oxide (WO), kindly supplied by BEFESA ZINC S.A. – ASER. The experimental methods were described for each designed and studied stage. Hence, the characteristics of the used reactors and process control tools were analysed in this chapter:

3.1.1. LEACHING, OXIDATION AND CEMENTATION STAGE WITH AMMONIA LIQUORS

All leaching and cementation experiments were carried out in 5 litter glass reactor with mechanic stirring. The reactor works in a thermostatic bath and it is operated closed in order to avoid ammonia losses by evaporation. The experiments of the oxidation stage were carried out in a 2 litter glass reactor with mechanic stirring. In this case, the stirrer is perforated in order to permit the gas injection. The gas is injected from the laboratory compressed air line and a Dwyer serie STFO is used as a flowmeter. The reactor works in a thermostatic bath.

An Orion Star A329 Multiparameter meter was used as pH and temperature controller. The pH control of the leaching stage was carried out automatically by acid/alkali addition through a peristaltic pump coupled to the Multiparameter.

A Millipore ASME-MU High pressure filter was used for solid/liquid separation so as to take the samples which were analyzed.

3.1.2. THE FINISHING STAGES FOR OBTAINING ZINC OXIDE

The experimental strategy in this step was divided in two difference parts:

- Precipitation stage: The chemical precipitation experiments were carried out in a patented reactor for solid-liquid-gas reactions (Núñez, J. Et al., 2006, **WO2007085671**).

  An Orion Star A329 Multiparameter meter was used as pH and temperature controller. The pH control of the leaching stage was carried out automatically by the acid/alkali addition through a peristaltic pump of the Multiparameter.

A Millipore ASME-MU High pressure filter was used to solid/liquid separation so as to take the samples which were analyzed.

- Calcination stage: The calcination experiments were carried out using a muffle furnace as equipment to maintain the temperature of the tests. Additionally, a Mettler Micro TGA analyzer was used to get the results.

3.1.3. AMMONIA RECOVERY STAGE

All solid waste treatment experiments were carried out in 2 litter glass reactor with mechanic stirring. The reactor works in a thermostatic bath.

A Millipore ASME-MU High pressure filter was used to solid/liquid separation so as to take the samples which were analyzed.

The ammonia stripping experiments were carried out in a 2 litter glass reactor with mechanic stirring. In this case, the stirrer is perforated in order to permit the gas injection. The gas has been injected from the laboratory compressed air line and using a Dwyer serie STFO as a flowmeter. The reactor works in a thermostatic bath and the cover has a gas extraction system. The stripped ammonia was recovered in an absorption reactor.

An Orion Star A329 Multiparameter meter was used as pH and temperature controller.

A Millipore ASME-MU High pressure filter was used to solid/liquid separation so as to take the samples which were analyzed.

3.1.4. EXHAUSTED LIQUOR REGENERATION STAGE

The experimental strategy in this step was divided in two difference parts:

- Experimental study of gas-liquid transfer of NH_3 and CO_2 in aqueous solution: A laboratory refractometer and a Mach – Zehnder interferometer were the selected instruments in order to carried out these tests.
- The experimental part using a stirred tank: These experiments were carried out in a 2 litter glass reactor with mechanic stirring. In this case, the stirrer is perforated in order to permit the gas injection. The gas was injected from a CO_2 bottle and using a Dwyer serie STFO as a flowmeter. The reactor works in a thermostatic bath.

Temperature: A thermoregulation system controlling the temperature in the reaction tank.

pH: A pH-metre probe (Jeulin ESAO 4 plus) with continuous monitoring during absorption experiments (Serenis software).

CO_2: A dissolved CO_2 probe (Jeulin ESAO 4 plus) with continuous monitoring during absorption experiments (Serenis software).

Stirring speed: A mechanical shaker with a speed control (Heidolph RZR 2102 Control).

3.3. RESULTS AND DISCUSSION

3.3.1. LEACHING STAGE WITH AMMONIA LIQUORS

The first step of the designed hydrometallurgical process is the leaching stage. The solid zinc contained in the Waelz oxide is solved in aqueous phase using an ammoniacal solution (Nuñez, 2005 and Meseguer et al, 1996). The goal of this initial process is to find the best operation conditions in order to reach the highest solubility of the zinc.

3.3.1.1. Technical considerations of ammoniacal leaching

Leaching is a liquid-solid operation. The two phases are in intimate contact, the solute(s) can diffuse from the solid to the liquid phase, which causes a separation of the components originally in the solid. In the metals processing industry, leaching is used to remove the metals from their ores, which contains many undesirable constituents, as solute salts.

Raw material

(ZnO (s), ZnS (s), Zn_2SO_4 (s), ...)

+

Solvent

(Acids (l), alkalis (l), organics (l), ...)

=

Leaching liquor

(Zn^{2+} (aq), cations^{n+} (aq), anions^{n-} (aq), complex (aq), ...)

+

Solid waste

(Solids incapable of being dissolved)

The leaching stage is conditioned by the size of the solid, the ratio solid/liquid, the temperature, the solubility of the target product in the used solvent and the stirring speed in the reactor, among other operating parameters.

3.3.1.2. The main chemical reactions of Waelz oxide leaching involving ammoniacal liquors

The optimization of leaching stage is the result of experimental study of operation variables, which have a direct impact in these chemical reactions:

Leaching liquor equilibrium reactions:

$CO_2 + OH^- \Leftrightarrow HCO_3^-$

$HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

$H_2O \Leftrightarrow H^+ + OH^-$

Leaching of zinc oxide reactions in used leaching liquor:

$ZnO + H_2O \Leftrightarrow Zn(OH)_2$ (Surface hydroxylation)

$Zn(OH)_2 + 4NH_3 \Leftrightarrow Zn\,(NH_3)_4^{2+} + 2\,OH^-$ (Surface complexation)

$Zn(OH)_2 + 2OH^- \Leftrightarrow Zn(OH)_4^{-2}$ (Surface complexation)

Zinc leaching equilibrium reactions:

$Zn^{2+} + OH^- \Leftrightarrow ZnOH^+$

$Zn^{2+} + 3OH^- \Leftrightarrow Zn(OH)_3^-$

$Zn^{2+} + 4OH^- \Leftrightarrow Zn(OH)_4^{-2}$

$Zn^{2+} + NH_3 \Leftrightarrow Zn\,NH_3^{2+}$

$Zn^{2+} + 2NH_3 \Leftrightarrow Zn\,(NH_3)_2^{2+}$

$Zn^{2+} + 3NH_3 \Leftrightarrow Zn\,(NH_3)_3^{2+}$

$Zn^{2+} + 4NH_3 \Leftrightarrow Zn\,(NH_3)_4^{2+}$

Zinc solubility equilibrium reaction:

$ZnCO_3 \Leftrightarrow Zn^{2+} + CO_3^{2+}$

$Zn(OH)_2 \Leftrightarrow Zn^{2+} + 2\,OH^-$

3.3.1.3. Optimization of ammoniacal leaching stage

In this chapter the operation parameters of leaching liquor were studied. The highest solubility of zinc and the lowest reactants consumption were the main goal of this experimental work. Several parameters were studied:

3.3.1.4. Study of leaching liquor concentration

The influence of ammonium carbonate solution concentration in the zinc recovery was studied. These experimental tests were carried out under these following conditions that appear in Table 3.1:

Table 3.1: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	25
Water volume	L	1,5
Aqueous ammonia (25%) volume	L	0,5
Ammonium carbonate anhydrous weight	g	Changes every experiment
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The obtained results of these experimental tests are the following ones:

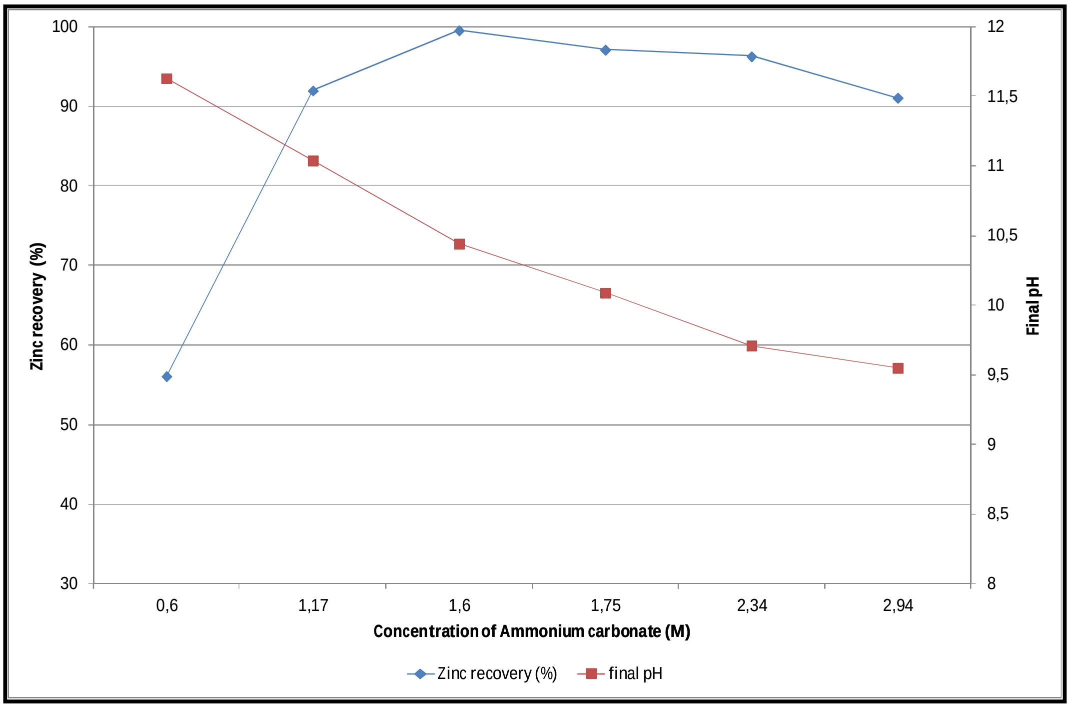

Figure 3.1: pH and zinc recovery as function of liquor concentration

The evolution of the zinc recovery by increasing the ammonium carbonate concentration was shown. The leaching yield increases until 1,6 M, but when this point is exceeded the zinc recovery has a softly decrease.

3.3.1.5. Optimization of liquid ammonia concentration

In this chapter, the influence of the liquid ammonia concentration in the zinc recovery was studied. So, the total carbonate concentration was constant during the different experimental works:

a. **Variation of liquid ammonia concentration by maintaining a steady concentration of ammonium carbonate solution in the optimum value**

The concentration of ammonium carbonate solution was maintained in the optimized point, so the concentration of liquid ammonia in the used liquor was the analyzed parameter. These experimental tests were carried out under these following conditions that appear in Table 3.2:

Table 3.2: Used experimental conditions

Parameter	Units	Quantity
Temperature	ºC	25
Volume of liquor	L	2
Aqueous ammonia (25%) volume	L	Changes every experiment
Concentration of ammonium carbonate solution	mol/L	1,6
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The obtained results of these experimental tests are the following ones:

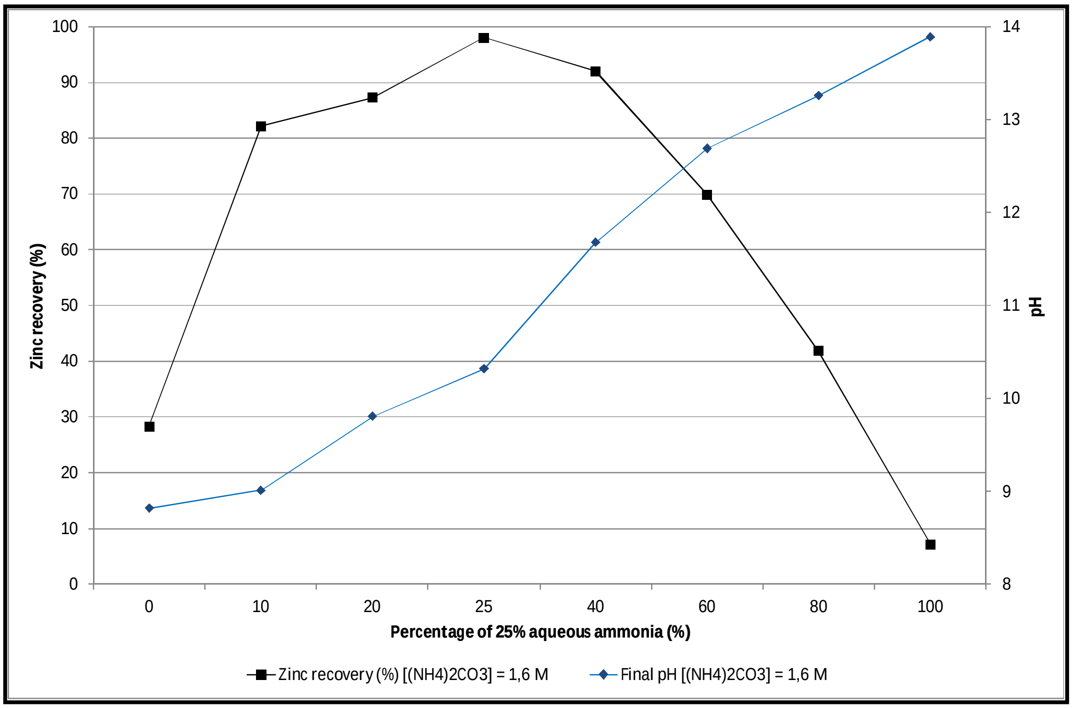

Figure 3.2: pH and zinc recovery as function of the ammonia concentration

The evolution of the zinc recovery and pH by increasing the ammonia concentration can be seen in Figure 3.2. The leaching yield increases until 25 % of ammonia, but when this point is exceeded the zinc recovery has a continuous decrease. Indeed, the zinc recovery is acceptable (near 90 %) can be detected between pH = 10 and pH = 12.

b. Variation of liquid ammonia concentration by maintaining a steady concentration of ammonium carbonate solution in a higher value of the optimum

The concentration of ammonium carbonate solution was maintained higher than the optimized point, therefore the influence of the liquid ammonia concentration and the total carbonate concentration were studied. These experimental tests were carried out under these following conditions that appear in Table 3.3:

Table 3.3: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	25
Volume of liquor	L	2
Aqueous ammonia (25%) volume	L	Changes every experiment
Concentration of ammonium carbonate solution	mol/L	2,5
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The obtained results of these experimental tests are the following ones:

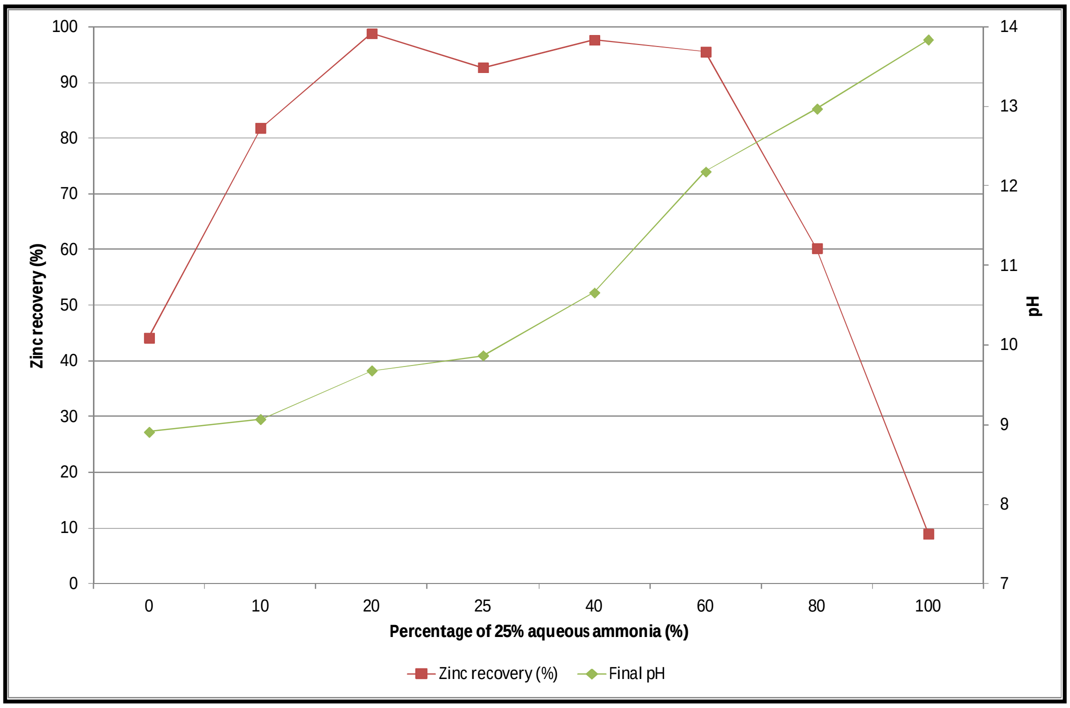

Figure 3.3: pH and zinc recovery as function of the ammonia concentration

The evolution of the zinc recovery and pH by increasing the ammonia concentration can be seen in Figure 3.3. The leaching yield increases until 20 % of ammonia and it is maintained until 60 %, after this point the zinc recovery has a softly decrease, but the zinc recovery is acceptable (near 90 %) between pH = 10 and pH = 12.

Thus, the both experimental test could be compared to reach important conclusions about the composition of the leaching solution, obtaining the following results:

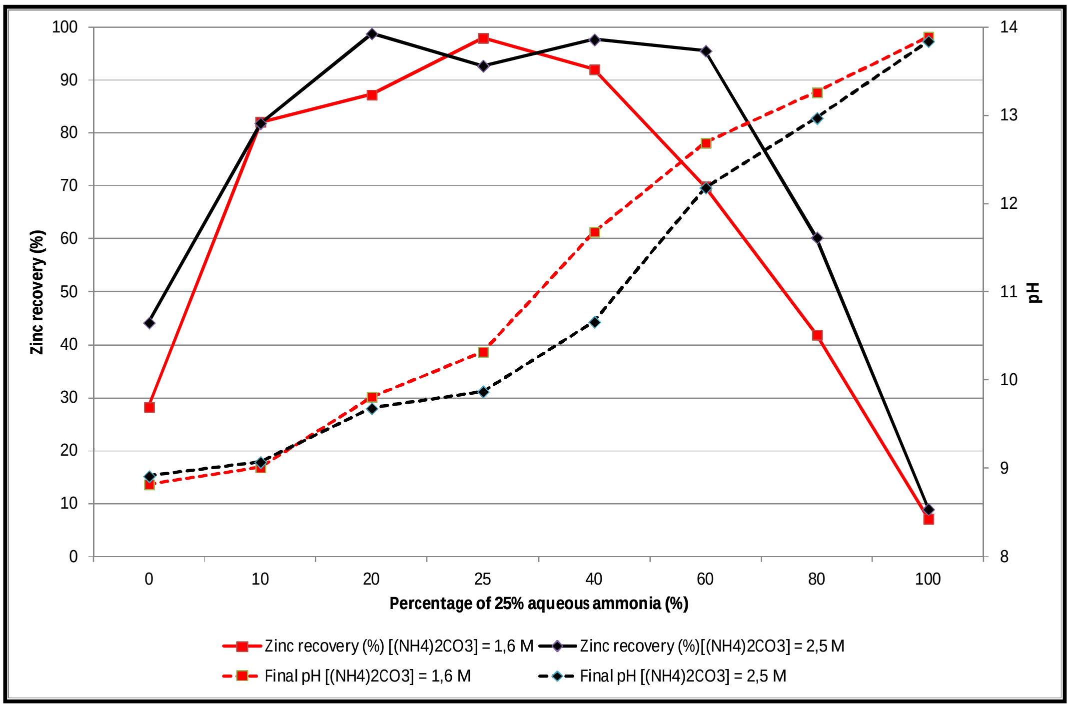

Figure 3.4: pH and zinc recovery as function of the ammonia concentration

3.3.1.6. Optimization of leaching temperature

The high volatility of ammonia is an important property in order to taken into account, so in this experimental part, the temperature of the leaching reaction was studied. These experimental tests were carried out using the optimized concentration of the liquor under these following conditions that appear in Table 3.4:

Table 3.4: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	Changes every experiment
Water volume	L	1,5
Aqueous ammonia (25%) volume	L	0,5
Ammonium carbonate anhydrous weight	g	270
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The obtained results of these experimental tests are the following ones:

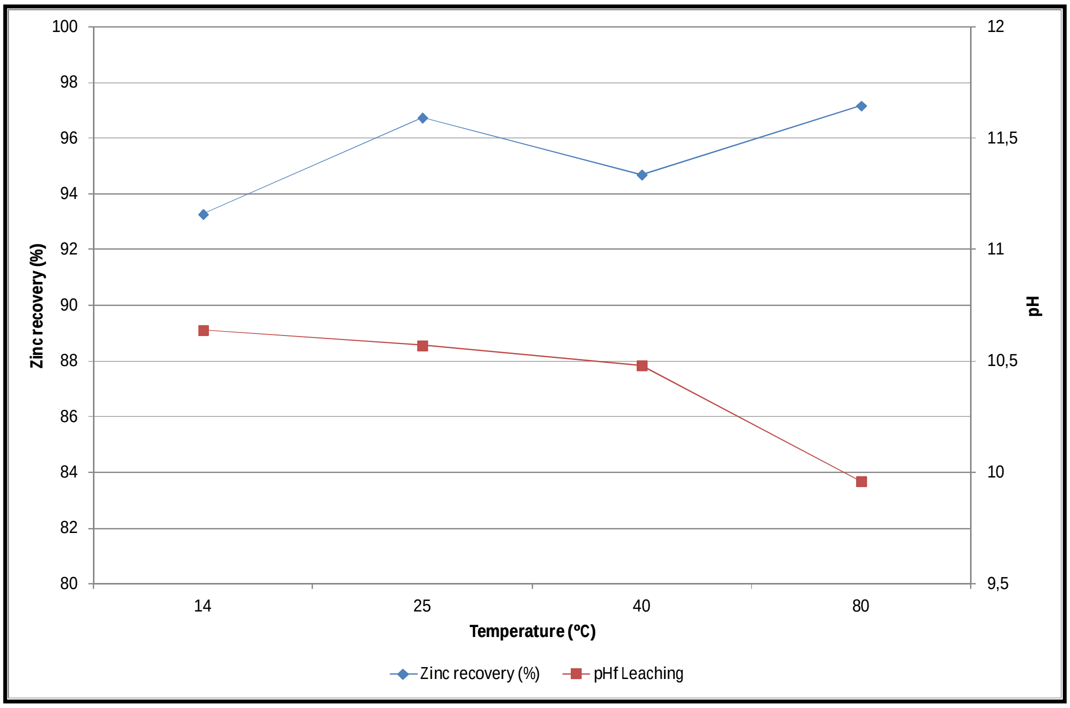

Figure 3.5: pH and zinc recovery as function of the temperature

The evolution of the zinc recovery and pH by increasing the temperature can be seen in Figure 3.5. The pH decrease uniformly until 40 ºC, but when this point is exceeded the pH has an important decrease. By contrast, the zinc recovery increase with the temperature rise, but this variation is not appreciable above the 25 ºC.

3.3.1.7. Study of leaching stage by simultaneous ammonia absorption

The regeneration of ammoniacal leaching liquors is one of the goals of this thesis, so the simultaneous ammonia absorption (as a recovery of ammonia losses) during leaching stage was analyzed in this experimental test. A sodium bicarbonate solution was used to leaching solution (as a exhausted liquor) and pure ammonia gas was injected. These experimental tests were carried out under these following conditions that appear in Table 3.5:

Table 3.5: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	Changes every experiment
Volume of liquor	L	2
Concentration of sodium bicarbonate solution	mol/L	1,34
Ratio S/L		0,15
NH_3 (g) flow	L/min	1
Stirring speed	r.p.m	700
Time	min	90

The obtained results of these experimental tests are the following ones:

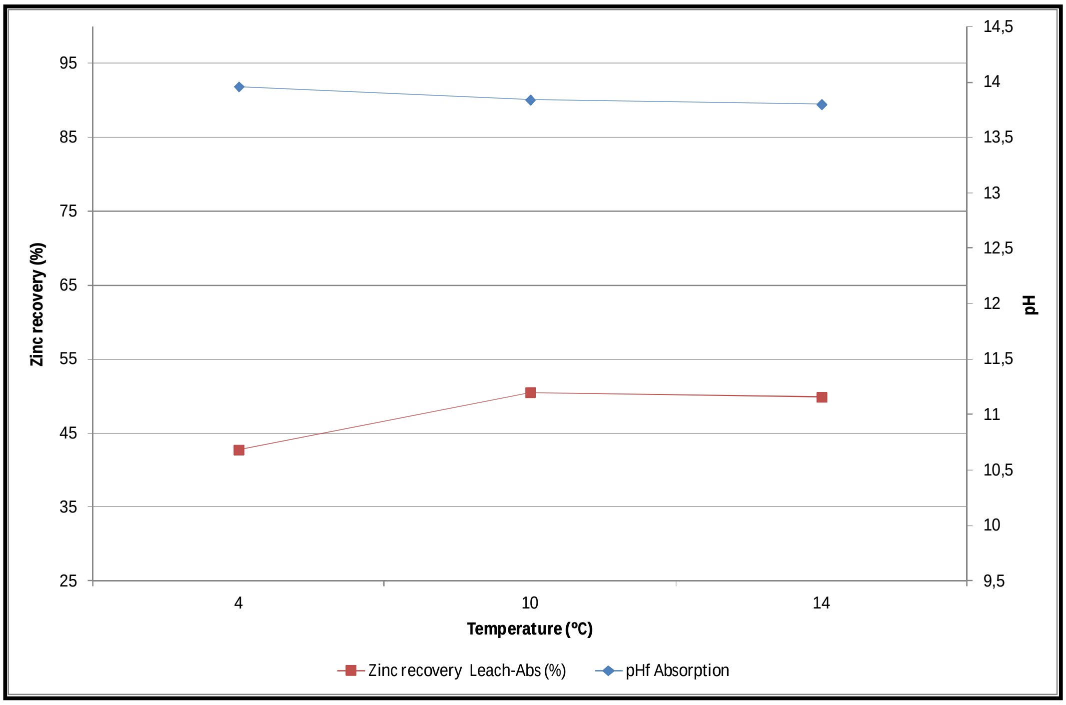

Figure 3.6: pH and zinc recovery as function of the temperature

The evolution of the zinc recovery and pH by increasing the leaching – absorption temperature can be seen in Figure 3.6. The pH decrease uniformly until 10 ºC, but when this point is exceeded the pH is kept constant. By contrast, the zinc recovery increase with the temperature rise, but this variation is not appreciable above the 10 ºC, during the temperature operation range in these experiments.

Hence, the obtained results in leaching-absorption and simple leaching experimental tests could be compared to show several conclusions, obtaining the Figure 3.7:

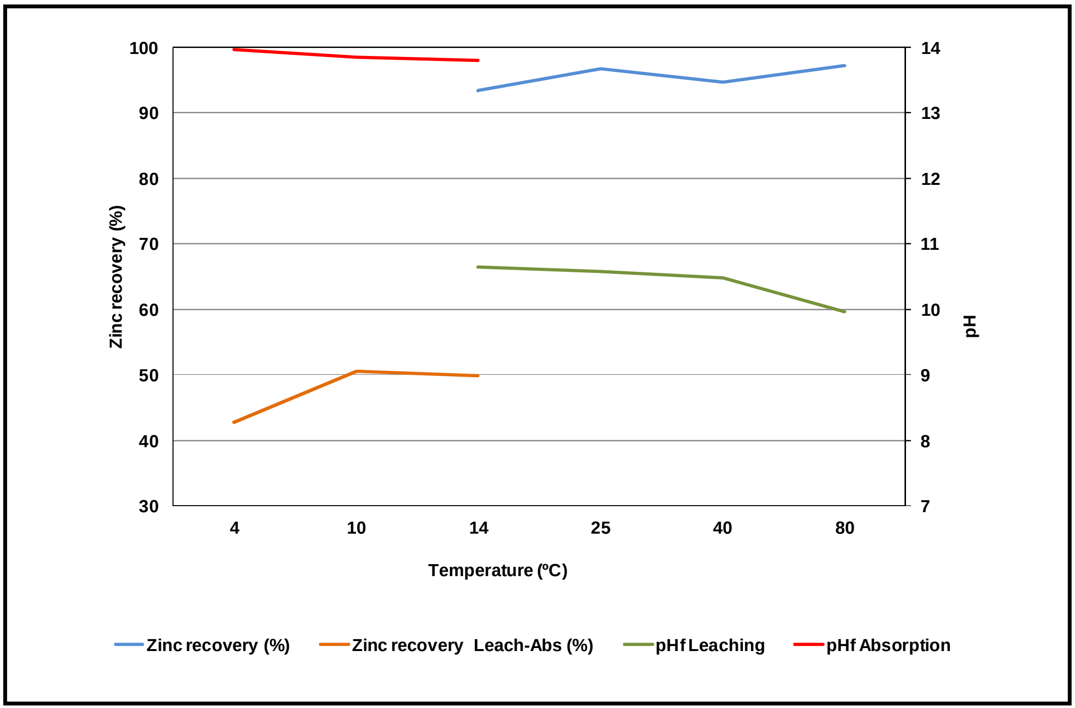

Figure 3.7: pH and zinc recovery as function of the temperature

After these tests, the influence of the sodium bicarbonate concentration in the zinc recovery was studied. For these experiments, the used conditions are following ones that appear in Table 3.6:

Table 3.6: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	25
Volume of liquor	L	2
Concentration of sodium bicarbonate solution	mol/L	Changes every experiment
Ratio S/L		0,15
NH_3 (g) flow	L/min	1
Stirring speed	r.p.m	700
Time	min	90

These are the obtained results after carried out the experimental works:

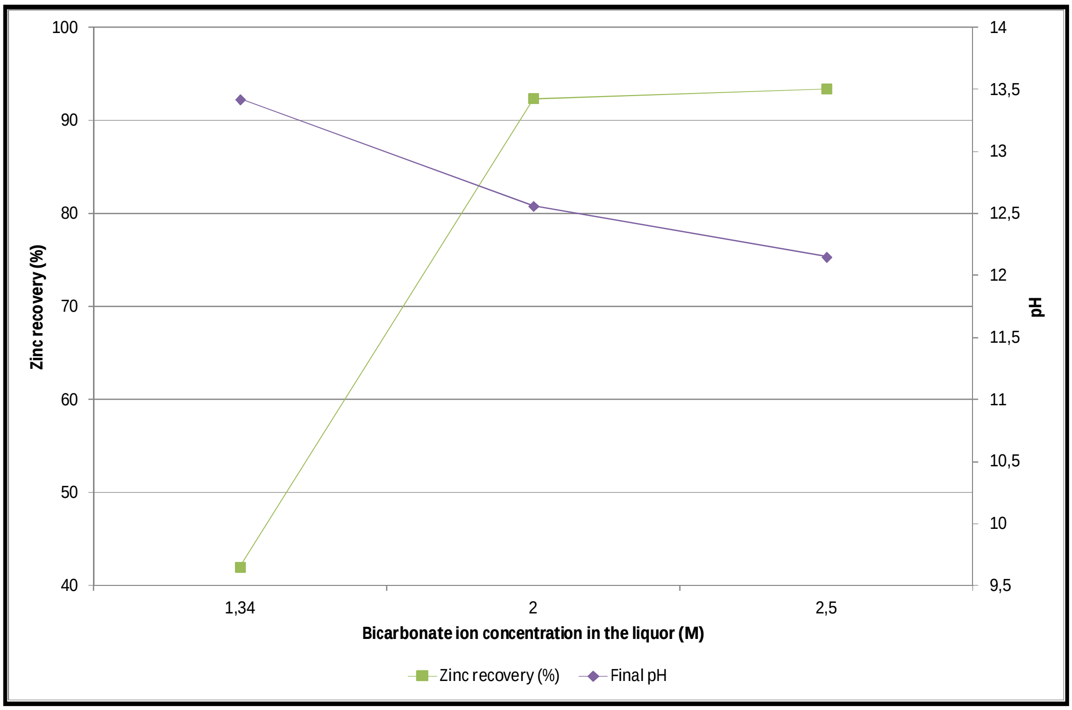

Figure 3.7: pH and zinc recovery as function of the bicarbonate concentration in the liquor

The evolution of the zinc and pH recovery by increasing the bicarbonate ion concentration can be seen in Figure 3.7. The leaching yield increases until 2 M, but when this point is exceeded the zinc recovery is kept constant.

3.3.1.8. Kinetic study of ammoniacal leaching stage

When the most important parameters of the leaching process are optimized, the kinetic of this step has to be analyzed. For these experiments, the used conditions are following ones that appear in Table 3.7:

Table 3.7: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	25
Volume of water	L	1,5
Volume of liquid ammonia (25%)	L	0,5
Concentration of ammonium carbonate solution	g	270
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	Changes every experiment

The obtained results of these experimental tests are the following ones:

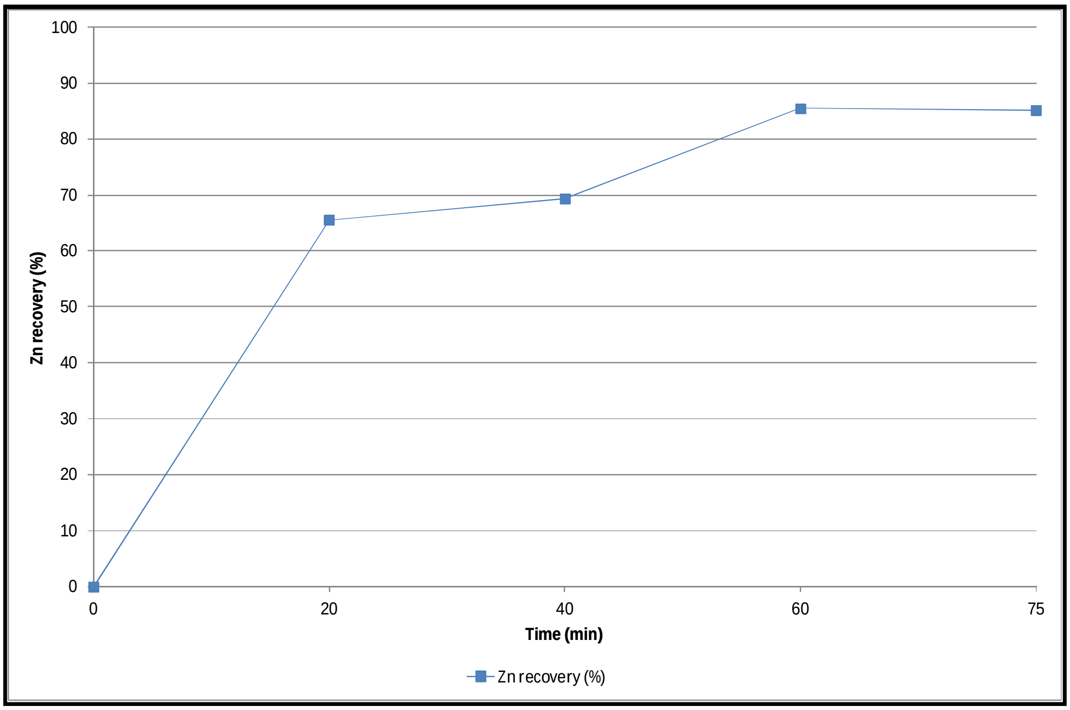

Figure 3.8: Time evolution of the zinc recovery

The time evolution of the zinc recovery can be seen Figure 3.8. The leaching yield increases until 60 minutes, but when this point is exceeded the zinc recovery is kept constant.

3.3.1.9. Characterization of optimized leaching stage

The optimal mass balance of the ammoniacal leaching stage can also be noted in the next figure:

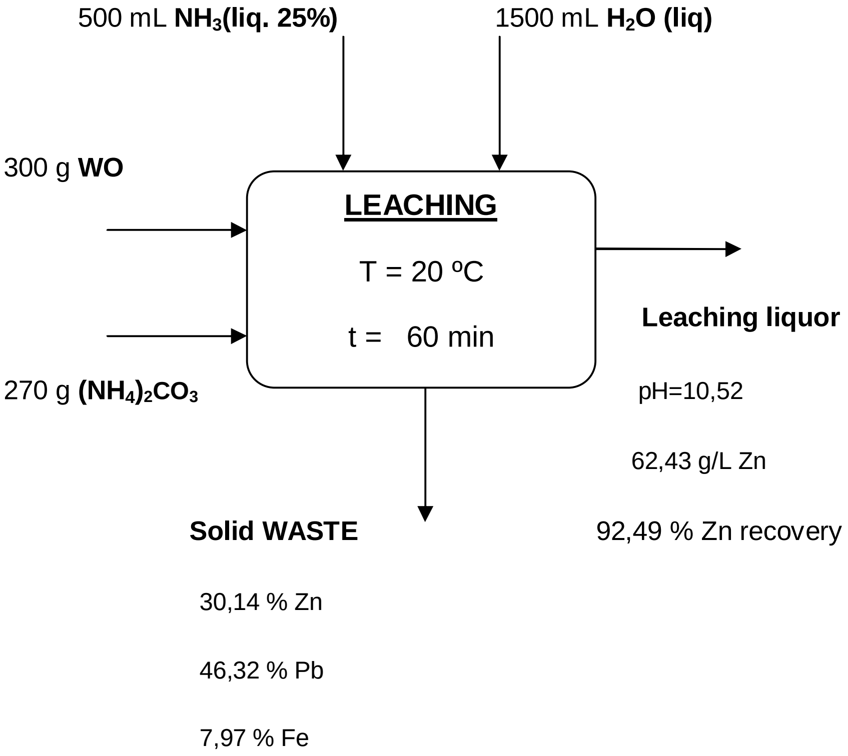

Figure 3.9: Process diagram of leaching stage

The characterization of product and waste of the optimal leaching step are noted in the Table 3.8, Table 3.9 and Table 3.10:

LEACHING LIQUOR

Table 3.8: Metallic composition

Element	**Concentration (mg / L)**	**Recovery (%)**
Cu	22,00	3,40
Zn	**62.430**	**92,49**
Ni	0,70	0,51
Cr	0,10	0,11
Mn	0,80	0,09
Fe	15,60	0,325
Cd	117,40	34,24
Sn	26,30	10,22
Pb	668,30	4,33

Table 3.9: Other composition parameters

Parameter	**Quantity**
pH	10,52
Total ammonia concentration	6,17 M*
Total CO_2 (comb.) concentration	1,61 M**

*Analyzed with ammonia ion selective electrode (Thermo Scientific ORION High Performance Ammonia ISE)

** Analyzed with combined CO_2 ion selective electrode (Thermo Scientific ORION High Performance CO_2 ISE)

SOLID WASTE

Table 3.10: Metallic composition

Element	**Concentration (% weight)**	**Concentration (g element/ g treated WO)**
Cu	0,2113	$2{,}54.10^{-4}$
Zn	30,1408	0,0362
Ni	0,5106	$6{,}13.\ 10^{-4}$
Cr	0,0704	$8{,}45.\ 10^{-5}$
Mn	0,5986	$7{,}18.\ 10^{-4}$
Fe	7,9754	$9{,}58.\ 10^{-3}$
Cd	0,0529	$6{,}34.\ 10^{-5}$
Sn	0,0003	$3{,}6.\ 10^{-7}$
Pb	**46,3205**	**0,0556**

3.3.2. OXIDATION STAGE OF AMMONIACAL LEACHING LIQUOR

When the maximum quantity of zinc was recovered from the Waelz oxide, this liquor must be purified in order to obtain a quality final product. The ammoniacal leaching of Waelz oxide is a good selective separation process for the zinc. But in this stage other metals (contained in the raw material) are also solved, which will impure the final product. So, some purification stages have to be designed before the termination process.

In this case, the target product is a high purity zinc oxide. Therefore its final quality demands some efficient removals of several impurities. The goal of the purification stages is to remove the impurities less quantity of zinc as possible from the leaching liquor. The most used of purification method in zinc hydrometallurgy is cementation. With this process the metallic impurities are removed, all metals with standard reduction potentials (volt), so iron, nickel and chromium will not be removed, decreasing the value of the final product. For this reason, an oxidation stage has to be analysed before the cementation process.

3.3.2.1. Election of oxidant agent

The oxidation process would be explained using the iron as an example:

$$\mathbf{n[Fe^{2+}\,(aq) \Leftrightarrow Fe^{3+}\,(aq) + 1e^{-}]}$$

$$\mathbf{Oxidant + ne^{-} \Leftrightarrow Oxidant^{-n}}$$

The iron is removed by precipitation, because $Fe(OH)_3$ has a very low solubility in the liquor.

So, first of all, the oxidant agent, that donates an electron must be chosen taking into account the target products quality and the economy of the industrial process.

In the zinc hydrometallurgy, some oxidant agents are used to remove the iron from the leaching liquors. The MnO_2 is the most common compound (Barakat et al, 2006 and Koleini et al, 2004) when the liquor could be tolerate concentrations of soluble Mn^{2+}, for example, the electrolytic metallic zinc production process (Mn^{2+} protects the aluminium cathodes). The hydrogen peroxide (Baik et al, 2000) is an efficient oxidant, which the oxidation process doesn't incorporate any impurity into the solution. But the use of H_2O_2 involves an exhaustive control of the pH adding chemical compounds, preferentially at acid pH. The other options for oxidation process of zinc hydrometallurgical liquors are carried out using oxidant gases. The most economic oxidation agent is oxygen and very high yields of iron removal can be achieved, around 99% (Ruiz eta al, 2007 and Nuñez, 2005), but always at higher temperatures than 25ºC. The oxidation stage with ozone has been studied (Nuñez, 2005) with satisfactory results, but it is an economically unsustainable process.

After these considerations, the most proper treatment for the obtained leaching liquors is an oxidation step using oxygen from the atmospheric air. The optimal operation conditions for this process have been studied in this chapter.

3.3.2.2. Technical considerations of ammoniacal liquor oxidation stage

High iron can generally be removed by oxidation to form an insoluble heavy substance that can be settled out and filtered. Aeration is frequently useful for the conversion or oxidation of iron. Aeration is normally too slow to be used with successful manganese oxidation unless the liquor's pH is very high. Aeration is used before other chemical treatment (cementation), since it is relatively inexpensive to operate and it can reduce the amount of chemicals that might subsequently be use.

3.3.2.3. Thermodynamic analyze of ammoniacal liquor oxidation stage

The optimization of oxidation stage is the result of experimental study of operation variables, which have a direct impact in these chemical reactions:

$$O_2 + \mathbf{3}H^+ + \mathbf{4}e^- \Leftrightarrow OH^- + H_2O$$

$$\mathbf{4}Fe^{2+} \Leftrightarrow \mathbf{4}Fe^{3+} + \mathbf{4}e^-$$

$$O_2 + 3H_2O + 4Fe^{2+} \Leftrightarrow 4Fe^{3+} + 4OH^- + H_2O$$

$$O_2 + 3H_2O + 4Fe^{2+} + 8OH^- \Leftrightarrow 4Fe(OH)_3(\downarrow) + H_2O$$

GLOBAL REACTION: $\mathbf{O_2 + 4Fe^{2+} + 10H_2O \Leftrightarrow 4Fe(OH)_3 + 8H^+}$

After the stoichiometric equations were showed, the Nernst's equation can be used to analyze the oxidation process.

$$E = E^o - (RT/nF)(Ln([H^+]^8/P_{O2}[Fe^{2+}]^4))$$

When: $E^o_{Fe2+/Fe3+} = 0{,}77\ V$

$E^o_{O2/H2O} = 1{,}23\ V$

$$E^o = E^o_{cathode} – E^o_{anode} = 1{,}23\ V – 0{,}77\ V = 0{,}46\ V$$

Nernst's equation applied to the global reaction:

$$E = 0{,}46 – (8{,}314*T/4*96500)(Ln([H^+]^8/P_{O2}[Fe^{2+}]^4))$$

$$\mathbf{E = 0{,}46 – 2{,}153886.10^{-5}T(Ln([H^+]^8/0{,}21[Fe^{2+}]^4))}$$

The objective of the thermodynamic study is to find the adequate ranges for the operation parameters, which would turn the process into a spontaneous one.

$$\Delta G < 0 \text{ (spontaneous reaction)} \rightarrow E > 0$$

$$\mathbf{0{,}46 > – 2{,}153886.10^{-5}T\ (Ln([H^+]^8/0{,}21[Fe^{2+}]^4))}$$

Therefore, the temperature of the process, the range of pH and the iron concentration in the liquor must be studied in order to obtain an efficient purification step.

3.3.2.4. Optimization of the ammoniacal oxidation stage

In this chapter the operation parameters of the oxidation step were studied. The highest removal of iron and the lowest zinc loss were the main goals of this experimental work. Several parameters were studied:

a. Optimization of oxidation temperature

The influence of the temperature is an important parameter in the thermodynamic of the operation and in the kinetic of the oxidation reaction. The experimental work to study this influence was carried out under following conditions that appear in Table 3.11:

Table 3.11: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	Changes every experiment
Volume of leaching liquor	L	1,8
Air flow	L/min	1,25
Diffusion volume	cm^3	270
Diffusion area	cm^2	0,15
Stirring speed	r.p.m	700
Gas injector size:		
Φ_{ext}	mm	4
Φ_{int}	mm	6
Time	min	100

The obtained results of these experimental tests are the following ones:

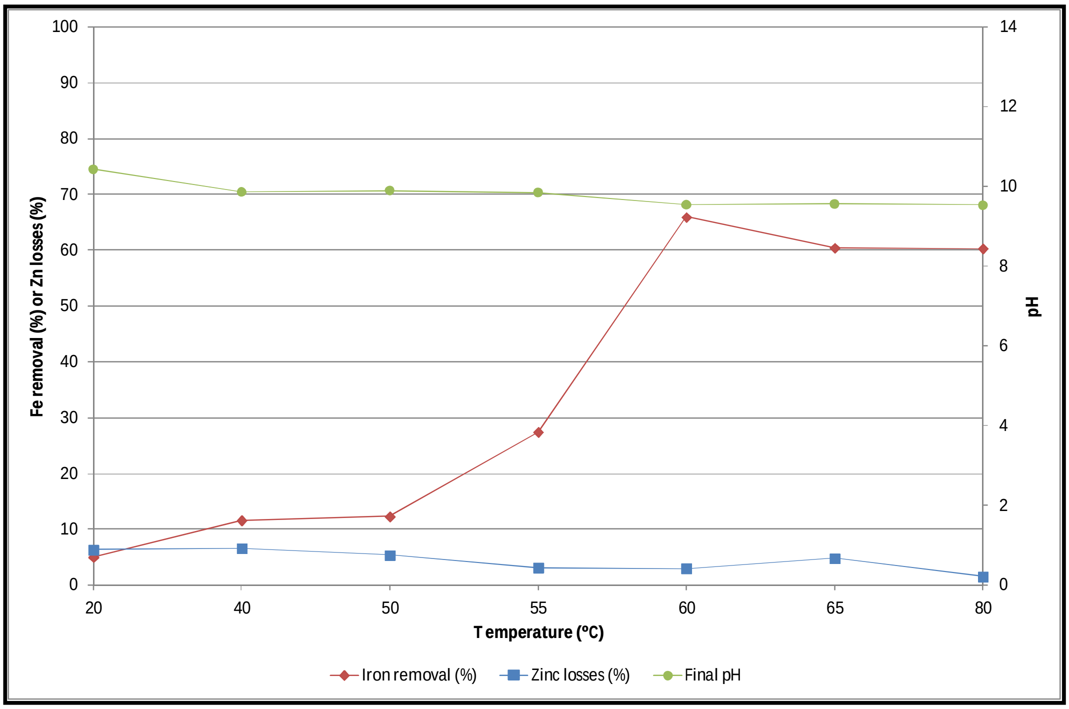

Figure 3.10: pH, iron removal and zinc losses as function of temperature

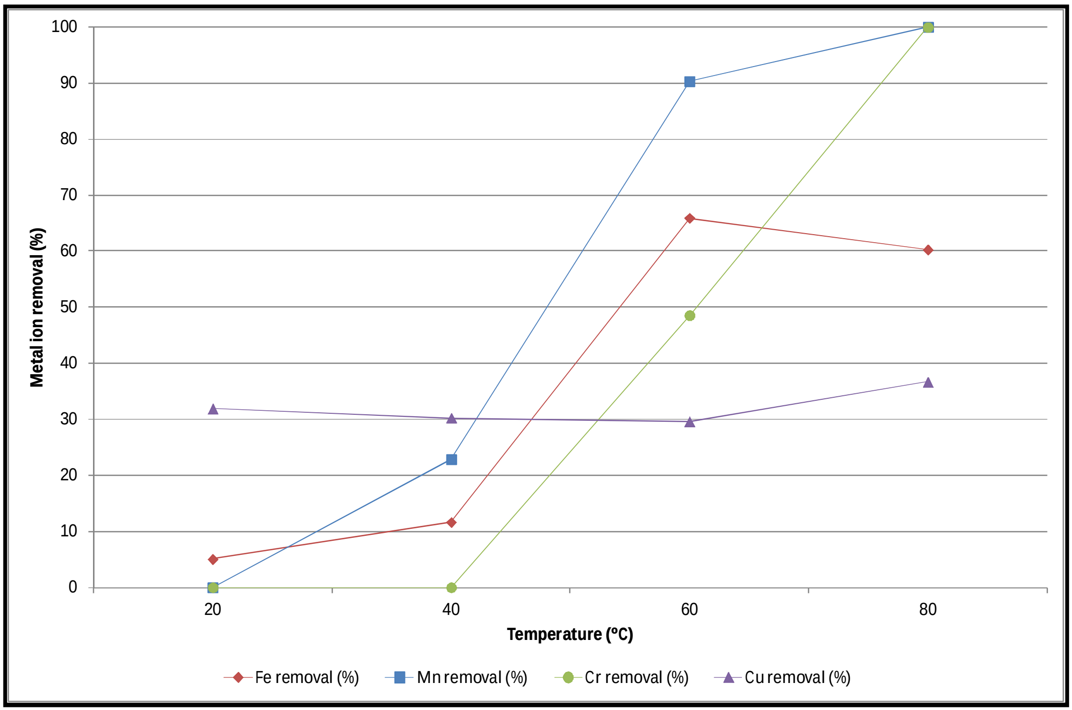

Figure 3.11: Iron, manganese chromium and cooper removal as function of temperature

The evolution of the zinc loss, iron and other metal ions removal and pH by increasing the temperature was shown. The pH decreases uniformly until 80 ºC. By contrast, the iron removal increase with the temperature rise, but the yield is acceptable between 60 ºC and 80 ºC.

b. Optimization of air flow rate

The used air flow rate is an important parameter in order to design an industrial process. But the experimental tests must be carried out, taking into account the influence of the temperature. As these tests were carried out under the same conditions than those of the previous experiments, the results were plotted in the Figure 3.12:

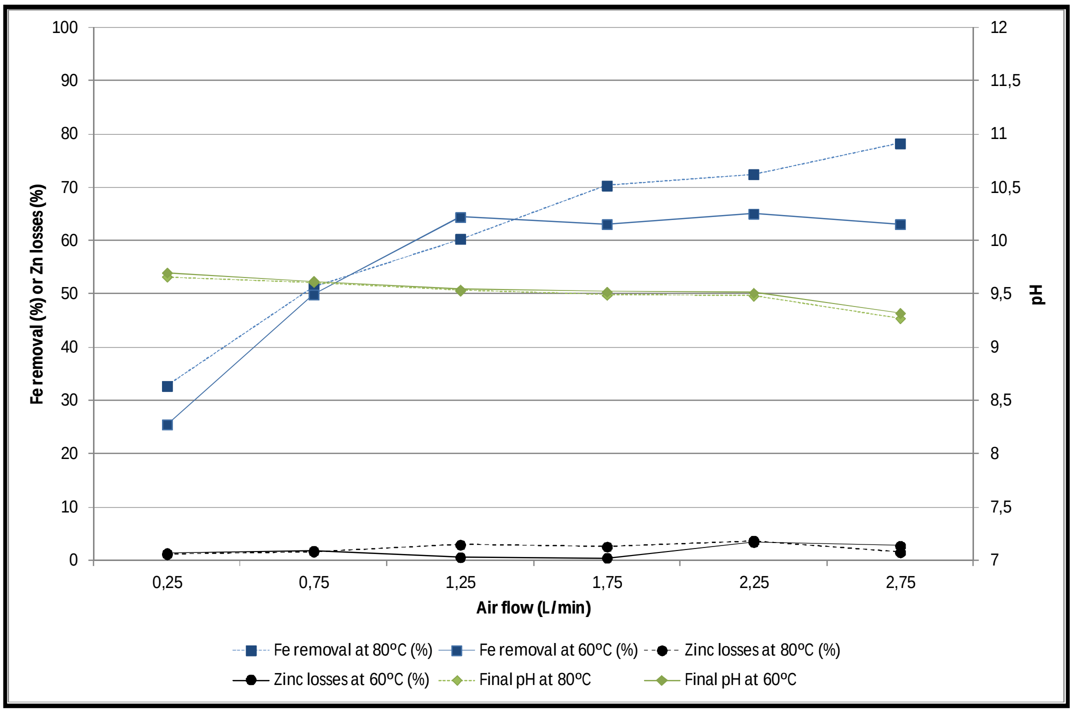

Figure 3.12: Iron removal and zinc losses at 60ºC and 80ºC as function of the used air flow

The evolution of the zinc loss, iron removal and pH at 60ºC and 80 ºC by increasing the air flow rate can be seen in Figure 3.12. The pH at 80 ºC decreases uniformly until 9,5 and more significantly after this point and it is the same at 60 ºC. By contrast, the iron removal increase with the air flow rate and the zinc losses was maintained below 5 %.

3.3.2.5. Kinetic study of ammoniacal oxidation stage

When the most important parameters of the oxidation process are optimized, the kinetic of this step has to be analyzed. The kinetic study was carried out taking into account two different temperatures, the chosen temperature will depend on the target quality of the final product.

a. Kinetic study at 60ºC

For these experiments, the used conditions are the following ones that appear in Table 3.13:

Table 3.13: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	60
Volume of leaching liquor	L	1,8
Air flow	L/min	1,25
Diffusion volume	cm^3	270
Diffusion area	cm^2	0,15
Stirring speed	r.p.m	700
Gas injector size:		
Φ_{ext}	mm	4
Φ_{int}	mm	6
Time	min	Changes every experiment

These are the obtained results after carried out the experimental works:

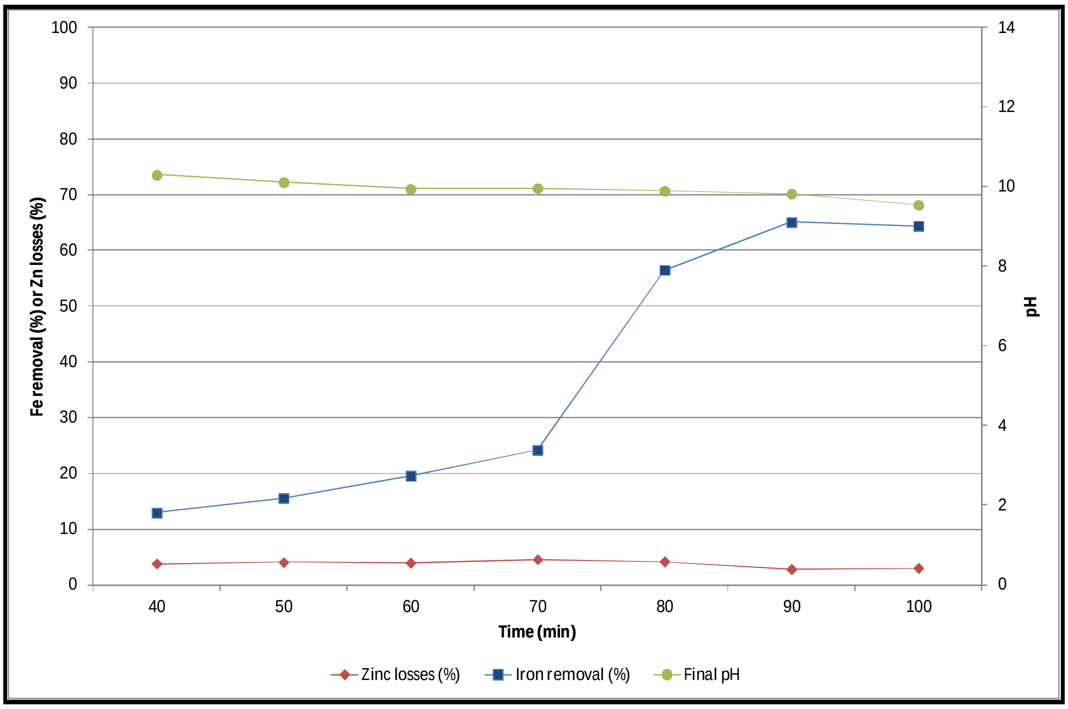

Figure 3.13: Time evolution of the iron removal, the zinc losses and the pH at 60ºC

The time evolution of the iron removal can be seen in Figure 3.13. The oxidation yield increases until 90 minutes, but when this point is exceeded the iron removal is kept constant.

b. Kinetic study at 80°C

For these experiments, the used conditions are the following ones that appear in Table 3.14:

Table 3.14: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	80
Volume of leaching liquor	L	1,8
Air flow	L/min	2,25
Diffusion volume	cm^3	270
Diffusion area	cm^2	0,15
Stirring speed	r.p.m	700
Gas injector size:		
Φ_{ext}	mm	4
Φ_{int}	mm	6
Time	min	Changes every experiment

These are the obtained results after carried out the experimental works:

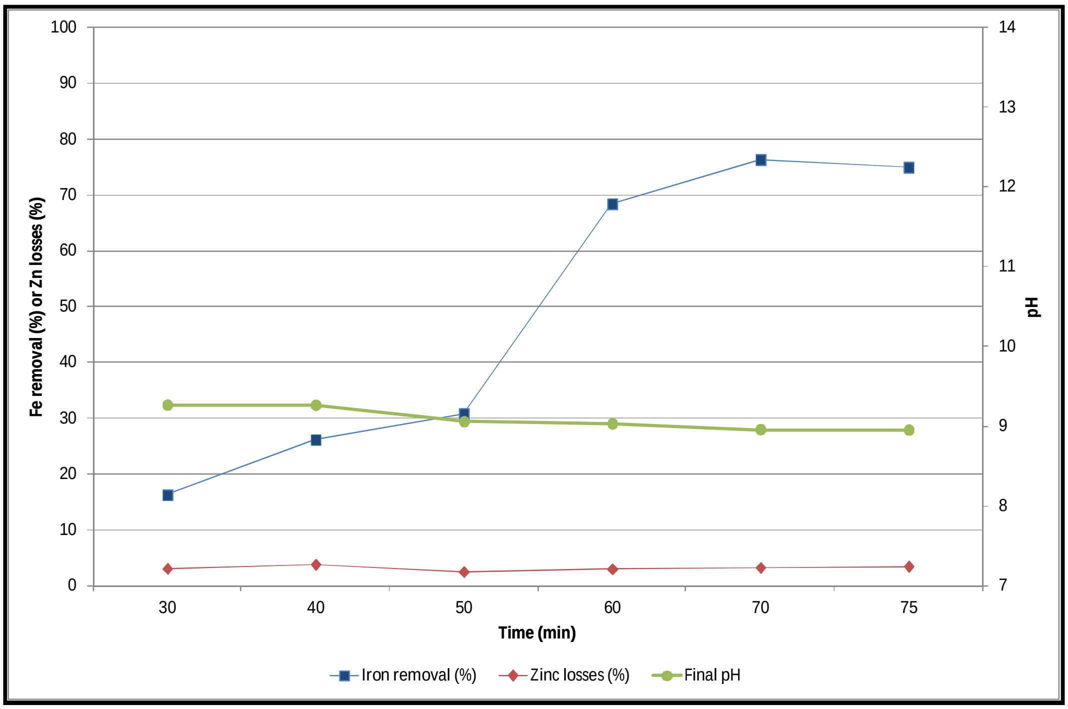

Figure 3.14: Time evolution of the iron removal, the zinc losses and the pH at 80ºC

The time evolution of the iron removal can be seen in Figure 3.14. The oxidation yield increases until 70 minutes, but when this point is exceeded the iron removal is kept constant.

3.3.2.6. Characterization of optimized oxidation stage

The optimal mass balance of the ammoniacal oxidation stage can be observed in the Figure 3.15:

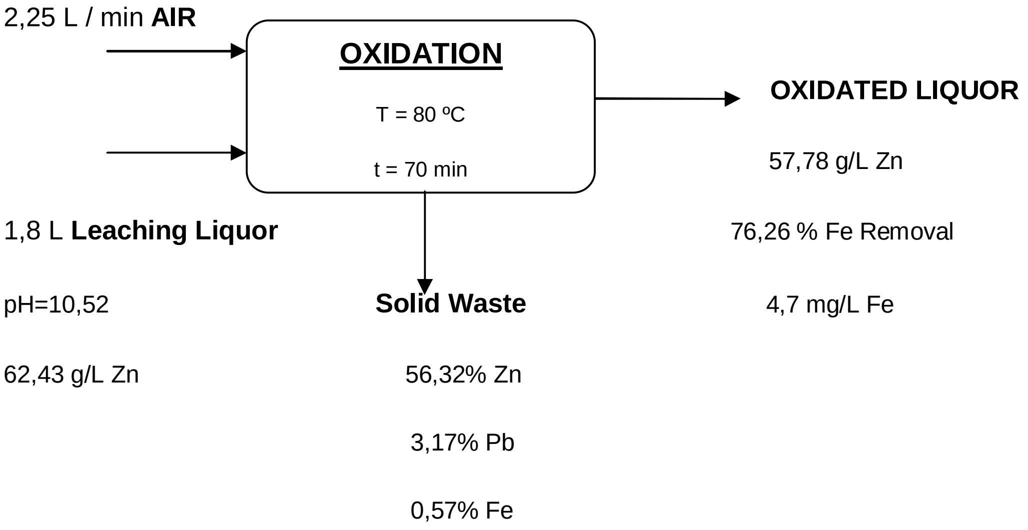

Figure 3.15: Process diagram of oxidation stage

WATER EVAPORATION

During this optimized oxidation stage, an important quantity of water is evaporated. This is an important parameter to design the ammonia recovery process, because the stripped ammonia stream is going to sweep along water to the absorption step.

H = Air humidity = Kg H_2O / Kg dry air = $(18,02 / 28,97)(P_A / P_T - P_A)$

H_S = Saturation humidity = $(18,02 / 28,97)(P_{AS} / P_T - P_{AS})$

Evaporated water quantity

$\dot{m}_{H2O\ evap} = \dot{m}_{da}(H_F - H_o)$

When: $\dot{m}_{H2O\ evap}$ = evaporated water quantity (Kg); $\dot{m}_{da}$ = dry air quantity (Kg); H_F = final humidity (Kg H_2O / Kg air); H_o = initial humidity (Kg H_2O / Kg air)

H_0 = (101,3 KPa, 20 ºC and 70 % humidity) = 0,012 = (18,02 / 28,97) (P_A / P_T - P_A)

P_{A0} = 1,9925 KPa

P_{AS}(80ºC) = 47,34 KPa → H_F (sat, 80ºC) = (18,02/28,97)(47,34/101,3 – 47,34) = 0,54571

$\dot{m}_{da}$ = optimized air flow . ρ_{air} (80ºC) = 2,25 10^{-3} m^3/min . 0,9109 Kg

$\dot{m}_{H2O\ evap} = \dot{m}_{da}(H_F - H_o)$ = 1,094 10^{-3} L_{H2O} / min

Total evaporated water quantity = (1,094 10^{-3} L_{H2O}/min)(70 min) = **0,0767 L**

The characterization of product and waste of the optimal oxidation step are noted in the Table 3.15, Table 3.16 and Table 3.17:

OXIDATED LIQUOR

Table 3.15: Metallic composition

Element	Concentration (mg / L)	Recovery (%)
Cu	16,53	24,43
Zn	**57.780**	**3,25**
Ni	1,4	0
Cr	0	100
Mn	0	100

Fe	**4,7**	**69,01**
Cd	109,9	3,71
Sn	31,2	0
Pb	579,1	10,87

Table 3.16: Other composition parameters

Parameter	**Quantity**
pH	10,04
Total ammonia concentration	4,59 M*
Total CO_2 (comb.) concentration	1,29 M**

*Analyzed with ammonia ion selective electrode (Thermo Scientific ORION High Performance Ammonia ISE)

** Analyzed with combined CO_2 ion selective electrode (Thermo Scientific ORION High Performance CO_2 ISE)

SOLID WASTE

Table 3.17: Metallic composition

Element	**Concentration (% weight)**	**Concentration (g element/ g treated WO)**
Cu	0	0
Zn	**56,3218**	**0,0033**
Ni	0	0

Cr	0	0
Mn	0,2528	$1{,}49.\ 10^{-5}$
Fe	0,5747	$3{,}388.\ 10^{-5}$
Cd	0	0
Sn	0	0
Pb	**3,1724**	$\mathbf{1{,}87.\ 10^{-4}}$

3.3.3. CEMENTATION STAGE OF AMMONIACAL LEACHING LIQUOR

The last purification step to reach the target quality of the hydrometallurgical liquor is the cementation stage. The goal of this process is to remove the remaining metallic impurities (after oxidation) solved in the liquor. The operation is used to precipitate metallic ions from the solution onto another cementation agent that is more electropositive.

3.3.3.1. Election of cementation agent

The election of cementation agent is very easy in the zinc hydrometallurgy, because the zinc metal itself is more electropositive than the most of the dissolved metal impurities. In addition, the oxidation of metal zinc dust enriches the liquor and the yield of the global process. Therefore, the zinc dust is the chosen cementation agent.

$$\mathbf{Zn^0\ (s) \Leftrightarrow Zn^{2+}\ (aq) + 2e^-}$$

$$\mathbf{Me^{n+}\ (aq) + ne^+ \Leftrightarrow Me^0\ (s)}$$

3.3.3.2. Technical considerations of ammoniacal liquor cementation stage

The cementation stage is a purification process based on redox reactions. The metal ionic impurities are removed through precipitation of their reduced forms. The cementation process inevitably occurs in the presence of a surface scale, where the surface of the reducing metal is covered by porous layers of the cemented metal. Therefore, the porous cemented metal must be electronic conductive and so it favours further dissolution of the reducing metal (Noubactep, C., 2010).

All impurities which are less electropositive than the metallic zinc dust (Zn^0) can be electrochemically precipitated in metallic form from the hydrometallurgical liquor. And the zinc dust is oxidized to Zn^{2+} and this ion is soluble in the solution, this reaction increases the zinc recovery yield of this recycling process.

In the Table 3.18 the difference of reduction potentials with respect to the zinc are shown:

Table 3.18: Difference of reduction potentials values

Ox. / Red. Species	**$\Delta E^0 = E_i^0 - E^0_{Zn(II)/Zn(0)}$ (V)**
Pb^{+4}/Pb^{+2}	+2,45
Mn^{+3}/Mn^{+2}	+2,27
Fe^{+3}/Fe^{+2}	+1,53
Cu^{+}/Cu^{0}	+1,28
Cu^{+2}/Cu^{0}	+1,10
Sn^{+4}/Sn^{+2}	+0,91
Pb^{+2}/Pb^{0}	+0,63
Sn^{+2}/Sn^{0}	+0,62
Ni^{+2}/Ni^{0}	+0,51
Fe^{+2}/Fe^{0}	+0,32
Cd^{+2}/Cd^{0}	+0,26

Cr^{+3}/Cr^{+2}	+0,25
Zn^{+2}/Zn^{0}	0
Cr^{+2}/Cr^{0}	-0,15
Mn^{+2}/Mn^{0}	-0,42

3.3.3.3. Optimization of the ammoniacal cementation stage

In this chapter different operation parameters of the cementation step was studied. The highest removal of metallic impurities and the lowest zinc dust addition was the main goals of this experimental work. Several parameters were studied:

a. Optimization of metallic zinc dust addition

Zinc dust consumption is an important parameter to fix the cost of this purification operation. The experimental work to study this influence was carried out under following conditions that appear in Table 3.19:

Table 3.19: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	20
Volume of leaching liquor	L	1,8
Stirring speed	r.p.m	700
Zinc dust addition	g	Researched parameter

The obtained results of these experimental tests are the following ones:

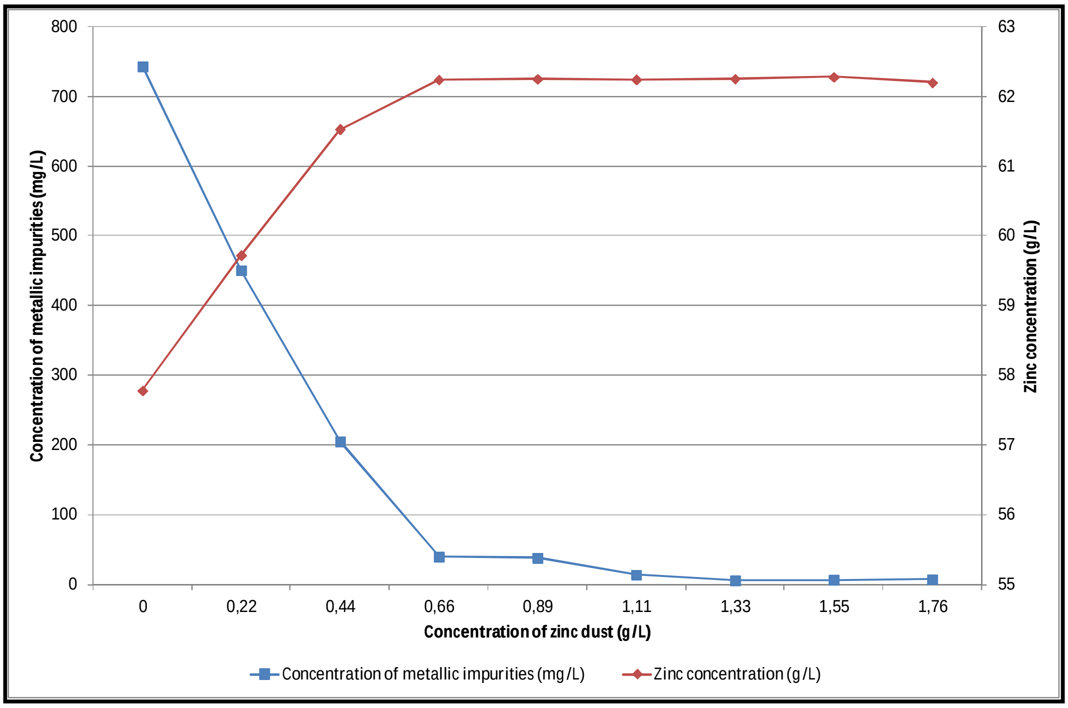

Figure 3.15: Concentration of metallic impurities and zinc concentration as function of zinc dust addition

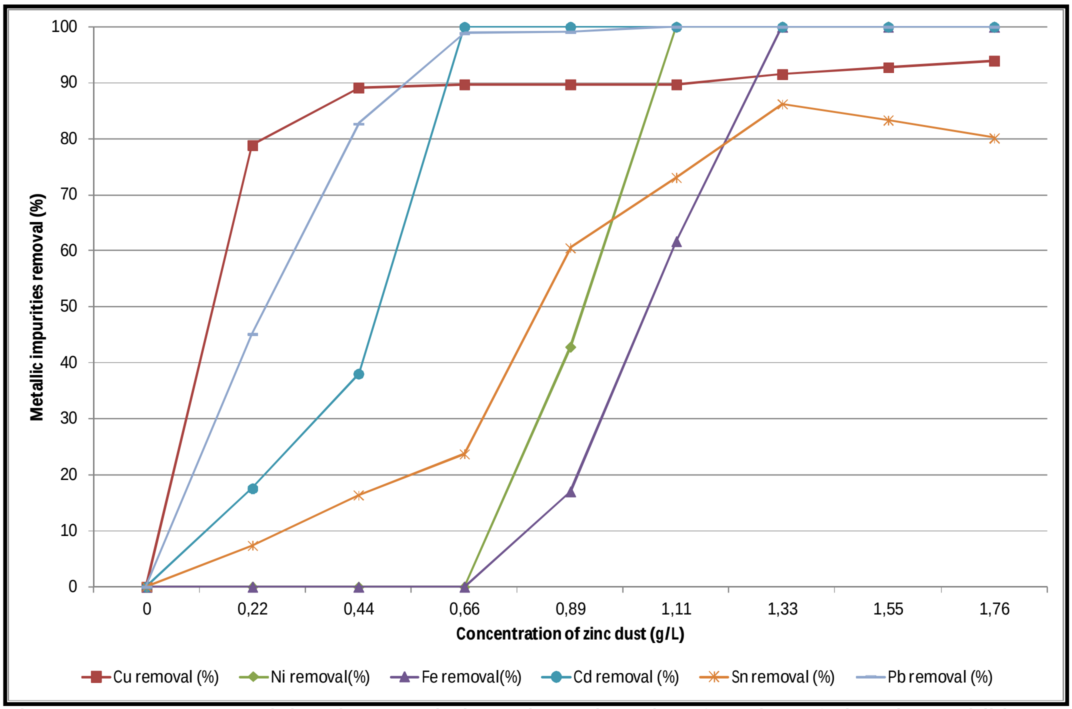

Figure 3.16: Cooper, nickel, iron, cadmium, tin and lead as function of zinc dust addition

The evolution of the metal impurities concentration and dissolved zinc concentration by increasing the zinc dust addition can be seen in Figure 3.15. The impurities removal increases until the zinc dust concentration reach 1,33 g/L, at the same time the zinc concentration in the liquor increase with the zinc dust addition. On the other hand, in the Figure 3.16 the removal of metallic impurities, one by one, in function of the concentration of zinc dust was represented.

3.3.3.4. Kinetic study of ammoniacal cementation stage

The influence of time of reaction is also an important parameter to estimate the cost of the purification operation. The experimental work to study this influence was carried out under following conditions that appear in Table 3.20:

Table 3.20: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	20
Volume of leaching liquor	L	1,8
Stirring speed	r.p.m	700
Zinc dust concentration	g/L	1,33

The obtained results of these experimental tests are the following ones:

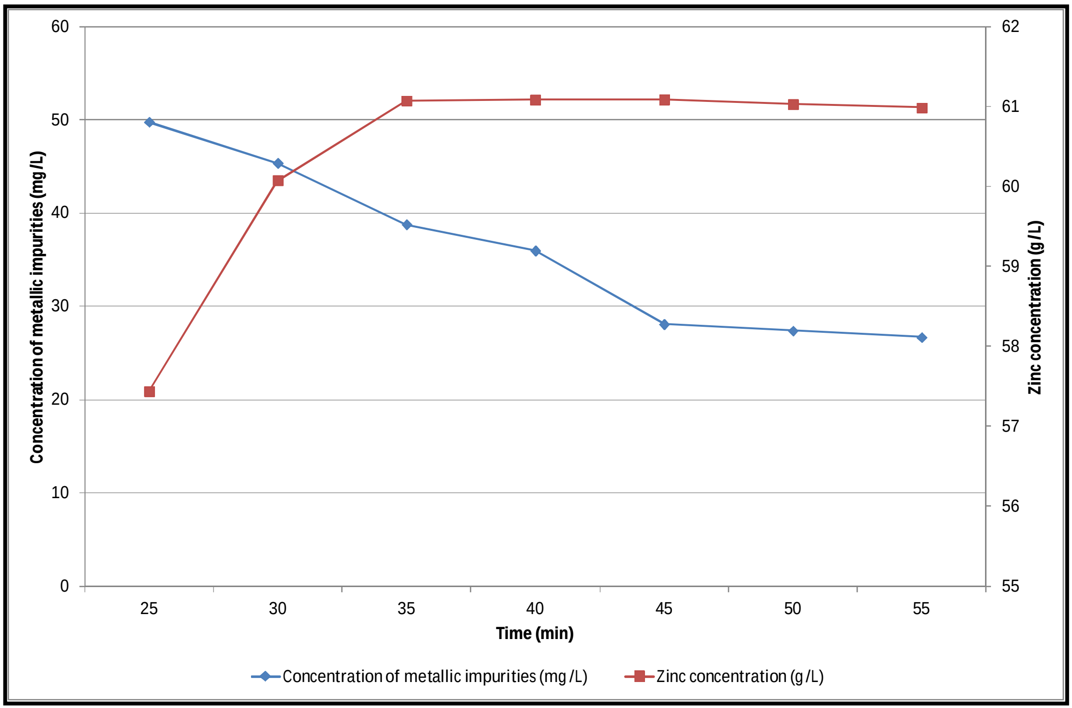

Figure 3.17: Time evolution of concentration of metallic impurities and zinc concentration

The time evolution of the metallic impurities removal can be seen in Figure 3.17. The cementation yield increases until 45 minutes, but when this point is exceeded the impurities removal is kept constant.

3.3.3.5. Characterization of optimized cementation stage

The optimal mass balance of the ammoniacal cementation stage can also be observed in the Figure 3.18:

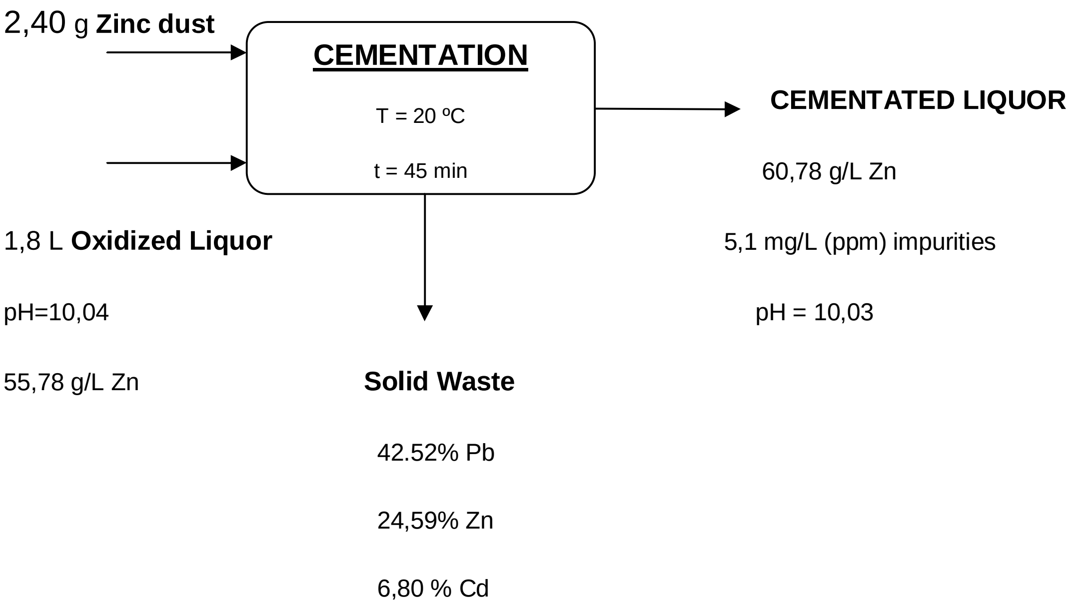

Figure 3.18: Process diagram of cementation stage

The characterization of product and waste of the optimal cementation step are shown in the Table 3.21, Table 3.22 and Table 3.23:

CEMENTATED LIQUOR

Table 3.21: Metallic impurities

Element	Concentration (mg / L)	Recovery (%)
Cu	1,1	93,35
Zn	**60.782**	**-3,41**
Ni	1,3	7,14
Cr	0,6	0
Mn	0,3	0

Fe	1,0	78,72
Cd	0	100
Sn	0	100
Pb	0,7	99,88

Table 3.22: Other composition parameters

Parameter	**Quantity**
pH	10,03
Total ammonia concentration	4,41 M*
Total CO_2 (comb.) concentration	1,35 M**

*Analyzed with ammonia ion selective electrode (Thermo Scientific ORION High Performance Ammonia ISE)

** Analyzed with combined CO_2 ion selective electrode (Thermo Scientific ORION High Performance CO_2 ISE)

SOLID WASTE

Table 3.23: Metallic impurities

Element	**Concentration (% weight)**	**Concentration (g element/ g treated WO)**
Cu	0,8269	$1,376.\ 10^{-4}$
Zn	**24,596**	**0,0041**
Ni	0,0769	$1,281.\ 10^{-5}$

Cr	0	0
Mn	0	0
Fe	0,0961	1,603. 10^{-5}
Cd	6,8076	0,0012
Sn	0,0385	6,417. 10^{-6}
Pb	**42,5192**	**0,0071**

3.3.4. THE FINISHING STAGES FOR OBTAINING ZINC OXIDE

After the purification stages the result is an ammonium carbonate liquor with a high concentration of zinc ions. So, to produce the target product the dissolved zinc has to be recovered from the liquor. The adopted strategy in this case is to recover the zinc in solid phase as zinc carbonate and zinc hydroxide and a subsequent thermal treatment of these solids. Therefore, in this chapter both finishing steps are studied.

3.3.4.1. Chemical precipitation of dissolved zinc with CO_2

Several options exist to recover the dissolved zinc from the liquor: evaporation, crystallization, precipitation… In this case, the selected operation is the chemical precipitation, because the characteristics of the final product make other options energetically unsustainable.

The studied solution for zinc recovery in this stage is the chemical precipitation with CO_2 by absorption in the cementated liquor, so the pH of the solution decreases and also the zinc solubility. The solubility of carbonates in the solution will be increased until it exceeds the saturation conditions, so the zinc is going to be recovered as zinc carbonate and zinc hydroxide.

a. Thermodynamic analyze of chemical precipitation with CO_2

Precipitation of metallic compounds from aqueous solution can often be accomplished by simple pH adjustment (Fuerstenau, M. C. Et al., 2003). The amount of metal ions removable from solution can be estimated by considering the solubility products of metal hydroxides and metal carbonates.

The solubility of metal oxides, hydroxides and carbonates at any particular pH value in the absence of other ions and at constant temperature will by controlled by following equilibria, assuming a divalent cation (as zinc cation). (Adapted from Stumm and Morgan, 1970):

$H_2O \Leftrightarrow H^+ + OH^-$

$CO_2\ (g) + H_2O \Leftrightarrow H_2CO_3\ (aq)$

$H_2CO_3\ (aq) \Leftrightarrow HCO_3^- + H^+$

$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$

$MCO_3\ (s) \Leftrightarrow M^{2+} + CO_3^{2-}$

$MCO_3\ (s) + H^+ \Leftrightarrow M^{2+} + HCO_3^-$

$MCO_3\ (s) + H_2CO_3\ (aq) \Leftrightarrow M^{2+} + 2HCO_3^-$

$MCO_3\ (s) + H^+ \Leftrightarrow M^{2+} + H_2CO_3\ (aq)$

In the same way as solid hydroxides may be precipitated by hydrolysis, other ions may react to form solid precipitates. In the particular case of this research, the precipitation takes place for two clear reasons:

- Precipitation of hydroxides by changes in pH without changes in oxygen potential

- Precipitation of insoluble compounds or salts by addition of certain chemicals

a.1. Main chemical reactions to precipitate zinc cations involving ammoniacal liquors

The optimization of precipitation stage is the result of experimental study of operation variables, which have a direct impact in these chemical reactions:

Zinc solubility equilibrium reaction:

$ZnCO_3 \Leftrightarrow Zn^{2+} + CO_3^{2+}$

$Zn(OH)_2 \Leftrightarrow Zn^{2+} + 2\ OH^-$

Leaching liquor equilibrium reactions:

$CO_2 + OH^- \Leftrightarrow HCO_3^-$

$HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

$H_2O \Leftrightarrow H^+ + OH^-$

Therefore, the flow of CO_2 in the reactor and the range of pH in the liquor must to be studied in order to obtain an efficient zinc recovery step.

b. Optimization of the precipitation stage

In this chapter the operation parameters of the precipitation step were studied. The highest removal of zinc and the lowest ammonia loss were the main goal of this experimental work. Several parameters were studied:

b.1. Optimization of CO_2 (g) flow in the precipitation stage

The influence of the gas flow is an important parameter in this operation and in the kinetic of the zinc precipitation reactions. In order to carry out the study and design of this step in hydrometallurgical processes, a patented reactor for solid-liquid-gas reactions (Núñez, J. Et al., 2006, **WO2007085671**) was used. The experimental work to study this influence was carried out under the following conditions that appear in Table 3.25:

Table 3.24: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	20
Volume of leaching liquor	L	1,8
CO_2 (g) concetration	%	99,9
CO_2 (g) flow	L/min (CO_2, T=25ºC;P=1atm)	Changes every experiments
Gas density	Kg/m^3	1,87
Diffusion volume	cm^3	132
Diffusion area	cm^2	0,113
Stirring speed	r.p.m	700
Gas injector size:		
Φ_{ext}	mm	4
Φ_{int}	mm	6
Time	min	100

The obtained results of these experimental tests are the following ones:

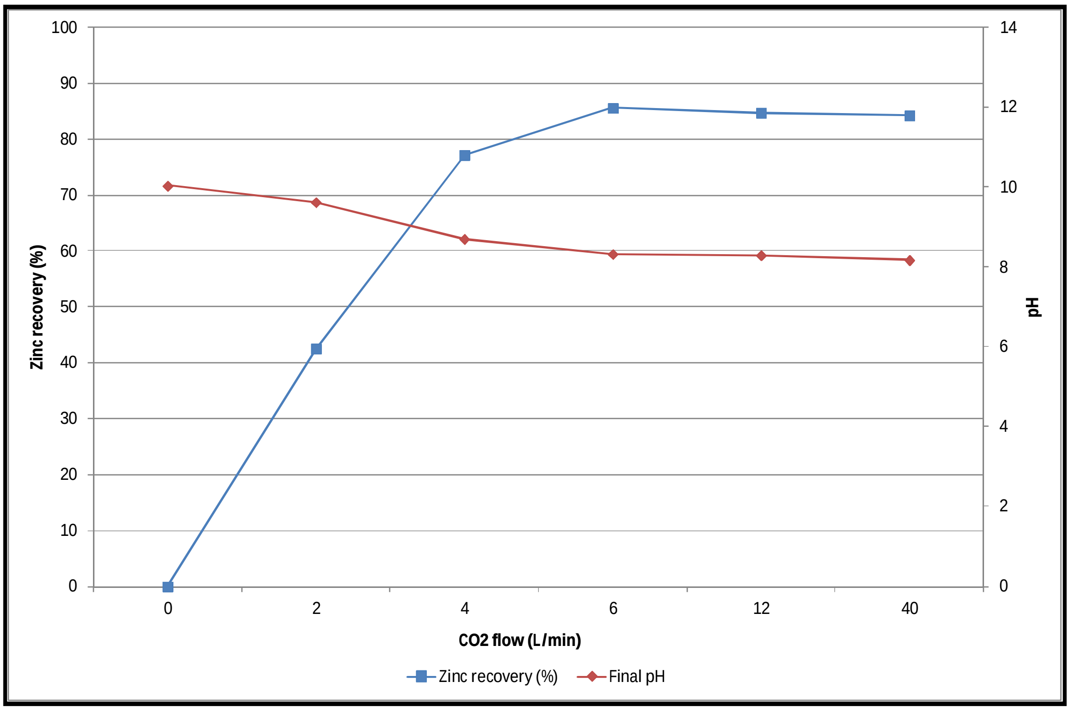

Figure 3.19: pH and zinc recovery as function of CO_2 flow

The evolution of the zinc recovery and pH by increasing the CO_2 flow rate can be seen in Figure 3.19. The pH decreases uniformly until 8,05 when the CO_2 injection is increased. So, the zinc recovery is increased until the 90 % due to this CO_2 flow rate.

b.2. Kinetic study of the precipitation stage

The influence of the time is an important parameter for the cost of the precipitation step and for the possible ammonia recovery. The experimental work to study this influence was carried out under the following conditions that appear in Table 3.25:

Table 3.25: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	20
Volume of leaching liquor	L	1,8
Stirring speed	r.p.m	700
CO_2 (g) flow	L/min (CO_2, T=25ºC;P=1atm)	6,0

The obtained results of these experimental tests are the following ones:

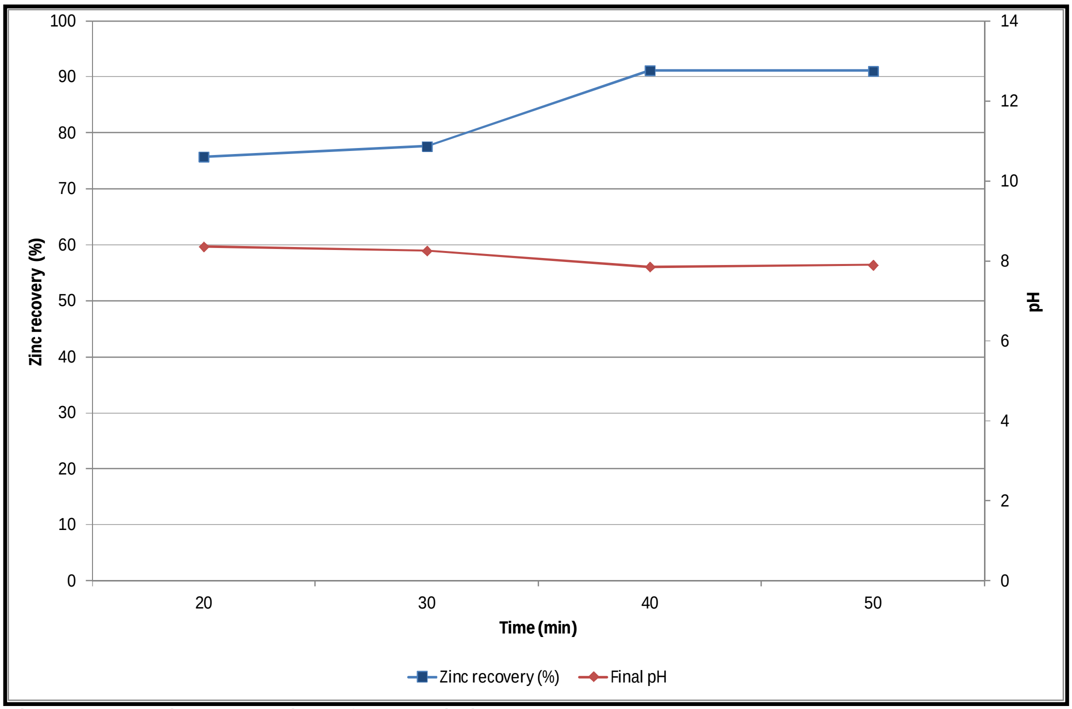

Figure 3.19: Time evolution of pH and zinc recovery

The time evolution of the zinc recovery can be seen in Figure 3.19. The zinc precipitation yield increases until the 40 minutes, but when this point is exceeded the recovery is kept constant.

c. Characterization of optimized precipitation stage

The optimal mass balance of the precipitation stage can also be noted in the Figure 3.20:

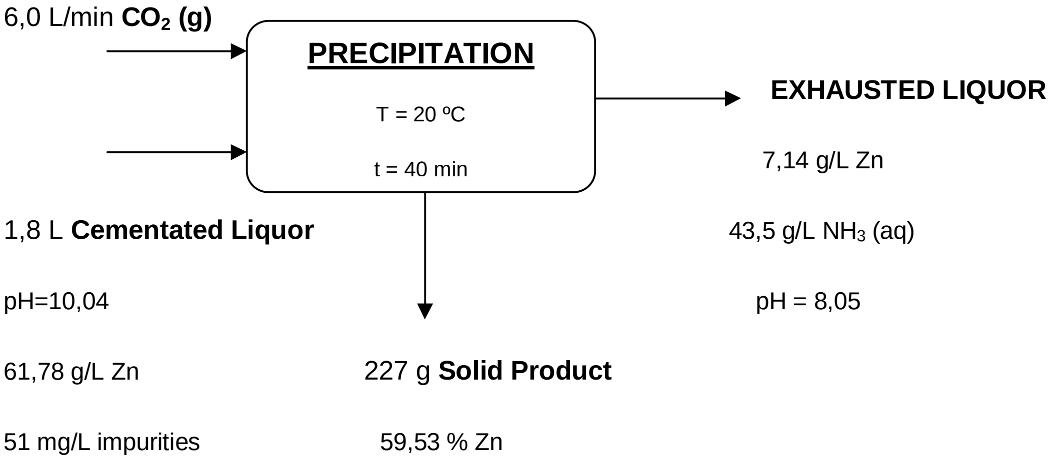

Figure 3.20: Process diagram of precipitation stage

The characterization of product and waste of the optimal precipitation step are noted in the Table 3.26 and Table 3.27:

EXHAUSTED LIQUOR

Table 3.26: Metallic impurities

Element	Concentration (mg / L)	Recovery (%)
Cu	0,1	91,81
Zn	7.138	91,22
Ni	0,5	65,38

Cr	0,1	85
Mn	0	100
Fe	2,3	0
Cd	1,4	100
Sn	0	100
Pb	4,9	0

Table 3.27: Other composition parameter

Parameter	**Quantity**
pH	8,05
Total ammonia concentration	2,83 M*
Total CO_2 (comb.) concentration	1,63 M**

*Analyzed with ammonia ion selective electrode (Thermo Scientific ORION High Performance Ammonia ISE)

** Analyzed with combined CO_2 ion selective electrode (Thermo Scientific ORION High Performance CO_2 ISE)

SOLID PRODUCT

After experimental work, the characterization of precipitated solid was carried out using a XRD analysis. The objective of this analysis is to recognise the compounds which are present in the solid product obtained in this stage. This information could be useful to study of the dissolved zinc recovery through precipitation with CO_2 (g) injection.

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
01-080-0074	75	Zinc Oxide	0,237	0,911	Zn O
01-072-1100	58	Hydrozincite	0,229	0,651	Zn5 (O H)6 (C O3)2

Figure 3.21: Results of XRD analysis

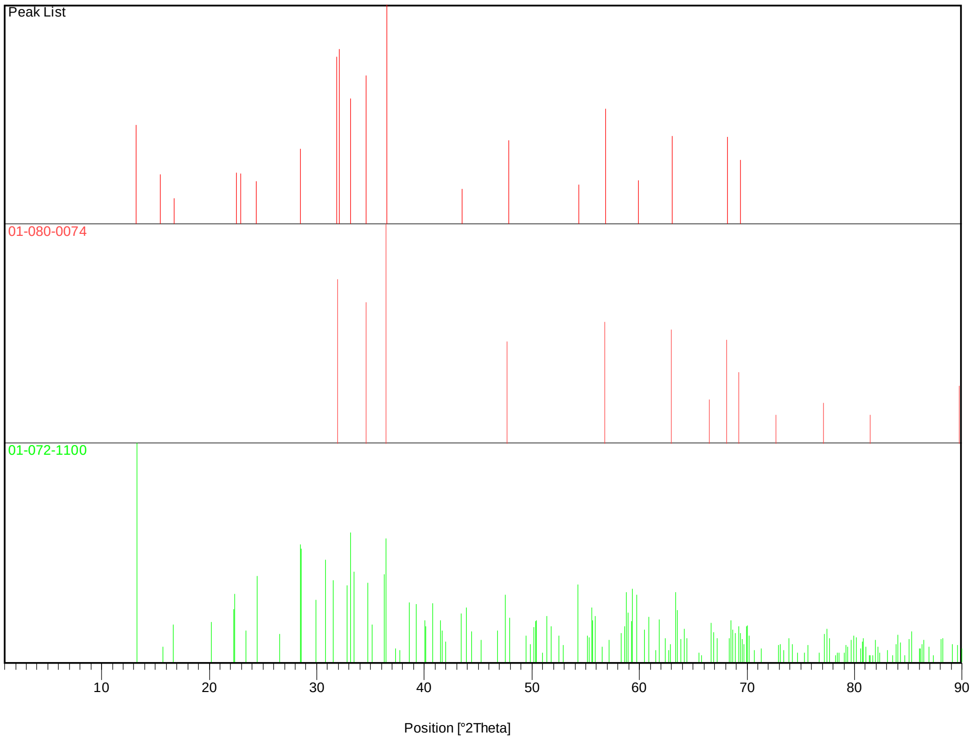

Figure 3.22: Difraction diagrams of indetified phases

3.3.4.2. Calcination stage of precipitated zinc compounds

After the recovery of dissolved zinc through precipitation in the previous step as hydrated zinc oxide and hydrozincite, the precipitated solid needs a thermal treatment that involves the removal of water, carbon dioxide, or other gases (because they are chemically bounded), in order to obtain the target product. Therefore, a calcination stage must be designed as a final step of this high purity zinc oxide fabrication process. So in this chapter a detailed study about the calcination of precipitated zinc compounds was carried out.

a. Technical considerations of calcination stage

In the calcination it is worth noticing that there is no sharp distinction between free and chemically bounded water. As the free water is removed from a substance, it gets into the range of absorbed water, then to relatively loosely bounds and finally the most strongly bound water. The decomposition pressure of the carbonates and hydrates depends on the temperature of the calcination. Calcination is more endothermic than drying. The rate of calcination seems to be governed primarily by the heat transfer limitations.

For an industrial application calcination may be carried out in a number of different furnaces. For material of mixed particle size or for lumps that disintegrate during the process, a rotary kiln may be used and for material of uniform, small particle size the calcination may be done in a fluidized bed. Depending on what is available, the fuel may be gas, oil or coke (Rosenqvist, T., 2004).

The main reactions which take place in this calcination step of the zinc precipitated compounds are:

$$\mathbf{Zn(OH)_2.n\ H_2O\ (s) \Leftrightarrow ZnO\ (s) + (n+1)\ H_2O\ (g)}$$

$$\mathbf{ZnCO_3.n\ H_2O\ (s) \Leftrightarrow ZnO\ (s) + CO_2\ (g) + n\ H_2O\ (g)}$$

b. Optimization of calcination stage

In this chapter the operation parameters of the calcination step were studied. The highest removal of water, CO_2 and other volatile impurities from the precipitated zinc compounds were the main goals of this experimental work. Several parameters were studied:

b.1. Optimization of the calcination temperature

The purity and quality of the zinc oxide and the energy expenditure per mass unit of product will be determined by the calcination temperature. So, this optimization was carried out using two kinds of procedures:

- **Micro TGA analysis:** A termogravimetric analysis was used to study the reactions during the calcination process observing the variation of the sample weight with the temperature through an instrumental measurement.

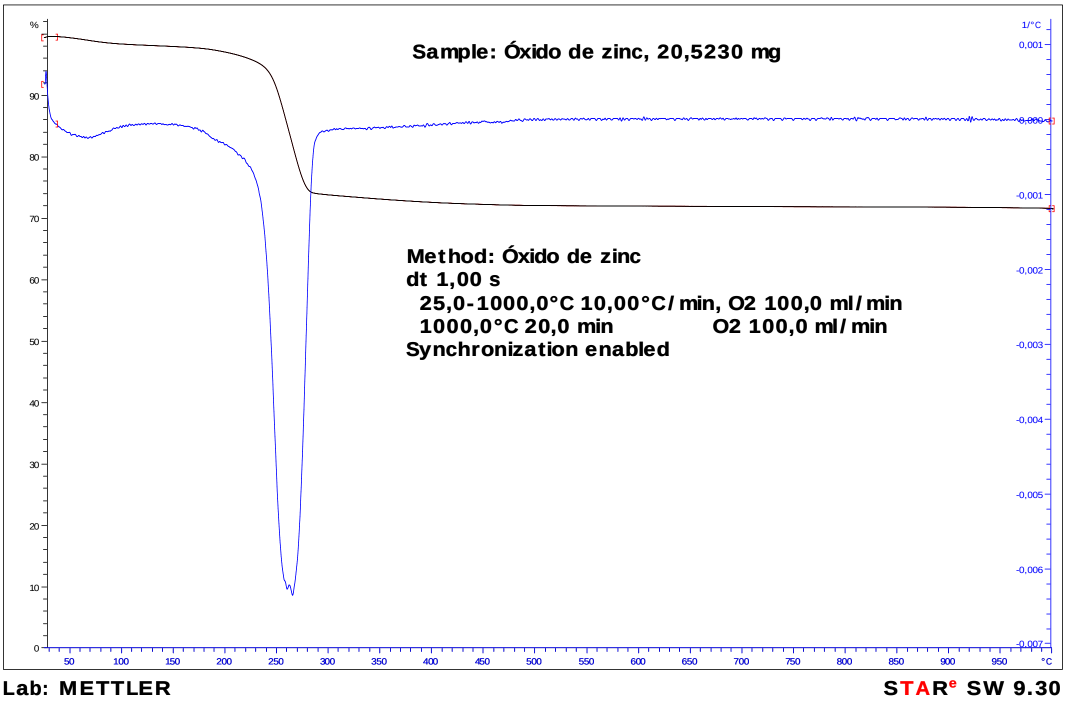

Figure 3.23: Weight variation as function of temperature

- **Batch test:** This experiment has taken place in a muffle furnace to simulate a industrial calcination and to estimate the optimal temperature at the following conditions that appear in Table 3.28:

Table 3.28: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	Studied parameter
Time	min	40
Weight of the sample	g	200

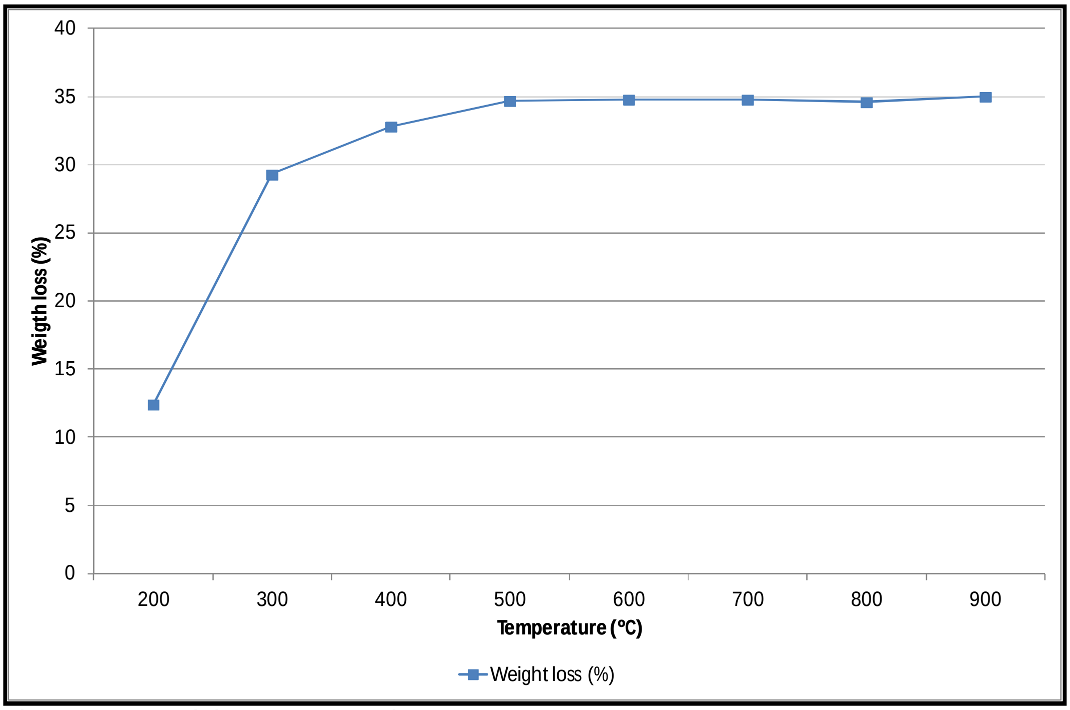

Figure 3.24: Weight loss as function of temperature

The evolution of the weight loss by increasing temperature can be seen in Figure 3.24. The calcination reactions evolve uniformly until 600 ºC when the 35 % of the weight loss is achieved.

b.2. Kinetic study of calcination step

The influence of the time is an important parameter for the cost of the calcination step and in the quality of the final product. The experimental work to study this influence was carried out under the following conditions that appear in Table 3.29, Table 3.30 and Table 3.31:

Table 3.29: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	500
Time	min	Studied parameter
Weight of the sample	g	200

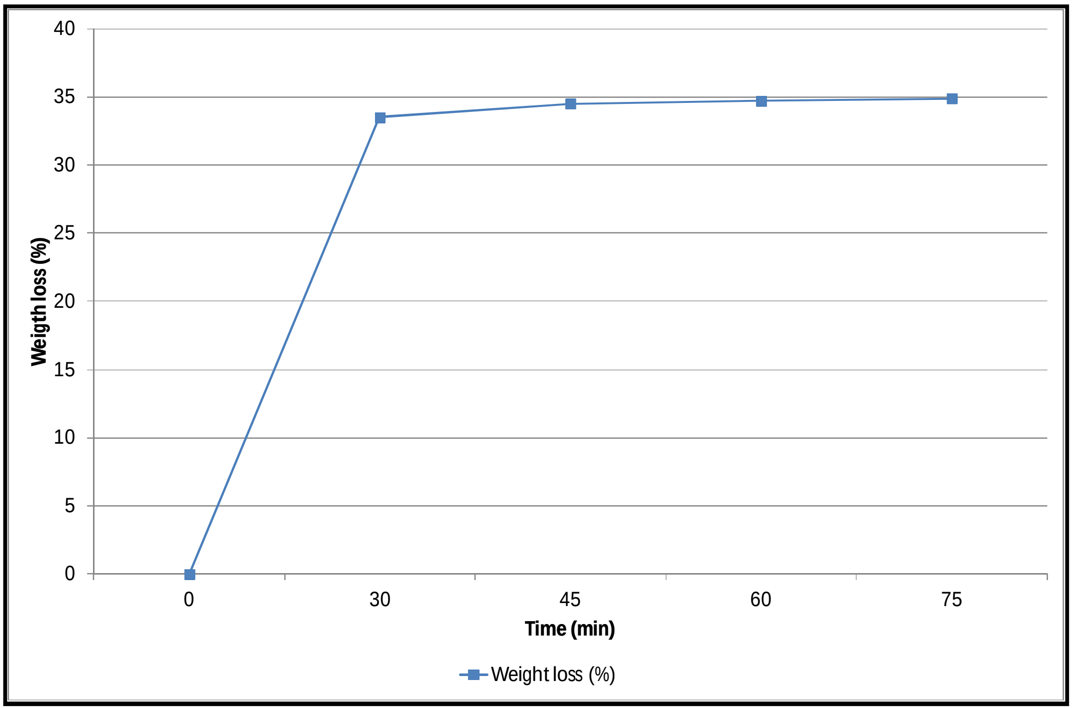

Figure 3.25: Weight loss as function of residence time at 500ºC

Table 3.30: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	600
Time	min	Studied parameter
Weight of the sample	g	200

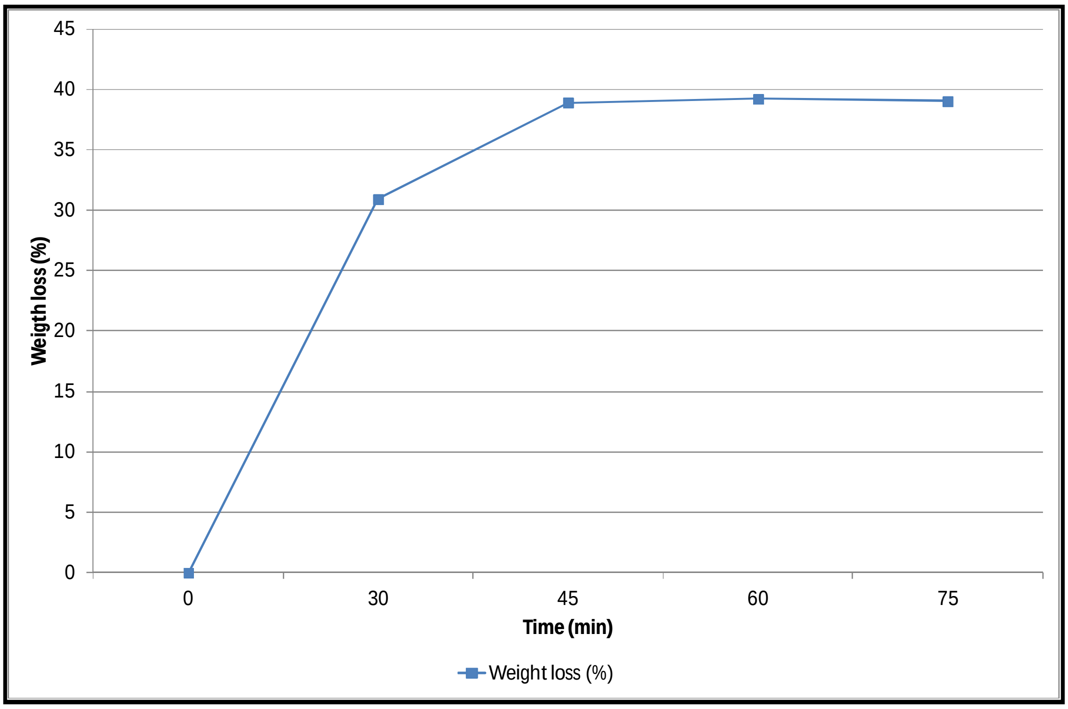

Figure 3.26: Weight loss as function of residence time at 600ºC

Table 3.31: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	800
Time	min	Studied parameter
Weight of the sample	g	200

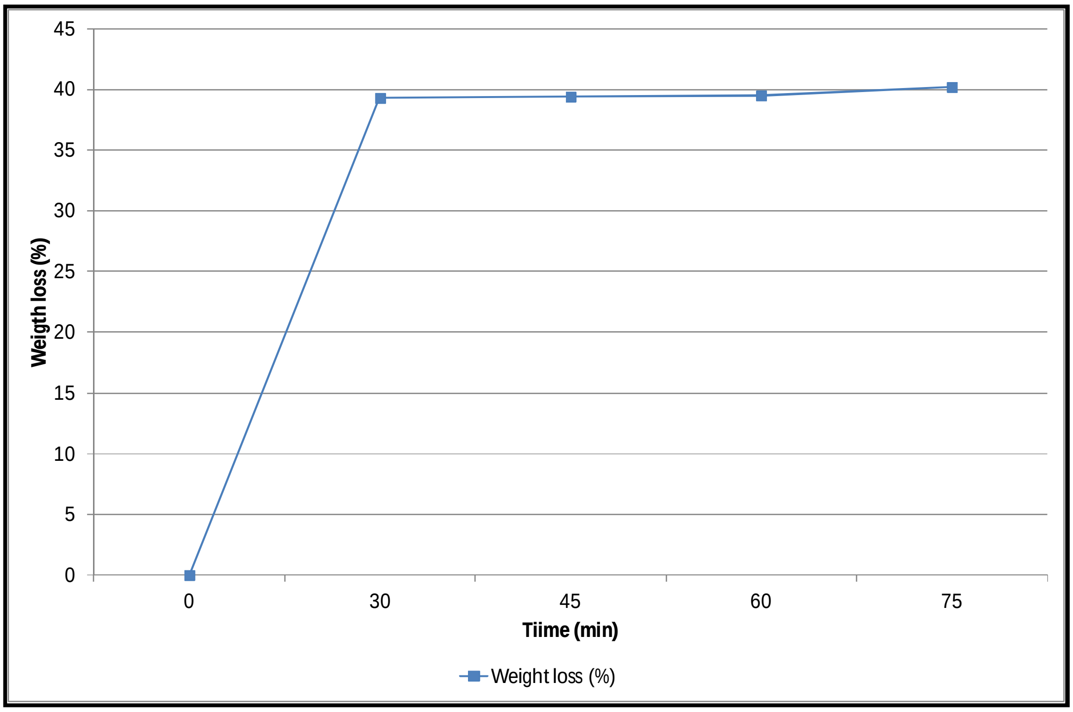

Figure 3.27: Weight loss as function of residence time at 800ºC

The time evolution of the precipitation stage at different temperatures has been shown. Each weight loss increases until a certain weight loss (depending of the used temperature), but when this point is exceeded the recovery is kept constant.

c. Characterization of optimized calcination stage

The optimal mass balance of the calcination stage can also be noted in the Figure 3.28:

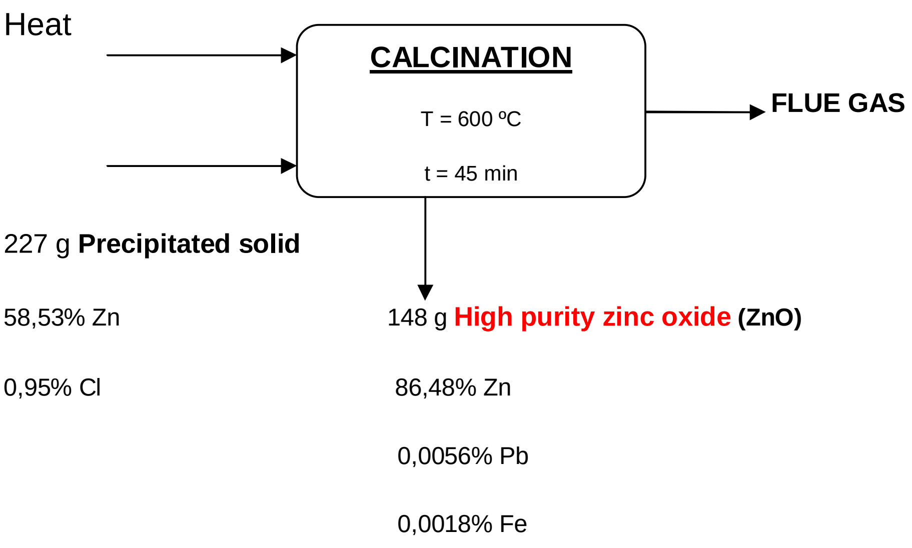

Figure 3.28: Process diagram of calcination stage

The characterization of final product obtained after the optimal calcination step are noted below:

HIGH PURITY ZINC OXIDE (ZnO)

To evaluate the achieved quality of the final product with the designed hydrometallurgical processes two different analytical methods were used:

- **Metallic composition by ICP – OES Analysis:**

Instrument: *Optima 8300 ICP-OES Spectometer Perkin Elmer*

Table 3.32: Metallic composition

Element	**Composition (%)**
Cu	0,0026
Zn	80,28

Ni	0,0011
Cr	0
Mn	0
Fe	0,0018
Cd	0
Sn	0
Pb	0,0056

- **Chemical analysis by XRF:**

Instrument: *WDXRF PANanalytical AXIOS (Rh tube and 3 detectors)*

Majority elements: (Expressed as oxide weight percentage)

Table 3.33: XRF results of majority elements composition

Sample	**SiO_2**	**Al_2O_3**	**Fe_2O_3t**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**
ZnOXID	0	0,09	0,06	0,01	0	0	ND	0,03	0,02	0,01

Trace elements: (Expressed as ppm)

Table 3.34: XRF results of trace elements composition

Sample	**Pb**	**Cu**	**Ni**	**F**	**S**	**Cl**
ZnOXID	0	302	150	285	386	0

3.3.5. AMMONIA RECOVERY STAGE

When the designed hydrometallurgical processes in order to obtain high quality zinc oxide were studied and optimized, the research work was focused on the economic and environmental impact of a possible future production plant. The goal of this chapter is to study the recovery of the higher possible quantity of the used raw materials during the production of target product, increasing the economical and environmental interest and viability of this technology.

The study of this recovery was carried out in two different steps:

- **Ammonia balance:** The identification of ammonia losses during the production process and the recoverable ammonia streams that can be reused in the process.

- **Ammonia recovery process:** The design of a process to recuperate ammonia from the exhausted liquor and to supply it to the fresh liquor feed in order to minimize the ammonia make up in the processing plant.

3.3.5.1. AMMONIA BALANCE

During the optimization of the hydrometallurgical stages all the ammonia losses were taken account and measured. In the Figure 3.28 they are summarized in order to identify the recoverable ammonia sources for spent liquor regeneration:

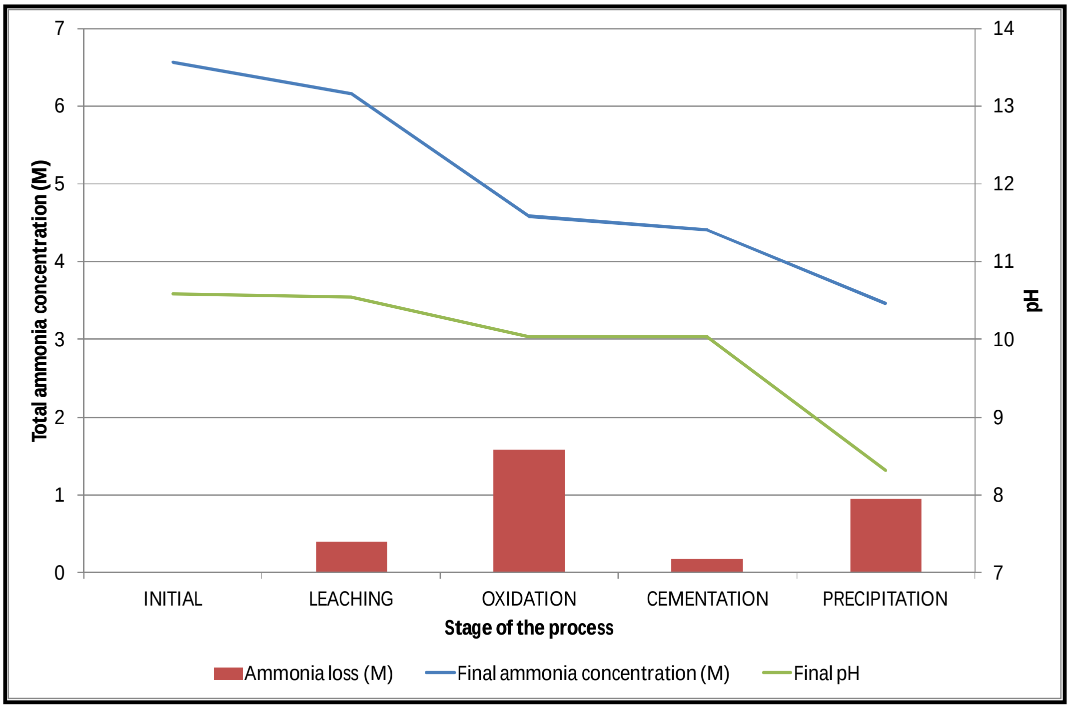

Figure 3.28: Mass balance of ammonia and pH in the all hydrometallurgical stages

In this graph two important ammonia losses (oxidation 1,58 M and precipitation 0,98 M) can be observed, both of them in the hydrometallurgical steps which use a gas injection. The ammonia is removed by stripping and there gas streams must be used in liquor regeneration stage. In the other hand, in the process two minor ammonia losses exist generated in the agitation, filtering and transfer operation in leaching (0,4 M) and cementation (0,18 M) stages. After this study the ammonia losses were classified in the Figure 3.29:

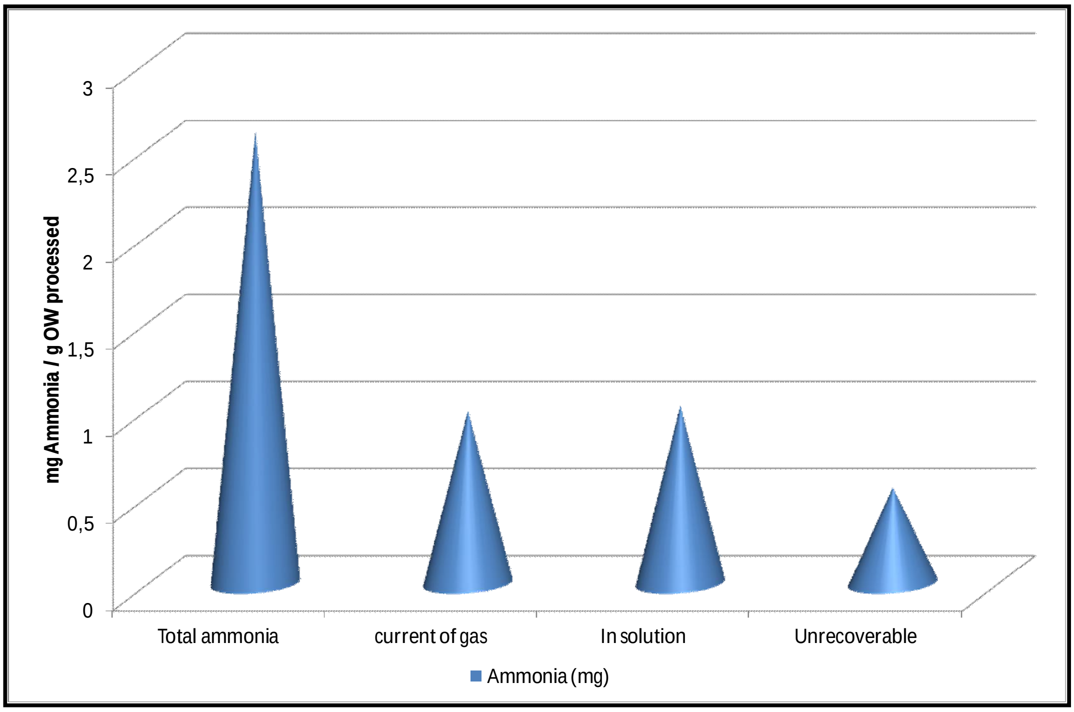

Figure 3.29: Total ammonia balance in the designed processes

3.3.5.2. AMMONIA RECOVERY PROCESS

The ammonia balance of the hydrometallurgical processes shows that the 80% of required ammonia could be recovered. But 44% of this ammonia has to be recovered from liquid phase in the exhausted liquor. Therefore, a process in order to recover this amount of ammonia has to be designed.

In this chapter, an ammonia recovery process was studied, obtaining an ammonia gas stream appropriated to feed the exhausted liquor regeneration stage.

a. Technical considerations of ammonia recovery process

The goals of this step are to recover the solved ammonia in the exhausted liquor and a second objective which is to obtain a zinc oxide with less quality by the generated precipitation when the ammonia is removed.

The dissolved ammonia in the exhausted liquor is as ammonium ions, NH_4^+, or as zinc ammonia complex ions. At pH = 11,5 – 12 almost only dissolved ammonia is present in an aqueous solution. Under the proper conditions this ammonia would be recovered in a useful gas stream. Therefore, the increase of exhausted liquor pH was carried out with a sodium hydroxide aqueous solution in order to maximize the quantity of dissolved ammonia. The stripping of this dissolved ammonia was also conducted through air injection at optimal conditions. Thus, these modifications in the exhausted liquor will also generate a zinc recovery by precipitation, increasing the economical yield and the efficiency of the recycling process.

- Main reactions in the liquor:

$\mathbf{NaOH \Leftrightarrow Na^{2+} + OH^-}$

$\mathbf{NH_4^+ + OH^- \Leftrightarrow NH_3 + H_2O}$

$H_2O \Leftrightarrow H^+ + OH^-$

$HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$

- Secondary reactions in the liquor:

$Zn^{2+} + OH^- \Leftrightarrow ZnOH^+$

$Zn^{2+} + 3OH^- \Leftrightarrow Zn(OH)_3^-$

$Zn^{2+} + 4OH^- \Leftrightarrow Zn(OH)_4^{-2}$

$Zn\ NH_3^{2+} \Leftrightarrow Zn^{2+} + NH_3$

$Zn\ (NH_3)_2^{2+} \Leftrightarrow Zn^{2+} + 2NH_3$

$Zn\ (NH_3)_3^{2+} \Leftrightarrow Zn^{2+} + 3NH_3$

$Zn\ (NH_3)_4^{2+} \Leftrightarrow Zn^{2+} + 4NH_3$

- Induced precipitation reactions:

$ZnCO_3 \Leftrightarrow Zn^{2+} + CO_3^{2+}$

$Zn(OH)_2 \Leftrightarrow Zn^{2+} + 2\ OH^-$

When the pH is increased above 11,5, two major factors affect the transfer rate of ammonia from water to the gas phase (Heggenan, M. H. Et al., 2001):

- The air-water surface tension
- The ammonia concentration gradient between gas stream and liquor

The designed processes must combine the gasification of solved ammonia and the stripping of the driven gaseous ammonia.

b. Optimization of ammonia recovery process

The recovery of ammonia from the exhausted liquor is going to be described and optimized in this chapter. Therefore, the necessity of alkaline solution in order to increase the pH of the exhausted liquor was previously concluded. Therefore, the generated solid residues during the main hydrometallurgical processes were treated with this alkaline solution, before to be employed in the ammonia recovery step.

So, the ammonia recovery stage was divided in two processes:

- **Solid waste treatment**
- **Ammonia stripping step**

b.1. Solid waste treatment

The chosen alkaline liquor, in order to treat the solid residue, was a caustic soda aqueous solution. The optimal concentration of the leaching liquor was searched in following experiments at the following conditions that appear in Table 3.35:

Table 3.35: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	25
Water volume	L	2
NaOH anhydrous weight	g	Changes every experiment
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The obtained results of these experimental tests are the following ones:

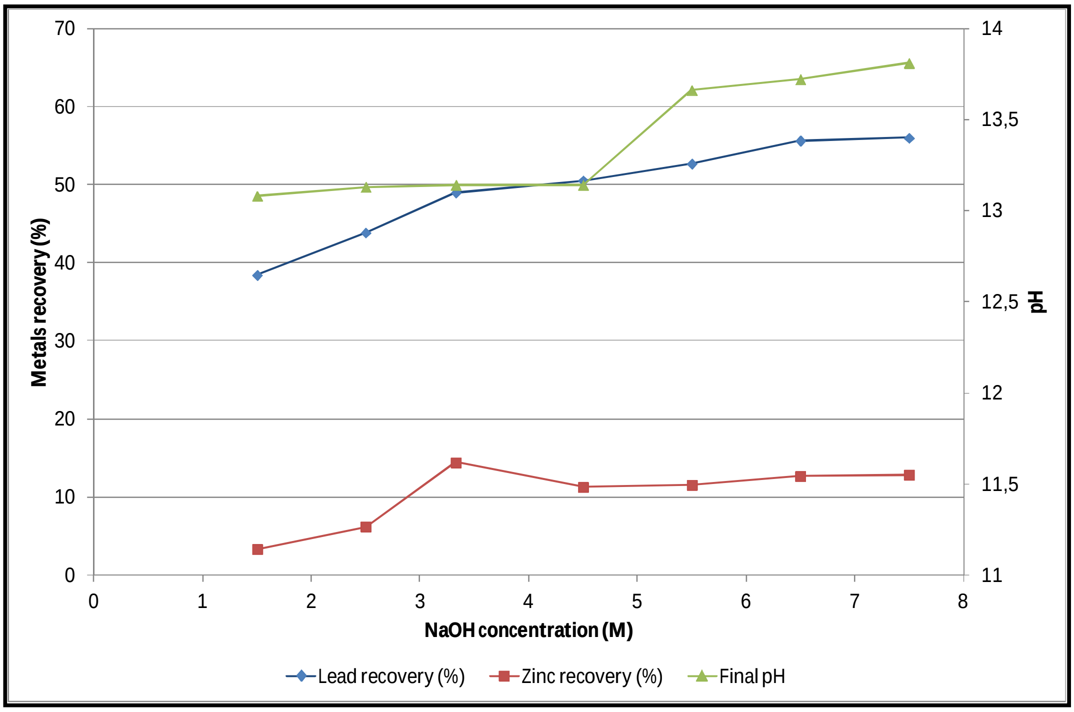

Figure 3.30: pH, lead and zinc recovery as function of NaOH concentration in the liquor

The evolution of the metals recovery and pH by increasing leaching liquor concentration can be seen in Figure 3.30. The lead recovery increases until the 55% when the NaOH (aq) concentration is 6,5 M and on the other hand, the zinc recovery increases until approximately 12% and when these points are exceeded the metals recovery are kept constant.

After the study of these results can be concluded that the optimal NaOH concentration to extract the maximum possible metals quantity from solid residues is 6,5 M. Then, the caustic soda solution / exhausted liquor mix ratio by volume was optimized, in order to maintain the pH over 11,5, in the following proportion:

1 Volume of exhausted liquor + ½ Volume of solid waste leaching liquor (6,5 M NaOH)

So, a combined solution with this mixing ratio must be fed to the ammonia stripping reactor, which is going to be optimized in the next chapter.

b.2. Ammonia stripping step

When the pH of the exhausted liquor was increased above 11,5, other operation condition of the ammonia stripping reactor have to be defined in order to optimize the ammonia recovery stage. The experimental work to study the influence of these conditions was carried out under following conditions that appear in Table 3.36:

Table 3.36: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	Studied parameter
Volume of liquor	L	1,8
Air flow	L/min	Studied parameter
Diffusion volume	cm^3	270
Diffusion area	cm^2	0,15
Stirring speed	r.p.m	700
Gas injector size:		

Φ_{ext}	mm	4
Φ_{int}	mm	6

b.2.1. Optimization of temperature in the ammonia recovery stage

The influence of the temperature is important for the thermodynamic of the operation and for the kinetic of this stage. The experimental work to study this influence was carried out under the following conditions that appear in Table 3.37:

Table 3.37: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	Studied parameter
Time	min	120
Stirring speed	r.p.m	700
Air (g) flow	L/min (Air, T=25ºC;P=1atm)	60

The obtained results of these experimental tests are the following ones:

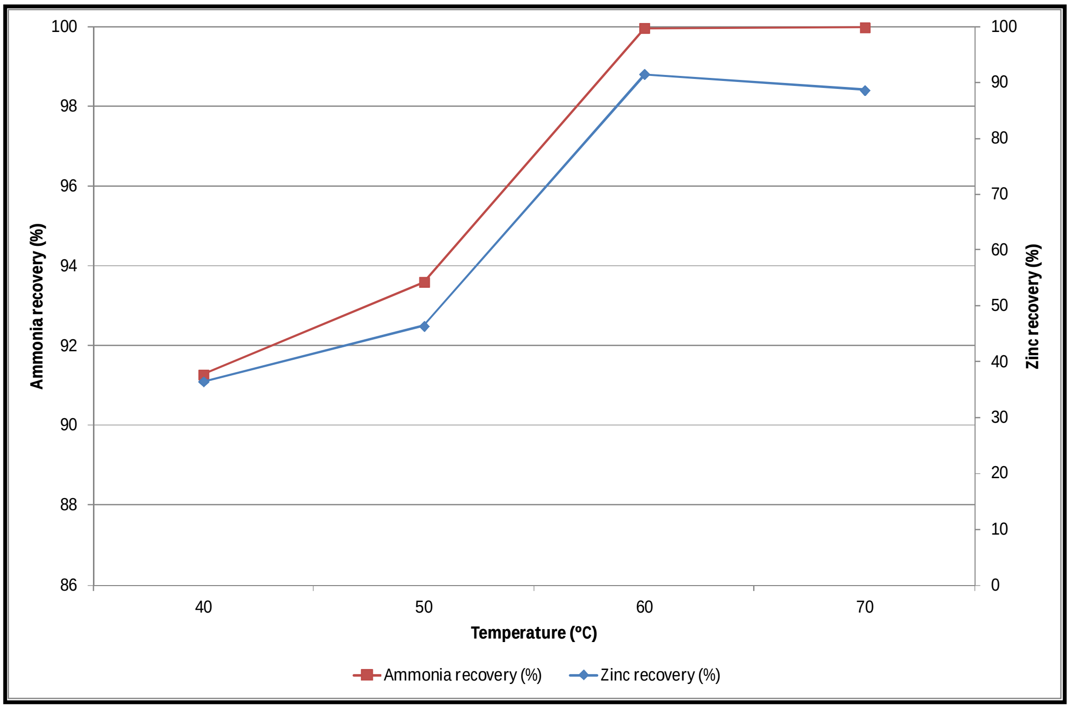

Figure 3.31: Ammonia and zinc recovery as function of temperature

The evolution of the ammonia and zinc recovery by increasing the temperature can be seen in Figure 3.31. Both of them increase until the 60 °C were achieved.

b.2.2. Optimization of air flow in the ammonia recovery stage

The influence of the gas flow rate is an other important parameter in the thermodynamic of the operation and in the kinetic of this stage. The experimental work to study this influence was carried out under the following conditions that appear in Table 3.38:

Table 3.38: Experimental conditions

Parameter	Units	Quantity
Temperature	°C	60
Time	min	120
Stirring speed	r.p.m	700

Air (g) flow	L/min (Air, T=25ºC;P=1atm)	Studied parameter

The obtained results of these experimental tests are the following ones:

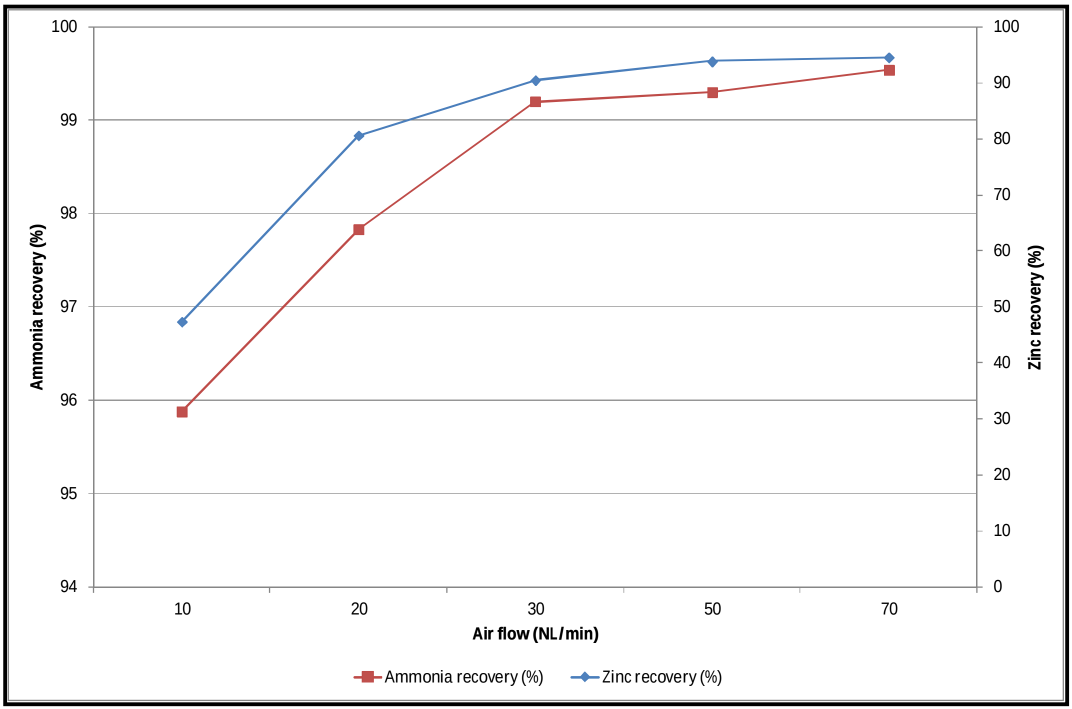

Figure 3.31: Ammonia and zinc recovery as function of used air flow rate

The evolution of the zinc and ammonia recovery at 60 ºC by increasing the air flow rate can be seen Figure 3.31. The recoveries increase uniformly until 30 NL/min and when this point is exceeded the ammonia and zinc recovery is kept constant.

b.2.3. Kinetic study of ammonia recovery stage

The influence of the stripping time is an important parameter in the cost of the ammonia recovery stage. The experimental work to study this influence was carried out under following conditions that appear in Table 3.39:

Table 3.39: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	60
Time	min	Studied parameter
Stirring speed	r.p.m	700
Air (g) flow	L/min (Air, T=25ºC;P=1atm)	30

The obtained results of these experimental tests are the following ones:

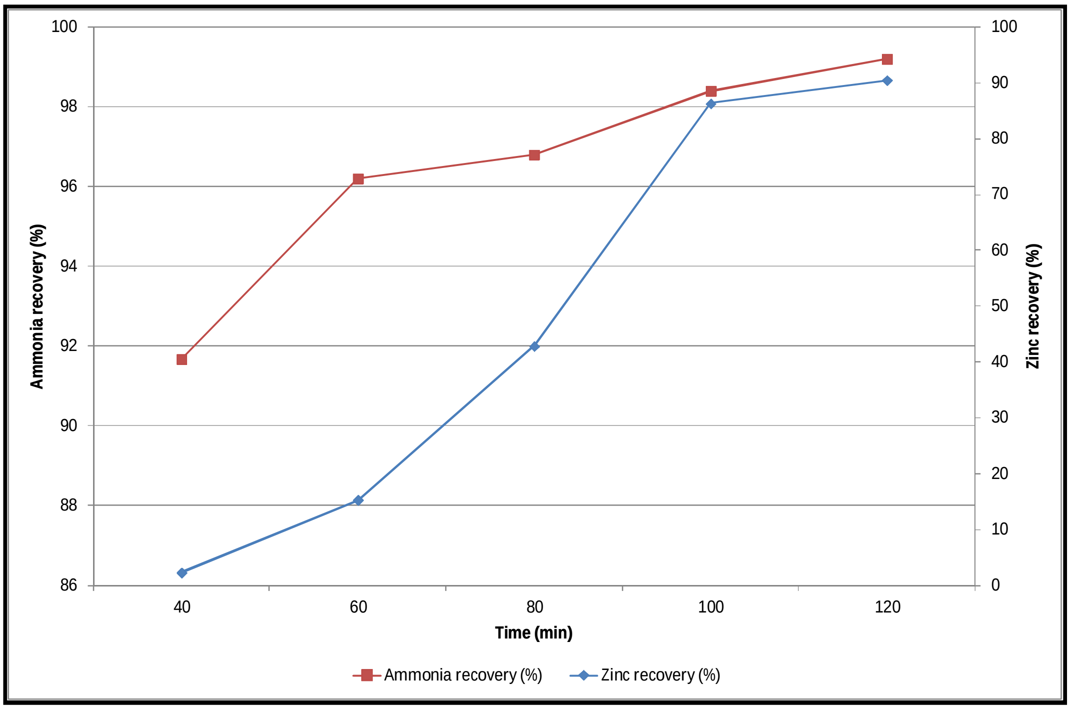

Figure 3.32: Time evolution of the ammonia and the zinc recovery

The time evolution of the ammonia recovery stage at optimal temperature can be seen in Figure 3.32. Both of the recoveries increases uniformly until the 100 minutes, but when this point is exceeded the recovery the ammonia and zinc recovery is not so significant.

c. The effect of a recovered ammonia absorption step in the ammonia recovery stage

After the study of the ammonia recovery stage, where the technical viability was shown, the absorption of the recovered ammonia is researched. This experimental work does not study the optimization of the absorption stage. It is just the research of the induced effects on the operation conditions.

This research was designed using an absorption reactor, in order to treat the obtained ammonia gas stream in the ammonia recovery stage. The experimental work to study the influence of these conditions was carried out in two connected reactors under the following conditions that appear in Table 3.40 and Table 3.41:

AMMONIA STRIPPING REACTOR

Table 3.40: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	60
Volume of liquor	L	1,8
Air flow	L/min	Studied parameter
Diffusion volume	cm^3	270
Diffusion area	cm^2	0,15
Stirring speed	r.p.m	700
Gas injector size:		
Φ_{ext}	mm	4
Φ_{int}	mm	6
Time	min	100

RECOVERED AMMONIA ABSORPTION

Table 3.41: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	15
Volume of water	L	1,8
Diffusion volume	cm^3	270
Diffusion area	cm^2	0,15
Stirring speed	r.p.m	700
Gas injector size:		
Φ_{ext}	mm	4
Φ_{int}	mm	6
Time	min	100

The obtained results of these experimental tests are the following ones:

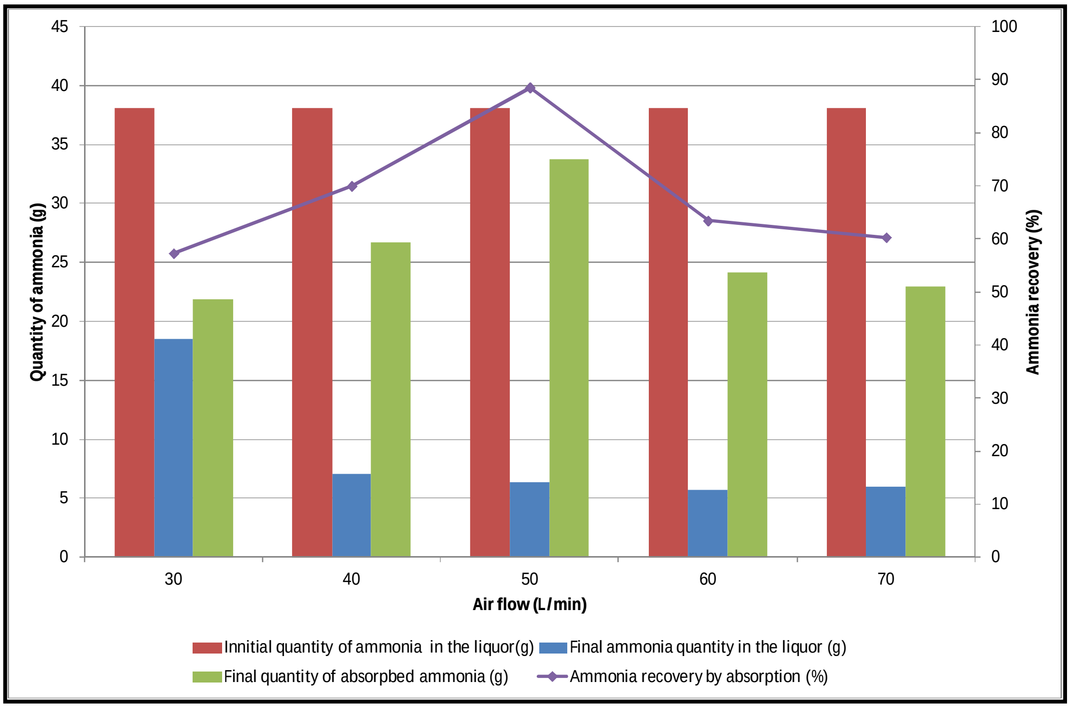

Figure 3.33: Mass balance of ammonia as function of used air flow rate

The evolution of the quantity of ammonia in the liquor and the ammonia recovery at 60 ºC by increasing the air flow rate can be seen in Figure 3.33. The recoveries increase uniformly until 50 NL/min and when this point is exceeded the ammonia and zinc recovery was a noticeable decreased.

3.3.5.3. Characterization of optimized ammonia recovery stage

The optimal mass balance of the calcination stage is also included in the Figure 3.34:

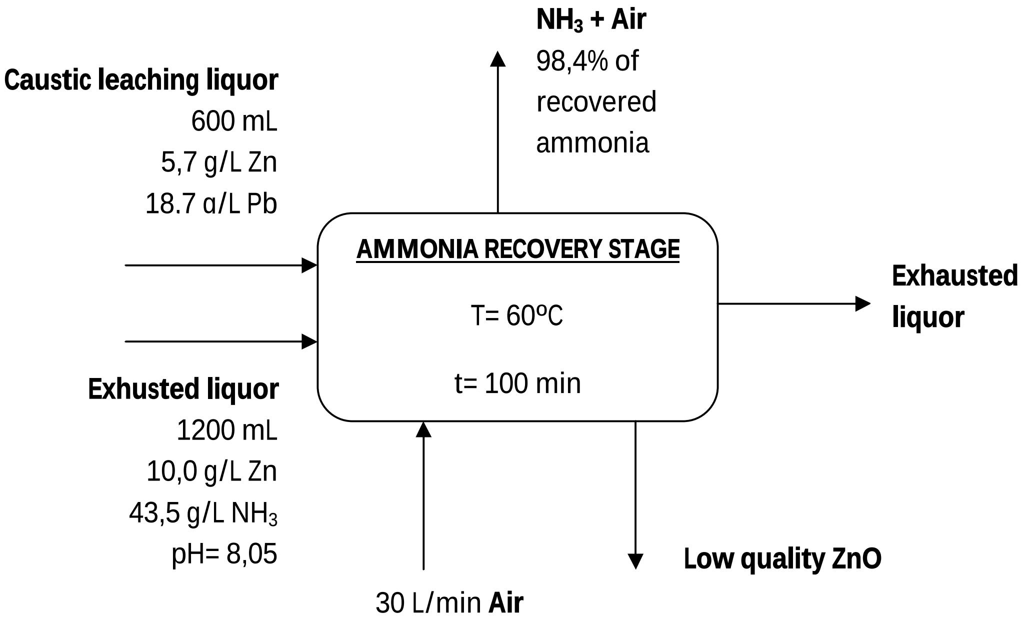

Figure 3.34: Process diagram of ammonia recovery stage.

The characterization of product and solid waste from the optimal ammonia recovery step are shown in the Table 3.42, Table 3.43 and Table 3.44:

EXHAUSTED LIQUOR

This liquor is the liquid waste after all the previous processes. The required treatment before its discharged must to be studied taking into account the environmental legislation.

Table 3.42: Compositions of main elements

Element	**Concentration (g/L)**
Pb	0,21
Zn	0,59
Cl	2

Table 3.43: Other composition parameters

Parameter	**Quantity**
pH	9,95
Total ammonia concentration	0,0179 M*
Total CO_2 (comb.) concentration	1,765 M**

*Analyzed with ammonia ion selective electrode (Thermo Scientific ORION High Performance Ammonia ISE)

** Analyzed with combined CO_2 ion selective electrode (Thermo Scientific ORION High Performance CO_2 ISE)

SOLID BY-PRODUCT

Table 3.44: Compositions of main elements

Element	**Composition (%)**
Pb	2,09
Zn	30,02
Fe	0,16
Na	5,01
F	0,0028
Cl	0,44
Carbonates	28,21

The usefulness and the economic value of this by-product will depend of the market, the possibilities could be:

- As feed of a zinc ore roasting
- As a low quality zinc oxide after calcination

3.3.6. EXHAUSTED LIQUOR REGENERATION STAGE

In this chapter the regeneration processes of the hydrometallurgical liquor is going to be studied. After the development and optimization of the high purity zinc oxide production process, using a mixture of aqueous ammonia and ammonium carbonate solutions as leaching liquor, the recovery of the ammonia losses and the regeneration of the leaching solution are the next steps in the research.

This research was carried out at the prestigious **Service TIPs** (Transferts, Interfaces et Procédés) in Brussels, headed by **Professeur Benoît Haut**. All experimental works, results and conclusions obtained in this chapter were supervised and led by the postdoctoral researcher **Dr. Ir. Christophe Wylock**.

The objective of this stage of the high purity zinc oxide production process is to minimize the environmental impact of future industrial plants and the reduction of production costs. The ammonia streams (recovered from the hydrometallurgical process) and the CO_2 emissions from Waelz furnace (the gasification of EAFD under reducing conditions) are the raw material sources of this step.

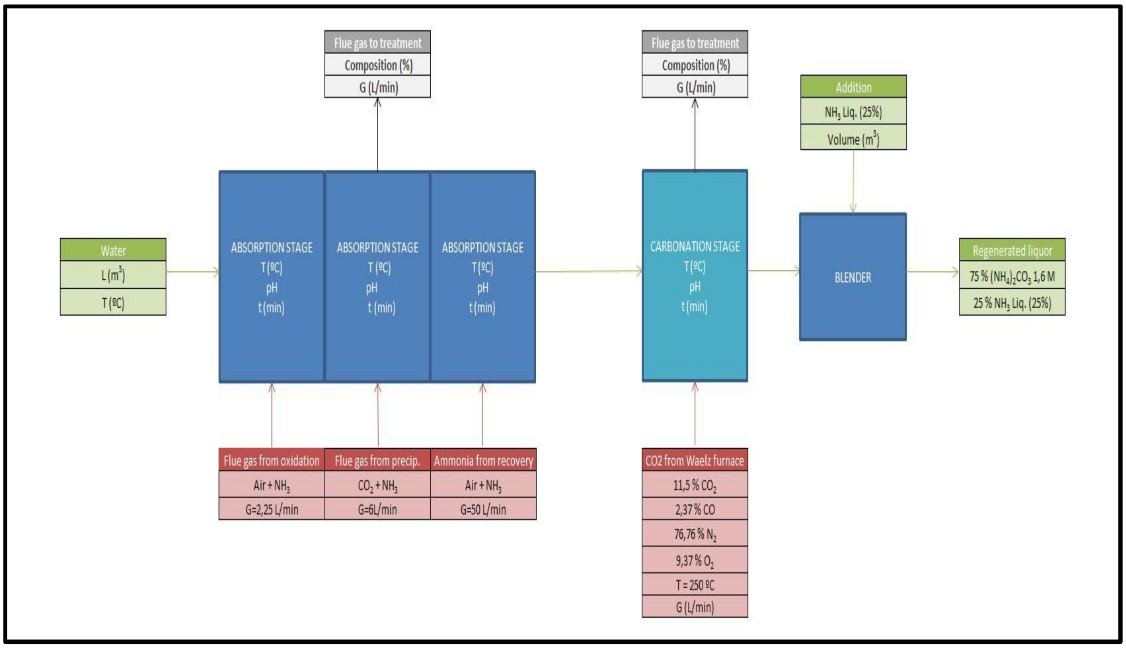

Figure 3.35: Studied process

The framework of this sub-project is to design an efficient industrial process in order to regenerate the used liquor, minimizing the make-up of liquid ammonia and ammonium carbonate solutions. Therefore, the study of the recovery system was carried out through the development of a model taking into account all the different operation parameters. The experimental part using a stirred tank was performed in a laboratory pilot plant. These tests must allow for validating the model that is going to use for an industrial design.

3.3.6.1. Technical considerations of exhausted liquor regeneration stage

Exhausted liquor regeneration through absorption is the target objective and it requires the design of a process which makes profitable and clean the future industrial hydrometallurgical process.

The gas absorption operation involves mass transfer from the gas phase to the liquid phase. That means the gas molecules must diffuse from the main body of the gas phase to the gas – liquid interface, then cross this interface into the liquid side, and finally diffuses from the main body of the liquid. Many theories have come up in explaining the mechanism of gas transfer and absorption of non – reacting gases in a liquid, therefore this gas – liquid system can be modelled using a simplified *TWO-FILM THEORY* as a basis for analysis as well as for the use of various correlations of mass transfer phenomena.

This theory assumes that at the interface between a gas and a turbulent liquid, through which the gas must pass by the relatively slow rate of molecular diffusion (Shashank, B. T. Et al., 2008).

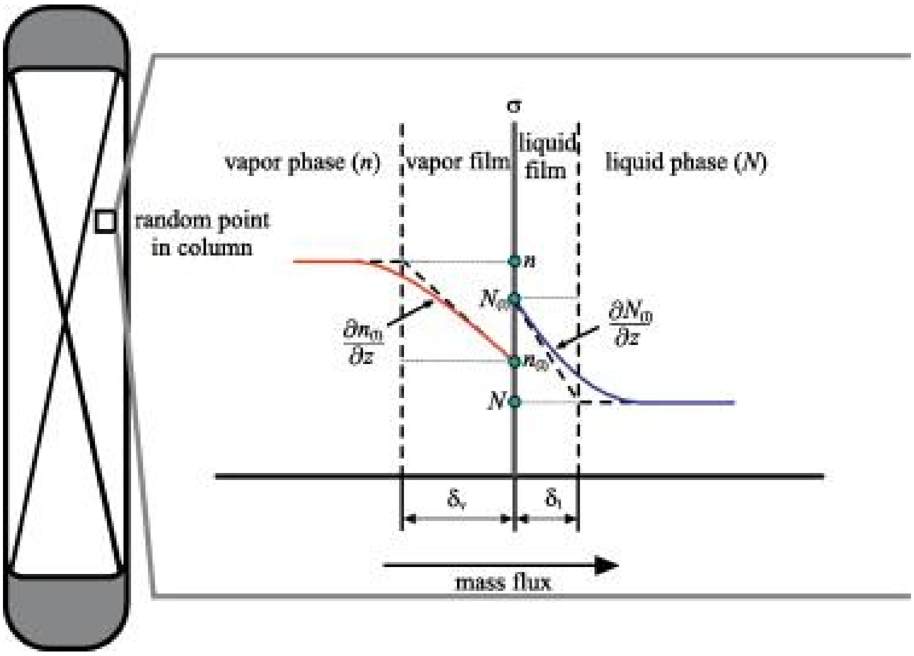

Figure 3.36: Graphic explanation of Two-film theory for a packet column (useful in any gas – liquid contactors)

Mass/concentration balance in an infinitesimal layer of fluid within the films leads to such partial differential equation:

$$\partial C/\partial t = D_i\,(\partial^2 C_i/\partial x^2) - r_i \ \text{(mol/dm}^3\text{.s)}$$

Mass transfer in the absorption process must take into account the physical absorption of the gas in the liquid phase (gas solubility in a liquid) and the chemical reaction rates and their limiting equilibrium in the liquid phase.

Diffusivity (valid for physical mass transfer only) is related to the Sherwood number, it can be calculated using empirical correlations *(Versteeg and Van Swaaij, 1988)*:

$$Sh = a\,Re^b\,S_c^{\,c}$$

With the dimensionless numbers given by:

$Sh = K.d/D$ $Re = \rho_L.v.d/\mu_L$

$Sc = \mu_L/\rho_L D$ $d = (3.\mu_L.Q_L/\rho_L.g.L)^{-3}$

$Pe = G.d/D = Re.Sc$

When: $\frac{d}{G}$ = Contact time; Sh = Sherwood number; Re = Reynolds number; Sc = Smith number; Pe = Pecklet; d = bubble diameter; D = diffusion coefficient; v = liquid velocity; Q_L = liquid flow; ρ_L = liquid density; μ_L = liquid viscosity; G = gas flow; g = gravity constant; K = mass transfer coefficient (using I.S units)

This information will be useful in order to carry out the mechanical design of the required contactors in the liquor regeneration stage, after the study of the absorption system.

The overall absorption flux generally written as:

- If there is no reaction (physical mass transfer)

$$\mathbf{N_i = kL.\Delta C_i}$$

When: kL = overall mass transfer coefficient specie i; ΔCi = Concentration gradient of specie i

- If chemical reactions exist, they tend to enhance the mass transfer rate. The fluxes are then expressed such as the product of the physical mass transfer rate multiplied by an enhancement factor E :

$$\mathbf{N_i = kL.E_i.\Delta Ci}$$

When: kL = overall mass transfer coefficient specie i; E_i = Enhancement factor; ΔCi = Concentration gradient of specie i

The enhancement factor is related to the Hatta number, which is defined as (Trambouze, P. Et al., 2008):

Ha = $\sqrt{(\boldsymbol{kr}.\boldsymbol{Da})}\,/\,\boldsymbol{kL}$ *(Whitman's two-film theory)*

and **E = Ha/tanh(Ha)** *for pseudo – first order reaction for a moderate reaction rate (0,3 ≥ Ha ≥ 5).*

When: D_a = Diffusion coefficient; k_L = liquid mass transfer coefficient; k_r = Kinetic constant

The measurement and estimation of the absorption flux and the mass transfer coefficients are the objectives of this research through theoretical and experimental studies.

3.3.6.2. The description of studied system

In this chapter the chemical reactions getting involved in liquor regeneration will be presented. The physicochemical absorption of CO_2 and ammonia in aqueous solution can be described by:

The equilibrium of CO_2 gas absorption in water as defined by Henry`s Law:

- $CO_2\,(g) + H_2O\,(l) \Leftrightarrow CO_2\,(aq)$ $\mathbf{h_{CO2} = [CO_2(aq)]/P_{CO2}}$ (dm^3.atm/mol)

The dissociation equilibriums of dissolved CO_2 in aqueous solutions are as follows:

- $CO_2 + OH^- \Leftrightarrow HCO_3^-$ $\mathbf{K_1 = [HCO_3^-]/[CO_2][OH^-]}$ (m^3/mol)

- $HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$ **$K_2=[CO_3^{2-}]/[HCO_3^-][OH^-]$** ($m^3/mol$)

The equilibrium of NH_3 gas absorption in water as defined by Henry`s Law:

- $NH_3\ (g) + H_2O\ (l) \Leftrightarrow NH_3\ (aq)$ **$h_{NH3}= [\ NH_3(aq)]/P_{NH3}$** ($mol/dm^3.atm$)

The dissociation equilibrium of dissolved NH_3 and $NH_3 - CO_2$ in aqueous solutions are as follows:

- $NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ **$K_3=[NH_4^+][OH^-]/[NH_3]$** ($mol/dm^3$)
- $NH_3 + HCO_3^- \Leftrightarrow NH_2COO^- + H_2O$ **$K_4=[NH_2COO^-]/[NH_3][HCO_3^-]$** ($mol/dm^3$)

The dissociation equilibrium of water is as follow:

- $H_2O \Leftrightarrow H^+ + OH^-$ **$K_W = [H^+][OH^-]$** (mol^2/dm^6)

These equations describe the CO_2 - H_2O - NH_3 absorption equilibrium system in accordance with equilibrium data (Satish Reddy, P. M. M. Et al., 2009; Park, J.M. Et al., 2011 and Thomsen, K. Et al., 2011).

After describing the equilibrium system, the study must be focused on the kinetic equations which govern the absorption process. Comparing equilibrium and kinetic constants of the reactions in the liquid phase, the following reactions were studied as the limiting ones:

- $CO_2\ (aq) + OH^- \leftrightarrow HCO_3^-$

$\mathbf{r_1} = k_1[CO_2][OH^-] - k_{-1}[HCO_3^-] = \mathbf{k_1([CO_2][OH^-] - [HCO_3^-]/ K_W)}$

- $NH_3 + CO_2 \rightleftharpoons NH_3^+COO^-$ k_2/k_{-2}

$NH_3^+COO^- + B \rightleftharpoons NH_2COO^- + BH^+$ k_B/k_{-B}

$\mathbf{NH_3 + CO_2 + B \rightharpoonup NH_2COO^- + BH^+}$ $\mathbf{k_B/k_{-B}}$

Where B could be NH_3 or H_2O. Therefore the kinetic equation using a termolecular mechanism *(Crooks and Donellan,1989 - Silva and Svendsen, 2004)* are:

- $2\ NH_3 + CO_2 \rightarrow NH_2COO^- + NH_4^+$

$\mathbf{r_{21}} = r_{NH3}^T = \mathbf{k_{NH3}^T[NH_3]^2[CO_2]}$

- $NH_3 + CO_2 + H_2O \rightarrow NH_2COO^- + H^+$

$\mathbf{r_{22}} = r_{H2O}^T = \mathbf{k_{H2O}^T[NH_3][CO_2][H_2O]}$

Finally, once the kinetic and equilibrium equations of the process were described, a deeper study would have taken into account the precipitation of four solid compounds in the system *(Thomsen et al, 2010)*:

- $NH_4^+ + HCO_3^- \leftrightarrow NH_4HCO_3$ (s)
- $NH_4^+ + NH_2COO^- \leftrightarrow NH_2COONH_4$ (s)
- $2\ NH_4^+ + CO_3^{2-} \leftrightarrow (NH_4)_2CO_3.H_2O$ (s)
- $4\ NH_4^+ + CO_3^{2-}\ 2\ HCO_3^- \leftrightarrow (NH_4)_2CO_3.2NH_4HCO_3$ (s)

3.3.6.3. Modelling of the absorption system in liquor regeneration stage

The transport - reaction equation system could be solved using the COMSOL Multiphysics software. The equations of the model were written as infinitesimal material balances in the diffusion layer.

A mass balance in a system may be written in the following general way:

Accumulation = generation - consumption + input - output

$\partial[A]/\partial t = D_A.\ \partial^2[A]/\partial x^2 + \sum_i \gamma A, i\ .ri + \sum_j \gamma A, j\ .\tau j$

<u>SYSTEM:</u>

$CO_2 + OH^- \rightleftharpoons HCO_3^-$	$\mathbf{r_1 = k_1([CO_2][OH^-] - [HCO_3^-]/ K_W)}$
$HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$	$\mathbf{K_2=[CO_3^{2-}]/[HCO_3^-][OH^-]}$
$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$	$\mathbf{K_3=[NH_4^+][OH^-]/[NH_3]}$
$NH_3 + HCO_3^- \Leftrightarrow NH_2COO^- + H_2O$	$\mathbf{K_4=[NH_2COO^-]/[NH_3][HCO_3^-]}$
$H_2O \Leftrightarrow H^+ + OH^-$	$\mathbf{K_W=[H^+][OH^-]}$
$2NH_3 + CO_2 \rightarrow NH_2COO^- + NH_4^+$	$\mathbf{r_{21} = k_{NH3}^T[NH_3]^2[CO_2]}$
$NH_3 + CO_2 + H_2O \rightarrow NH_2COO^- + H^+$	$\mathbf{r_{22} = k_{H2O}^T[NH_3][CO_2][H_2O]}$

The slave concentrations are the concentrations with time evolutions which are not explicitly computed from the dynamic equations but from the equilibrium equations. Therefore, their evolution is 'slaved' to the others. So, this is a 'numeric' consideration used to solve the equation system, in this case following ones were selected: HCO_3^-, CO_3^{2-}, NH_4^+ and H^+

After the equilibrium and reaction rates were described, the simulation of the diffusion must be added. The time evolution of the system is an interesting information in order to properly describe the absorption process under study. To simulate the transport – reaction system, the following equation system was set out:

DYNAMIC EQUATIONS:

$\partial[CO_2]/\partial t = - r_1 - r_{21} - r_{22} + k_{GL}([CO_2]_{eq}^{G} - [CO_2])$

$\partial[OH^-]/\partial t + \partial[CO_3^{-2}]/\partial t - \partial[NH_4^+]/\partial t - \partial[H^+]/\partial t = - r_1 - r_{21} - r_{22}$

$0 = [CO_3^{-2}] – K_2[OH^-][HCO_3^-]$

$0 = [NH_3] – K_3[OH^-][NH_4^+]$

$0 = [H^+][OH^-] - K_w$

$-\partial[HCO_3^-]/\partial t - \partial[CO_3^{-2}]/\partial t + \partial[NH_4^+]/\partial t + \partial[NH_3]/\partial t = - r_1 - r_{21} - r_{22} + k_{GL}([NH_3]_{eq}^{G} - [NH_3])$

$0 = [HCO_3^-][NH_3] - K_5[NH_2COO^-]$

$\partial[HCO_3^-]/\partial t + \partial[CO_3^{-2}]/\partial t + \partial[NH_2COO^-]/\partial t = r_1 + r_{21} + r_{22}$

These equations actually enable computing the time evolution of concentrations in a perfectly mixed system, because the selected contactor in order to check the model was a stirred tank.

MATRIX FORM:

These equations can be written in a matrix form in order to solve numerically the system with COMSOL Multiphysics software.

$$[\bar{A}].\ \partial/\partial t\ [\bar{u}] = [\overline{F}]$$

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & -1 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 & 1 \end{pmatrix} * \partial / \partial t \begin{pmatrix} [CO_2] \\ [OH-] \\ [HCO_3-] \\ [CO_3--] \\ [NH_4+] \\ [NH_3] \\ [H+] \\ [NH_2COO-] \end{pmatrix} =$$

$$\begin{pmatrix} -r_1 - r_{21} - r_{22} + r_{GLCO2} \\ -r_1 - r_{21} - r_{22} \\ [HCO_3-] - K_2[OH-][HCO_3] \\ [NH_3] - K_3[OH-][NH_4+] \\ [H+][OH-] - Kw \\ -r_1 - r_{21} - r_{22} + r_{GLNH3} \\ [HCO_3-][NH_3] - K_5[NH_2COO-] \\ r_1 + r_{12} + r_{22} \end{pmatrix}$$

3.3.6.4. *Modelling of NH$_3$ and CO$_2$ Gas – Liquid transfer using a film model*

The one - dimensional Film - Model of the absorption process under study that simulates the chemical diffusion – reaction for a differential element in a finite liquid is the following one:

$$\frac{\partial[CO_2]}{\partial t} + \frac{\partial[HCO_3^-]}{\partial t} + \frac{\partial\left[CO_3^{2-}\right]}{\partial t} + \frac{\partial[NH_2COO^-]}{\partial t} = \mathcal{F}_{CO_2}$$

$$\frac{\partial[NH_3]}{\partial t} + \frac{\partial\left[NH_4^+\right]}{\partial t} + \frac{\partial[NH_2COO^-]}{\partial t} = \mathcal{F}_{NH_3}$$

$$\frac{\partial[OH^-]}{\partial t} + \frac{\partial[HCO_3^-]}{\partial t} + 2\,\frac{\partial\left[CO_3^{2-}\right]}{\partial t} + \frac{\partial[NH_2COO^-]}{\partial t} - \frac{\partial\left[NH_4^+\right]}{\partial t} - \frac{\partial[H^+]}{\partial t} = 0$$

$$K_1[OH^-]\frac{\partial[CO_2]}{\partial t} + K_1[CO_2]\frac{\partial[OH^-]}{\partial t} - \frac{\partial[HCO_3^-]}{\partial t} = 0$$

$$K_2[\mathrm{OH}^-]\frac{\partial[\mathrm{HCO_3}^-]}{\partial t}+K_2[\mathrm{HCO_3}^-]\frac{\partial[\mathrm{OH}^-]}{\partial t}-\frac{\partial\left[\mathrm{CO_3}^{2-}\right]}{\partial t}=0$$

$$K_3[\mathrm{OH}^-]\frac{\partial[\mathrm{NH_3}]}{\partial t}+K_3[\mathrm{NH_3}]\frac{\partial[\mathrm{OH}^-]}{\partial t}-\frac{\partial\left[\mathrm{NH_4}^+\right]}{\partial t}=0$$

$$K_4\frac{\partial[\mathrm{NH_2COO}^-]}{\partial t}-[\mathrm{HCO_3}^-]\frac{\partial[\mathrm{NH_3}]}{\partial t}-[\mathrm{NH_3}]\frac{\partial[\mathrm{HCO_3}^-]}{\partial t}-=0$$

$$-[\mathrm{OH}^-]\frac{\partial[\mathrm{H}^+]}{\partial t}-[\mathrm{H}^+]\frac{\partial[\mathrm{OH}^-]}{\partial t}=0$$

And finally, the diffusive flux equations for the boundary conditions are:

$$\mathcal{F}_{\mathrm{CO_2}}=-\frac{\mathcal{A}_{G/L}}{\mathcal{V}_L}D_{\mathrm{CO_2}}\frac{\partial[\mathrm{CO_2}]}{\partial x}\bigg|_{x=0}$$

t = 0 $[CO_2] = [CO_2]_{bulk} = K_{CO2}.\ P_{CO2}$

t > 0 and x = 0 $[CO_2] = [CO_2]_{bulk} = K_{CO2}.\ P_{CO2}$

t > 0 and x = δ d[CO2]/dx = 0

$$\mathcal{F}_{\mathrm{NH_3}}=-\frac{\mathcal{A}_{G/L}}{\mathcal{V}_L}D_{\mathrm{NH_3}}\frac{\partial[\mathrm{NH_3}]}{\partial x}\bigg|_{x=0}$$

t = 0 $[NH_3] = [NH_3]_{bulk} = K_{NH3}.\ P_{NH3}$

t > 0 and x = 0 $[NH_3] = [NH_3]_{bulk}= K_{NH3}.\ P_{NH3}$

t > 0 and x = δ $d[NH_3]/dx = 0$

When: δ = film thickness

3.3.6.5. Experimental study of gas – liquid transfer of NH_3 and CO_2 in aqueous solution through Mach – Zehnder interferometry

Different experimental strategies to estimate the transport – reaction coefficients, which are necessary to design an industrial process of hydrometallurgical liquor regeneration stage, were used. The interferometry was the first technique used during this research in order to study the gas - liquid transfer in the hydrometallurgical liquors regeneration stage.

INTERFEROMETRY: refers to a family of techniques in which waves, usually electromagnetic, are superimposed in order to extract information about the waves (Bunch and Hellemans, 2004). Phenomena caused by the interference of light waves can be seen all around us.

Only a few colored fringes can be seen with white light. As the thickness of the film increases, the optical path difference between the interfering waves increases, and the changes of color become less noticeable and finally disappear. However, if monochromatic light is used, interference fringes can be seen with quite large optical path differences, this is the used light in the experimental part.

Since the wavelength of visible light is quite small (approximately half a micrometer for green light), optical interferometry permits extremely accurate measurements and has been used as a laboratory technique for almost a hundred years. Several new developments have extended its scope and accuracy and have made the use of optical interferometry practical for a very wide range of measurements.

Some of the current applications of optical interferometry are accurate measurements of distances, displacements and vibrations, tests of optical systems, studies of gas flows and plasma, microscopy, measurements of temperature, pressure, electrical and magnetic fields, rotation sensing, and high resolution spectroscopy. There is little doubt that the near future many more will be found (Hariharan, 1992).

This project tries, through interferometry, to measure the variation of the refraction index of an ammonia aqueous solution when CO_2 dissolves in it. This variation of refraction index can be transformed into a concentration of the aqueous solution. These techniques allow for studying the capture of CO_2 into ammonia solutions (Wylock, C. Et al., 2011).

In this chapter the optical experiments of gas – liquid transfer of CO_2 in liquid ammonia aqueous solutions will be presented.

a. Calibration of refraction index of ammonium in ammoniacal liquors

In the experiment through Mach – Zehnder interferometry, the gas diffusivity and interface-mass transfer coefficients in gas injections are calculated by means of a correlation with the measured refraction index and the density of the solution. Thus, the refraction index of the ammonia liquors has to be previously calibrated.

a.1. Pure ammonia aqueous solution

In the Figure 3.37 the correlation between measured density of a pure ammonia aqueous solution and ammonium concentration is shown:

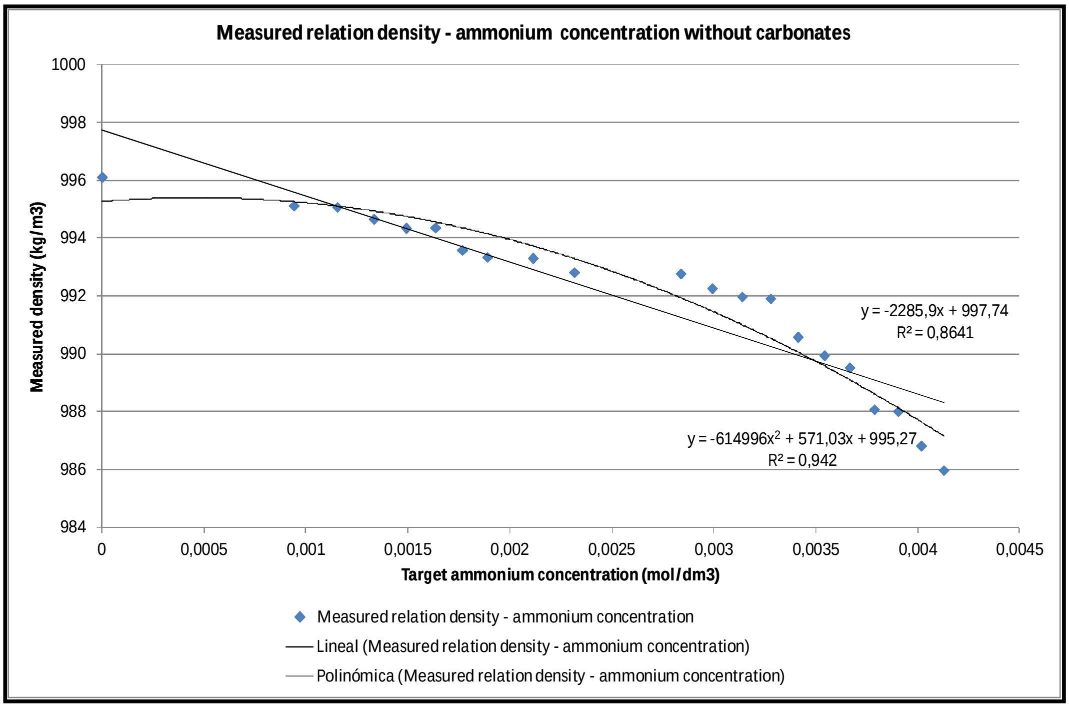

Figure 3.37: Measured density as function of the target ammonium concentration

The gas diffusion in liquid phase will be studied through the relation between refraction index and concentration. So, the calibration of refraction index of different ammonium concentration in pure ammonia solutions is the following one:

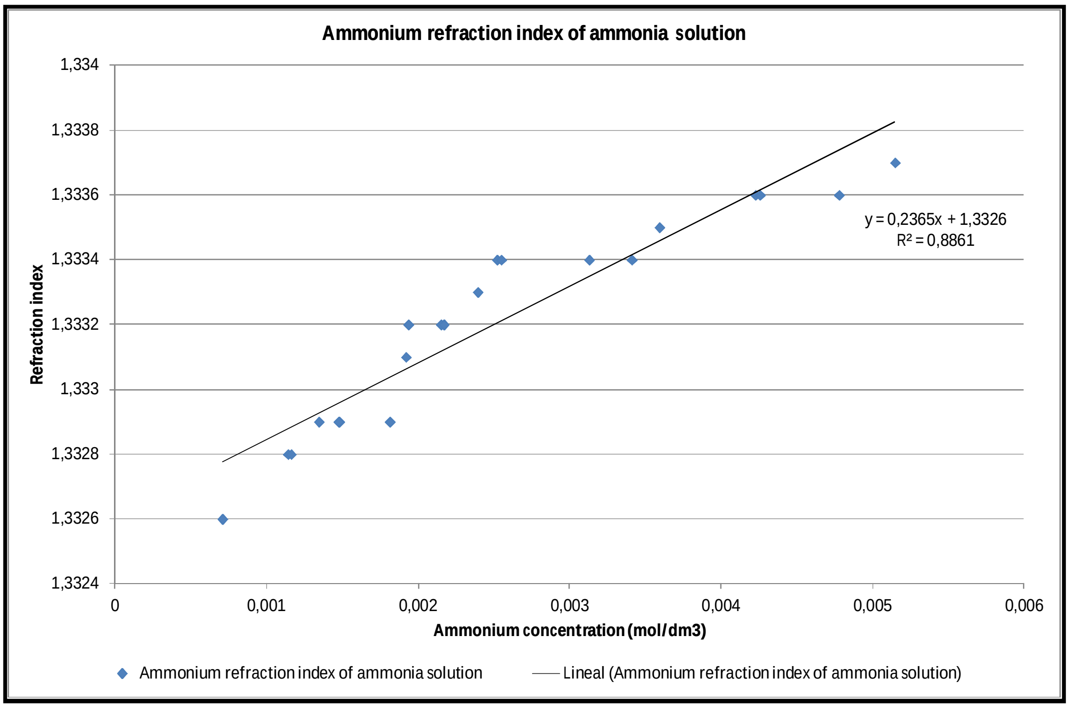

Figure 3.38: Refraction index as function of ammonium concentration

a.2. Pure ammonium carbonate aqueous solution

In the Figure 3.39 the correlation between measured density of a pure ammonium carbonate aqueous solution and ammonium concentration is shown:

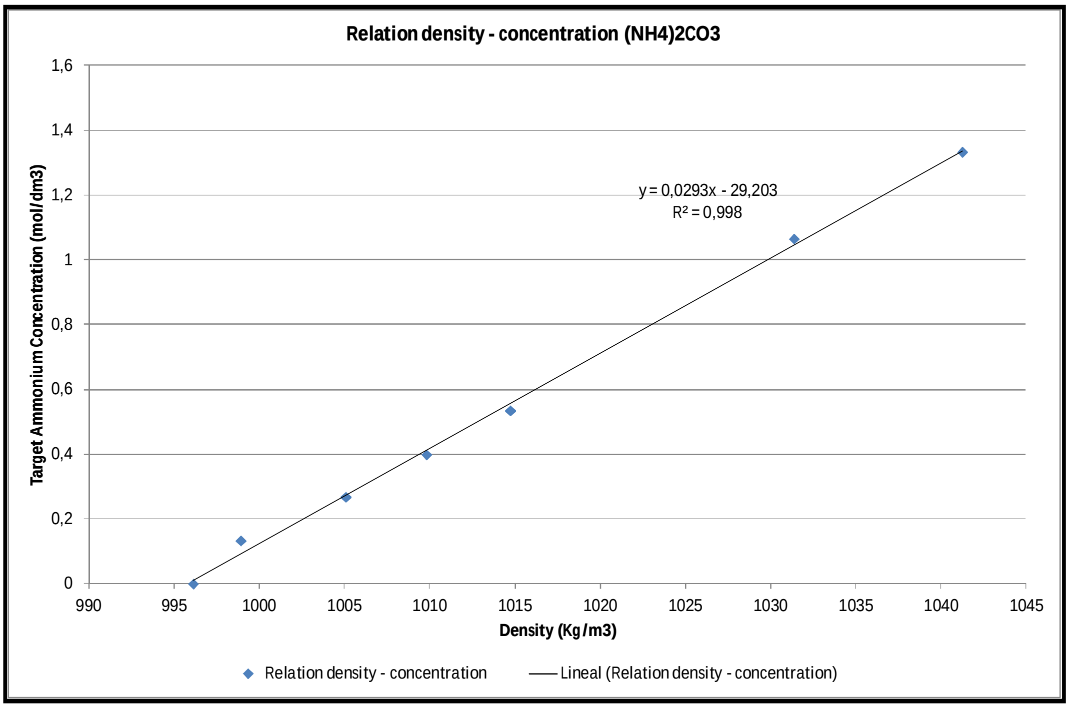

Figure 3.39: Target ammonium concentration as function of density

The gas diffusion in liquid phase will be studied through the relation between refraction index and concentration. So, the calibration of refraction index of different ammonium concentration in pure ammonium carbonate aqueous solutions is the following one:

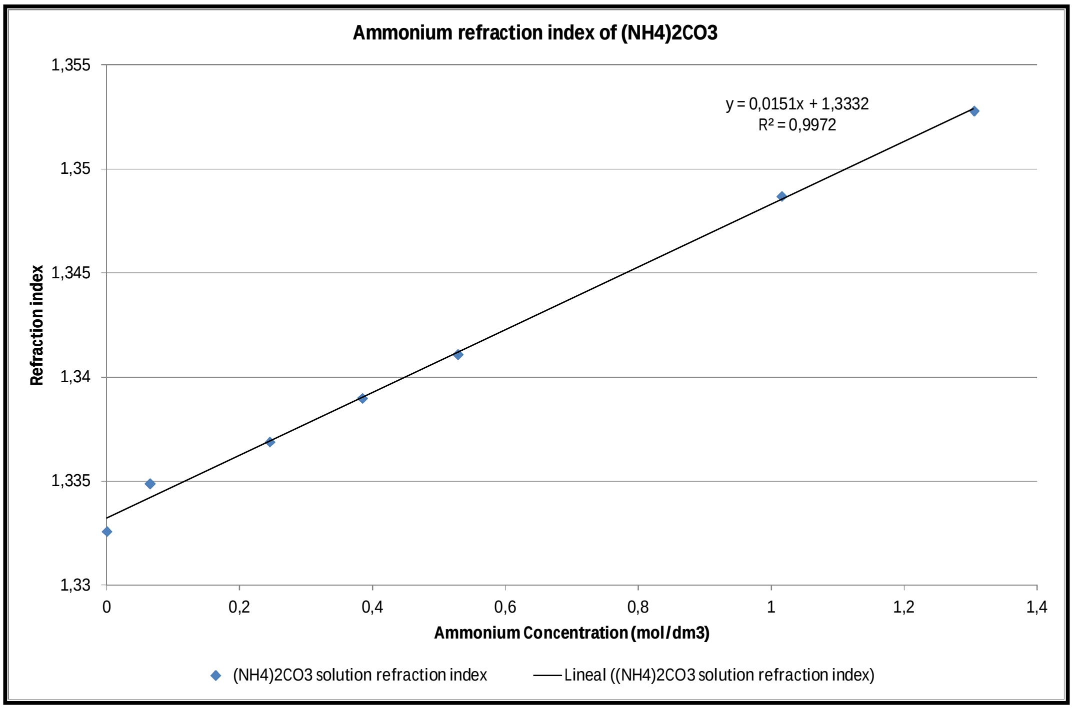

Figure 3.40: Refraction index as function of ammonium concentration

a.3. Pure ammonium bicarbonate aqueous solution

In the Figure 3.41 the correlation between measured density of a pure ammonium bicarbonate aqueous solution and ammonium concentration is shown:

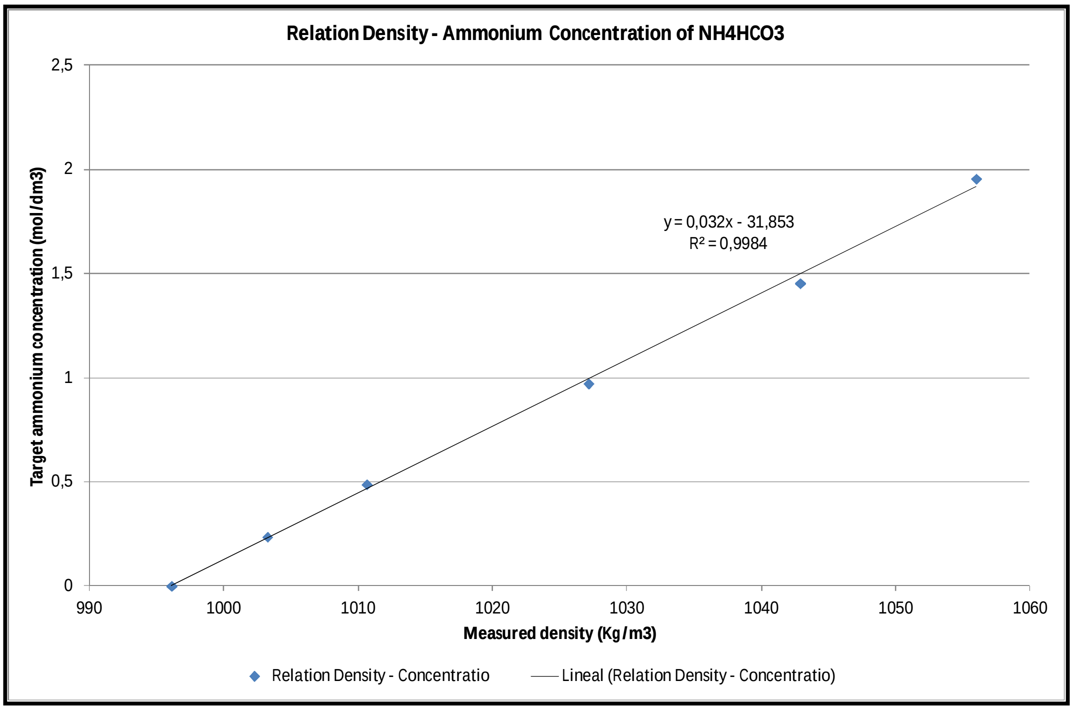

Figure 3.41: Target ammonium concentration as function of measured density

The gas diffusion in liquid phase will be studied through the relation between refraction index and concentration. So, the calibration of refraction index of different ammonium concentration in pure ammonium bicarbonate aqueous solutions is the following one:

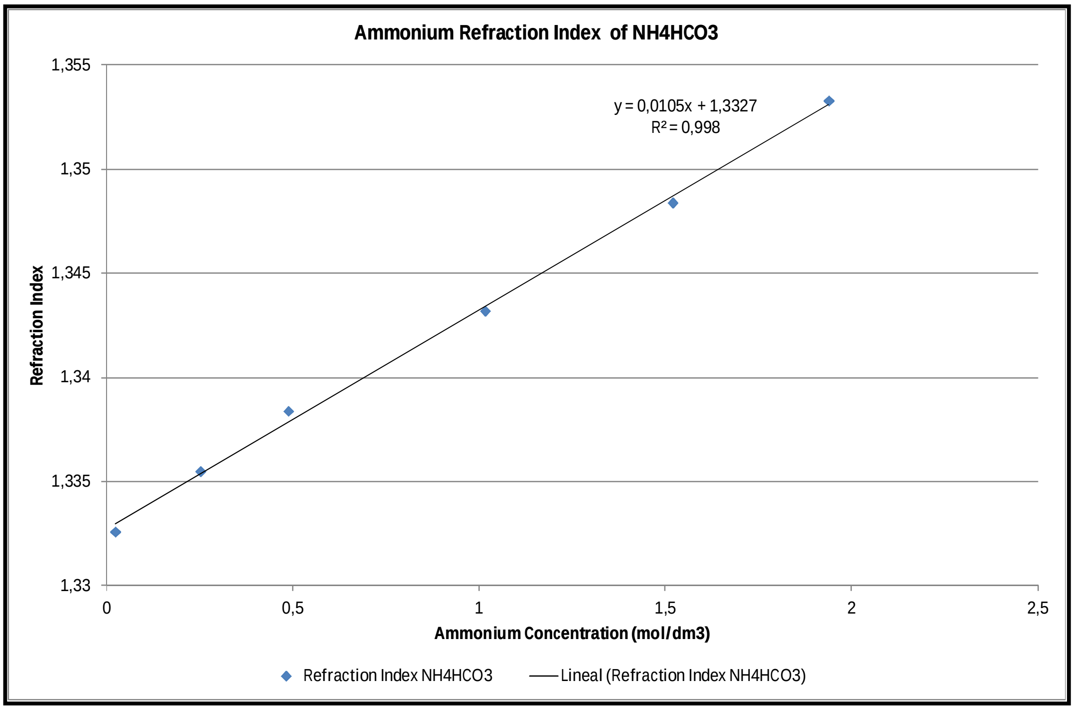

Figure 3.42: Refraction index as function of ammonium concentration

a.4. Aqueous solution of mixed ammonium salts

The relation between refraction index and different concentrations of mixed ammonium salts solutions was calibrated. First of all, the ammonium carbonate addition was maintained constant and the ammonium bicarbonate addition was increased. In the Figure 3.43 the correlation between measured density and ammonium concentration is shown:

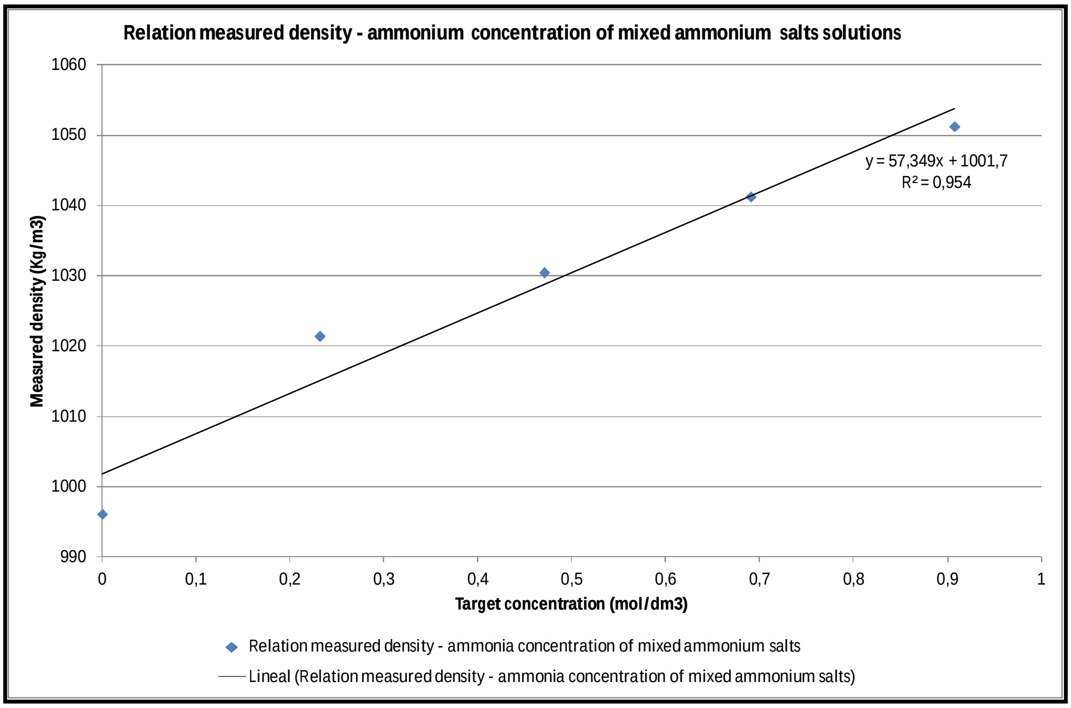

Figure 3.43: Measured density as function of target ammonium concentration

Secondly, the ammonium bicarbonate addition was maintained constant and the ammonium carbonate addition was increased. In the following Figure 3.44 the correlation between measured density and ammonium concentration is shown:

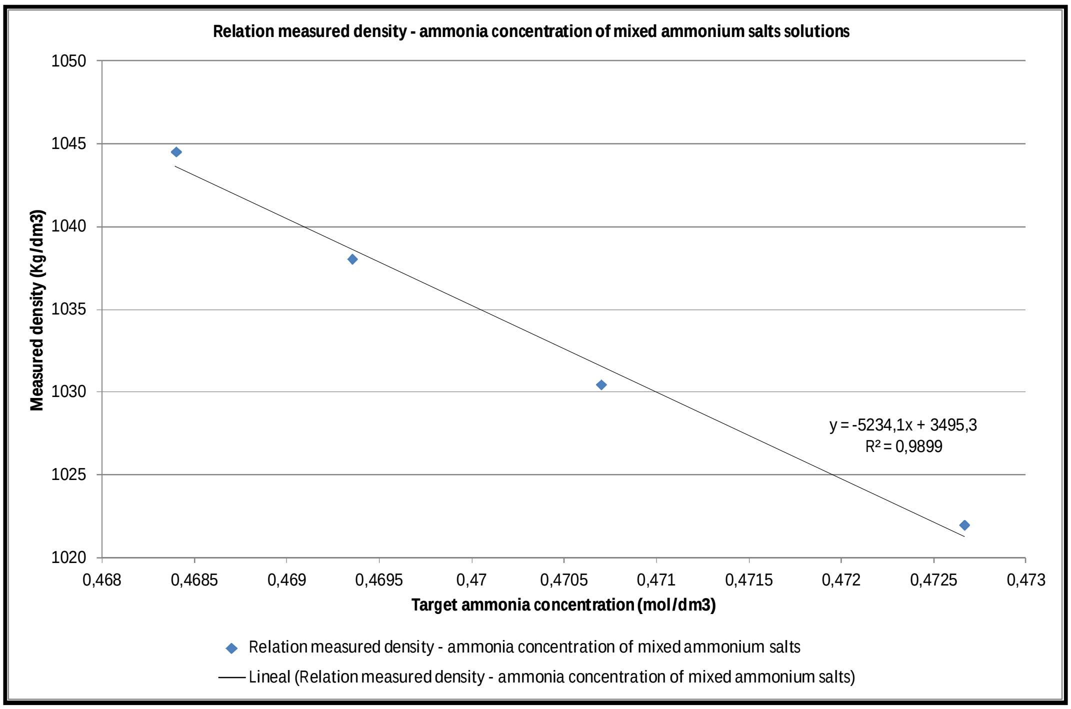

Figure 3.44: Measured density as function of target ammonia concentration

The gas diffusion in liquid phase was studied through the relation between refraction index and concentration. So, the calibration of refraction index of different ammonium concentration in mixed of ammonium bicarbonate and ammonium aqueous solutions is the following one:

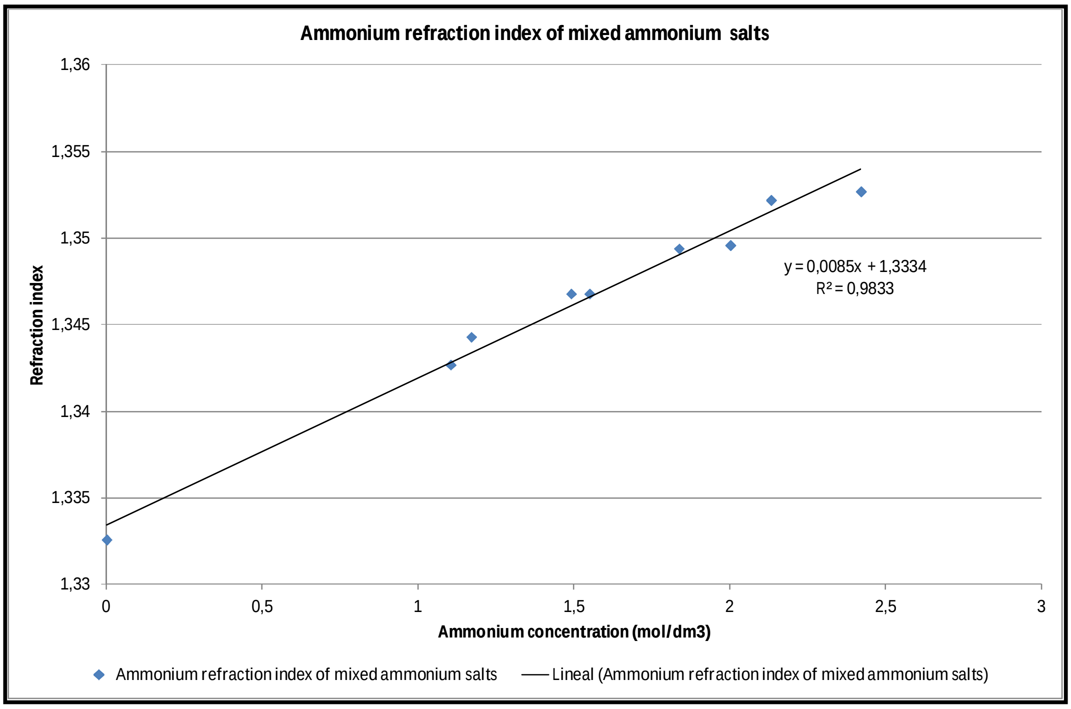

Figure 3.45: Refraction index as function of ammonium concentration

a.5. Aqueous solution of pure and mixed ammonium salts

After analysing the relation between the refraction index of ammonium salts aqueous solutions separately, the behaviour of the refraction index of pure and mixed ammonium salts in aqueous solutions was studied:

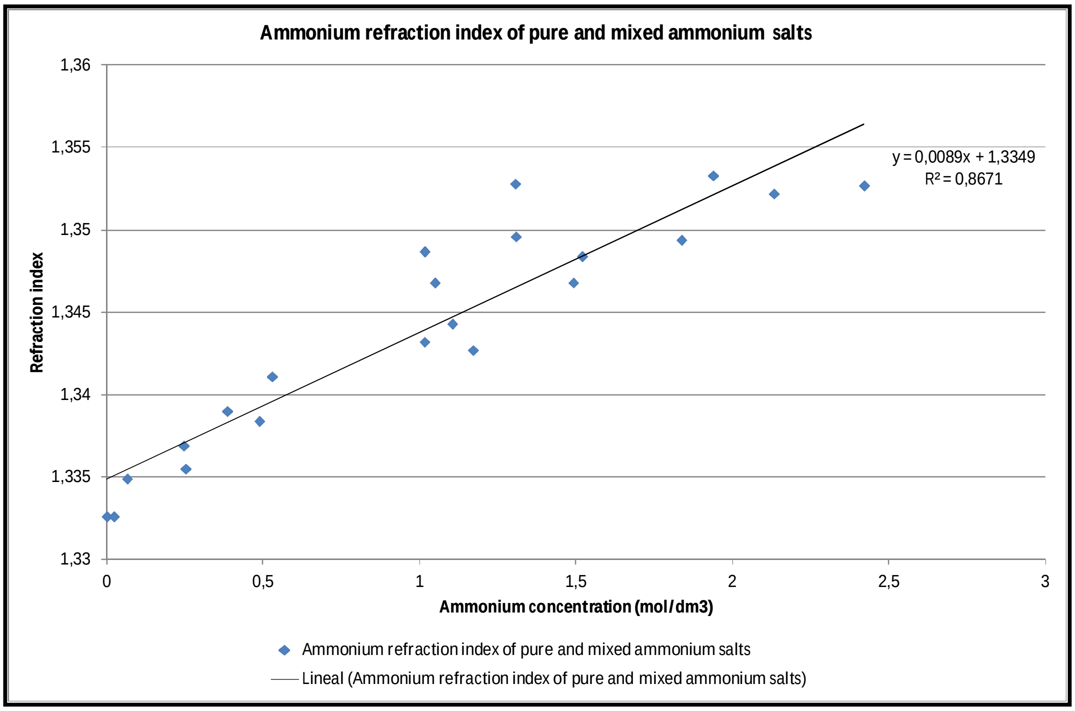

Figure 3.46: Refraction index as function of ammonium concentration

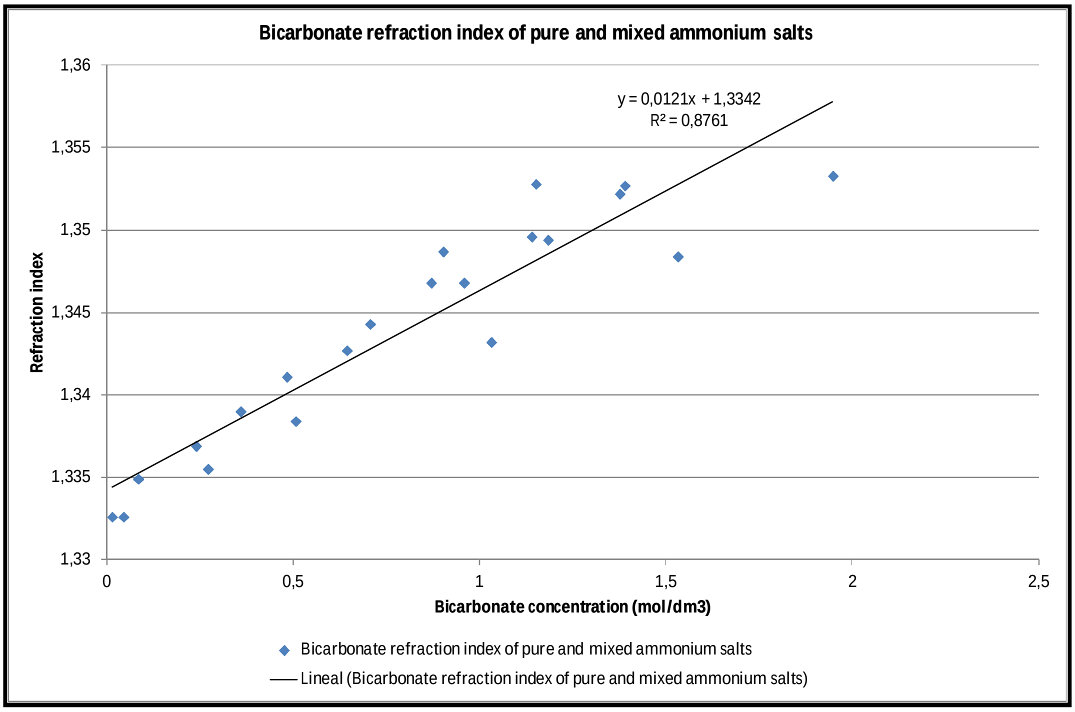

Figure 3.47: Refraction index as function of bicarbonate concentration

a.6. Other relations

Other relations between different combinations of various parameters with refraction index were studied, in order to find the most adjusted correlation.

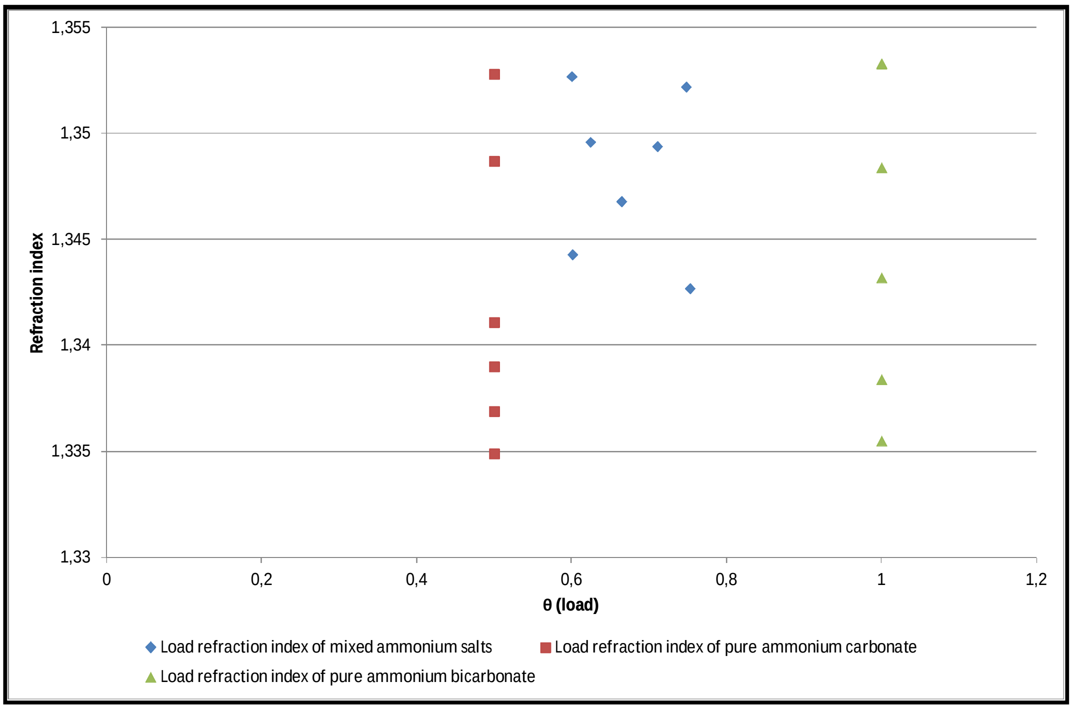

Figure 3.48: Refraction index as function of load

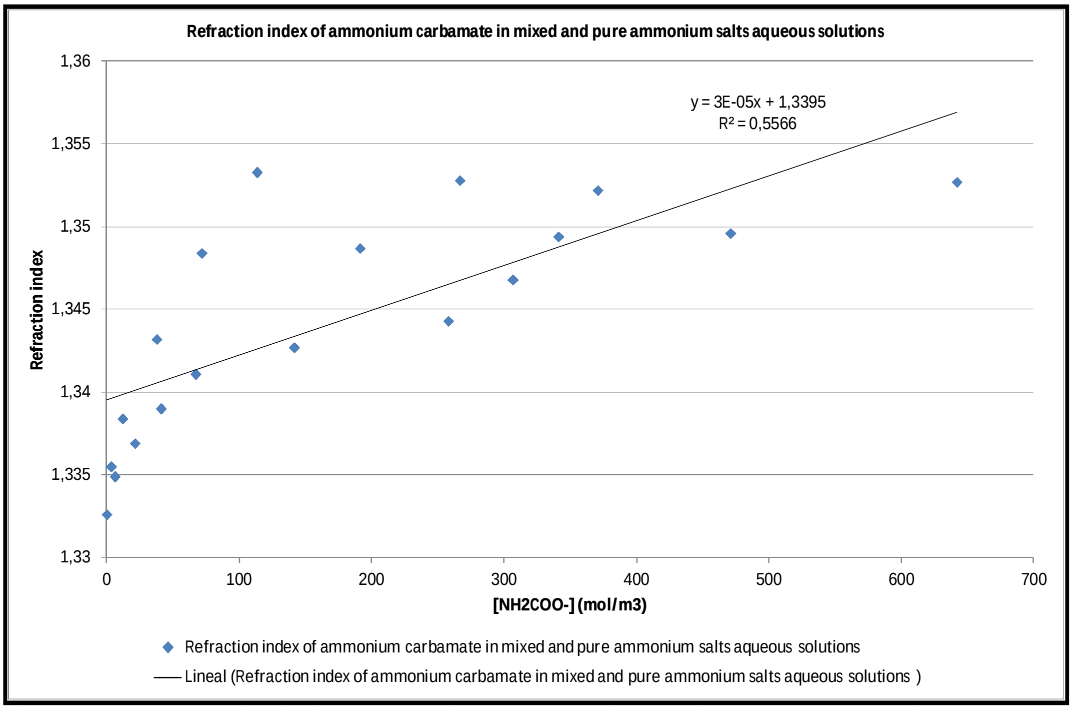

Figure 3.49: Refraction index as function of ammonium carbamate concentration

b. Conclusions after calibration

After the calibration of refraction index of the system $NH_3 - H_2O - CO_2$ was studied the following conclusions were obtained:

- The best linear correlation for ammonia gas absorption in water is the following relation between refraction index and ammonium concentration in the aqueous solution:

$R.I = 0,2365[NH_4^+] + 1,3326$ $R^2 = 0,8861$

The correlation between measured density and the real ammonium concentration in the aqueous solution is:

$\rho = - 2285,9[NH_4] + 997,74$ $R^2 = 0,8641$

- The better linear correlations for ammonia gas and CO_2 gas absorption in water are the following equations between refraction index and ammonium concentration or bicarbonate concentration in aqueous solutions:

$R.I = 0,0089[NH_4^+] + 1,3349$ $R^2 = 0,8671$
$R.I = 0,0121[HCO_3\text{-}] + 1.3342$ $R^2 = 0,8761$

- The variation of refraction index and the concentration of aqueous ammonia solutions and ammonium carbonate and bicarbonate solutions were experimentally measured. These data allow to acquire knowledge of the studied system. The correlation index of the obtained correlations are lower than 0,9 in all cases. Thus, the results obtained with Mach – Zehnder interferometry cannot be quantitative, only qualitative. But it could be possible to treat these values (statistically) or to find the relation between refraction index and other parameters that could allow using this technique.

3.3.6.6. Experimental study of Gas – Liquid transfer of NH_3 and CO_2 in aqueous solution in a stirred tank

In this chapter, the experimental absorption study in a pilot plant (Figure 3.50) carried out is presented. The goal of this work using a stirred tank is to obtain data to assess the mathematical model by comparison with experimental results, in order to be able to design an industrial plant to regenerate the exhausted liquor of the hydrometallurgical process.

The stirred tank used was designed with controllers of the following parameters:

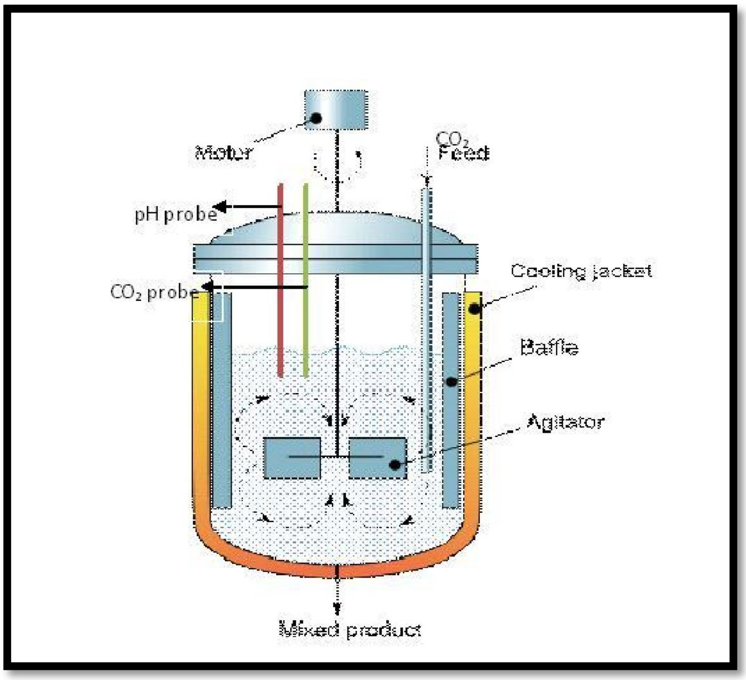

Figure 3.50: Scheme of the stirred tank

- Temperature: A thermoregulation system controlling the temperature in the reaction tank.
- pH: A pH-metre probe (Jeulin ESAO 4 plus) with continuous monitoring during absorption experiments (Serenis software).

- CO_2: A dissolved CO_2 probe (Jeulin ESAO 4 plus) with continuous monitoring during absorption experiments (Serenis software).
- Stirring speed: A mechanical shaker with a speed control (Heidolph RZR 2102 Control).

a. Experimental device

During this experimental work, the obtained data were monitored with the previously mentioned pH-metre probe and CO_2 probe. These controllers were calibrated before carrying out all tests.

a.1. pH-metre PROBE

The pH-metre probe is the reference 703119 of JEULIN. The resolution of this probe is 0,01 pH units with an accuracy of 1% and 5 second of the characteristic response time. This is fast enough regarding to the time evolution of pH to be considered as an instantaneous measure.

a.2. CO_2 PROBE

The CO_2 probe is the reference 453076 of JEULIN. It is an “Electrode of Severinghaus” type. The CO_2 measurements were carried out through the following reaction which happens in the electrolyte:

$CO_2 + H_2O \Leftrightarrow H^+ + HCO_3^-$

The equilibrium constant of this reaction is:

$K = [H^+][HCO_3^-]/[CO_2]$

If the concentration of CO_2 in the electrolyte is high with enough, the equation could be simplified as:

$$[H^+] = K^{'}[CO_2]$$

The time response of the probe was simulated, using the following equation:

$$dC_e/dt = (C_l - C_e)/\zeta$$

When:
C_e = Concentration of the probe's electrolyte
C_l = Concentration of dissolved CO_2 in the solution
t = Time
ζ = Characteristic response time of the probe

This equation must be used because there is a delay due to the characteristic response time. Due to the slow diffusion in the electrolyte between the probe membrane and the severing the electrode in it, it is known that this characteristic response time is significant and cannot be neglected regarding to the CO_2 time evolution rate,

To calculate this parameter, the CO_2 concentration being absorbed in distilled water was measured using the following experimental procedure:

1) The probe sensor is immersed in distilled water saturated with CO_2 (obtained by CO2 injection)

2) The probe sensor is immersed in distilled water free of CO_2

This way, the CO2 concentration in the solution is known:

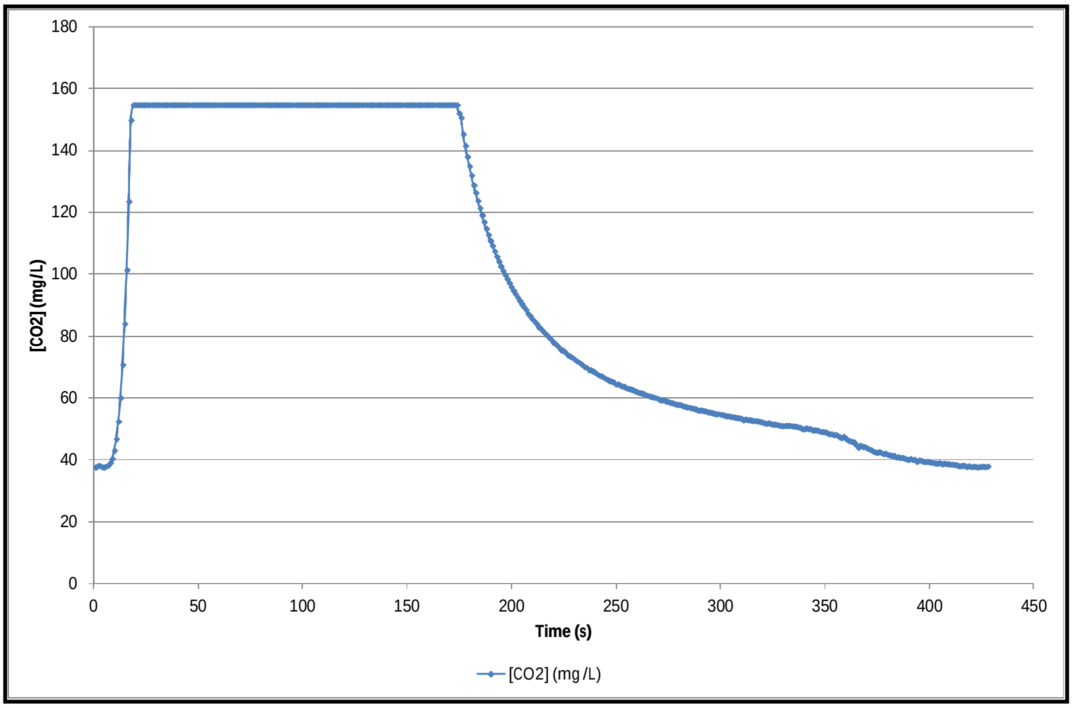

Figure 3.51: Time evolution of CO_2 concentration

The saturation concentration of CO_2 in water is $C_e(t = 0) = C_{sat} = 154{,}798$ mg/L. So the solution of the equation is the following one:

$$C_e(t) = C_e(t = 0)\exp(-t/\zeta)$$

The characteristic response time (ζ) of the used CO_2 probe during the experimental works is 173 seconds.

After this initial calibration of the controllers, the experimental tests were carried out.

b. Experimental study of water – CO_2 absorption system

First of all, the CO_2 (g) absorption in liquid water was studied in the stirred tank unit. Thus, this experimental part enables to calculate the $(kl.a/V_L)$ in the used stirred tank. The effect of some operation parameters in the studied absorption system in the reactor were analysed to improve the knowledge of the system.

b.1. Effect of CO_2 (g) flow

The experiments were carried out at the following conditions:

Temperature: 25ºC
Rotation speed: 300 r.p.m
Liquid volume: 5,5 L
CO_2 (g) concentration: 100%

The obtained results after the trials are the following:

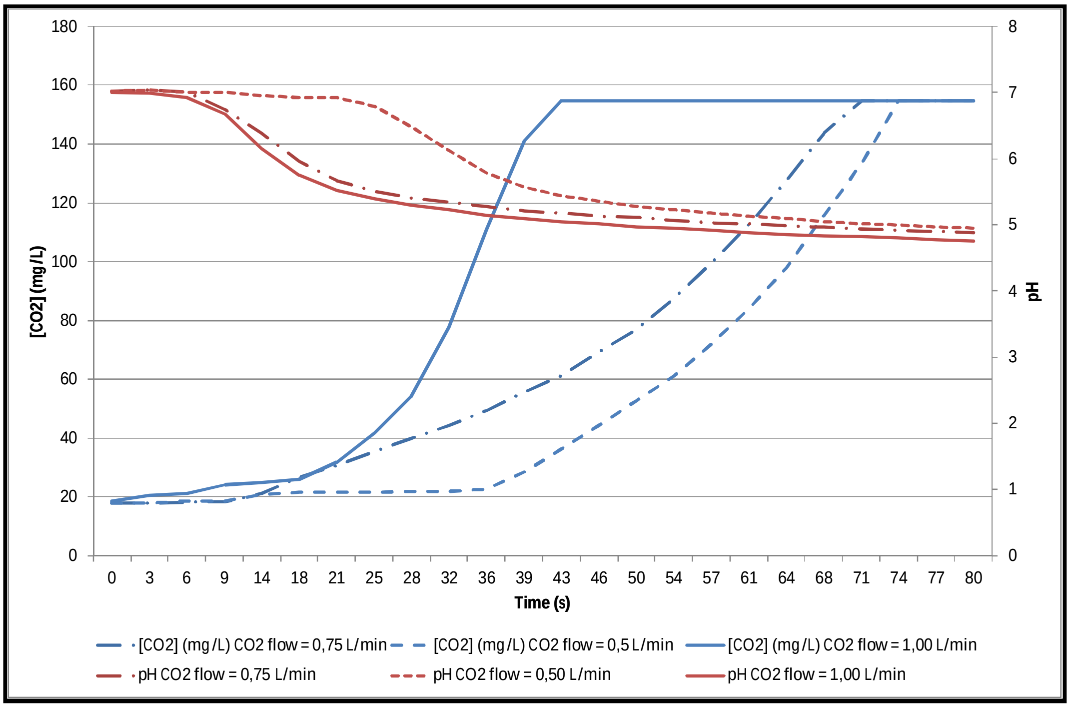

Figure 3.52: Time evolution of CO_2 concentration and pH

The time evolution of the CO_2 (aq) concentration and the pH can be seen in Figure 3.52. Both of the variables were studied changing the flow rate of the injected CO_2. The increase of this flow rate has a positive effect in the kinetic of the CO_2 absorption.

b.2. Effect of stirring speed

The experiments were carried out at the following conditions:

Temperature: 25ºC

Gas flow: 0,75 L/min

Liquid volume: 5,5 L

CO_2 (g) concentration: 100%

The obtained results after the trials are the following ones:

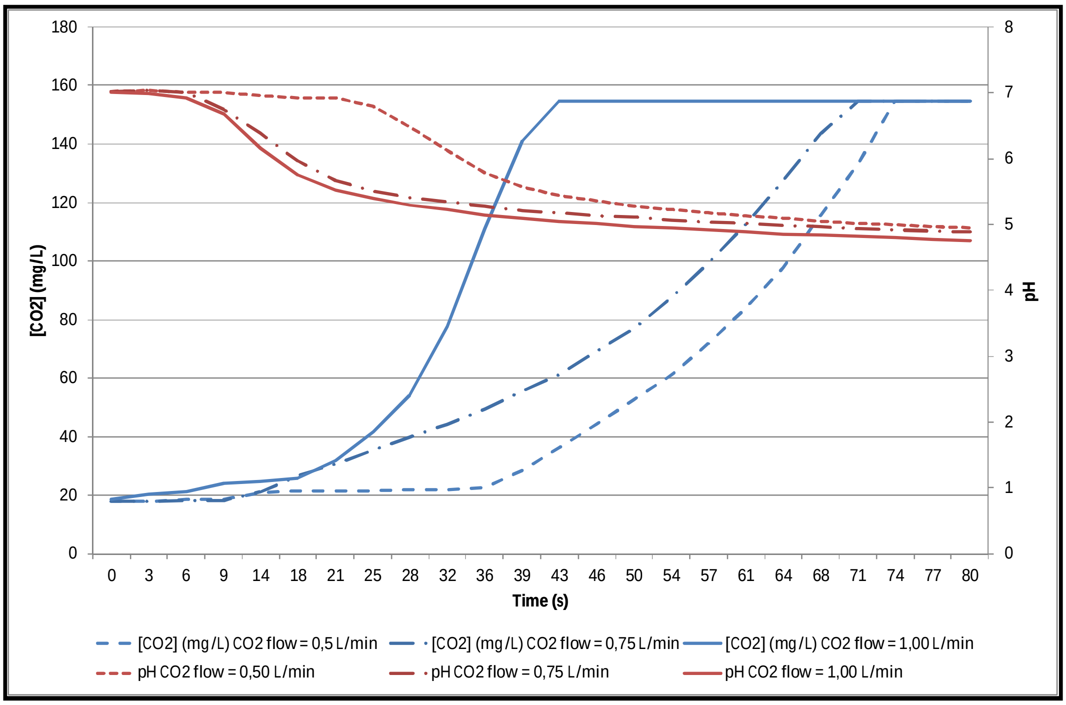

Figure 3.53: Time evolution of CO_2 concentration and pH

The time evolution of the CO_2 (aq) concentration and the pH can be seen in Figure 3.53. Both of the variables were studied changing the stirring speed of the reactor. The increase of the stirring speed has a positive effect in the kinetic of the CO_2 absorption.

b.3. The calculation of gas – liquid mass transfer coefficient in a stirred tank (k_L.a)

The main objective of this chapter was to find a value for the volumetric mass transfer coefficient referred to the liquid (k_L.a) using the laboratory scale stirred tank reactor.

Only the dynamics of liquid phase is considered in this work. The evolution of the dissolved CO_2 (assuming a well mixed model) can be expressed as:

$$\partial[CO_2]/\partial t=(k_L.a/V_L)([CO_2]_{int}-[CO_2])$$

$$\partial[CO_2]_{measured}/\partial t= - (1/\zeta)([CO_2]_{measured}-[CO_2])$$

Both equations constitute the model to interpret the experimental data. The analytical solution to find the values of $k_L.a$ ($k_L.a = D_{CO2}.a/x_L$) is:

$$[CO_2]_m=([CO_2]_{int}(1-\exp((-kl.a/V_L).t)+(\exp(t/\zeta)-1)(kl.a/V_L)\zeta)/(1+(kl.a/V_L)\zeta))$$

The experimental composition profiles resulting after the fitting of the experimental and the calculated data are represented in the Figure 3.54 and the Figure 3.55:

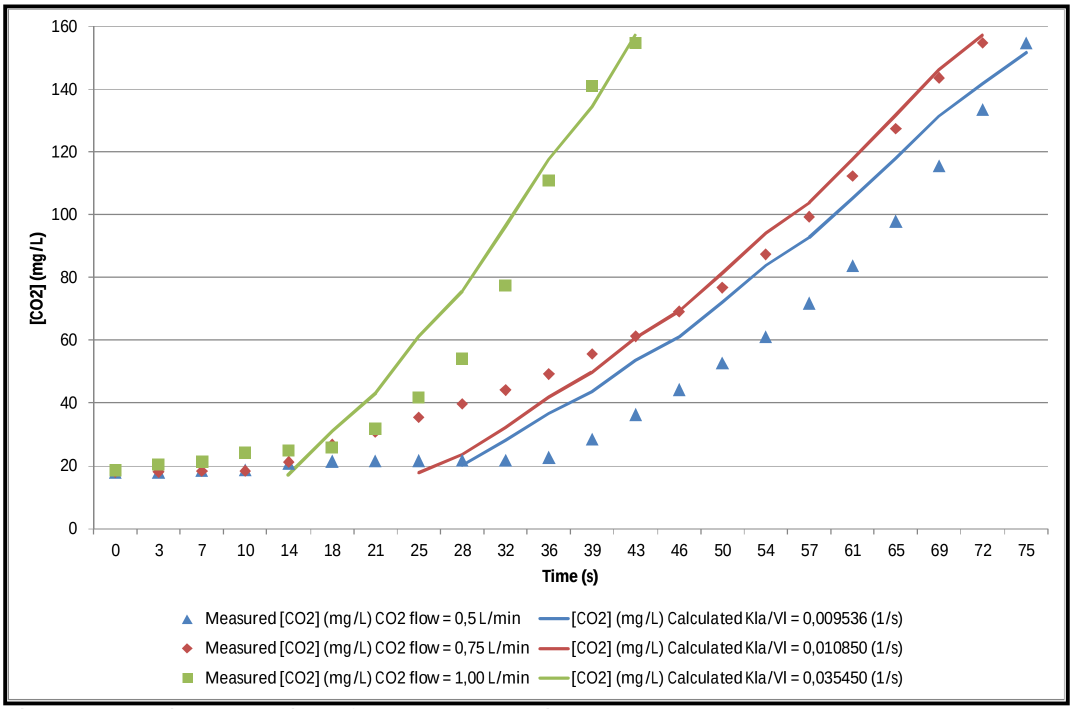

Figure 3.54: Time evolution of CO_2 concentration

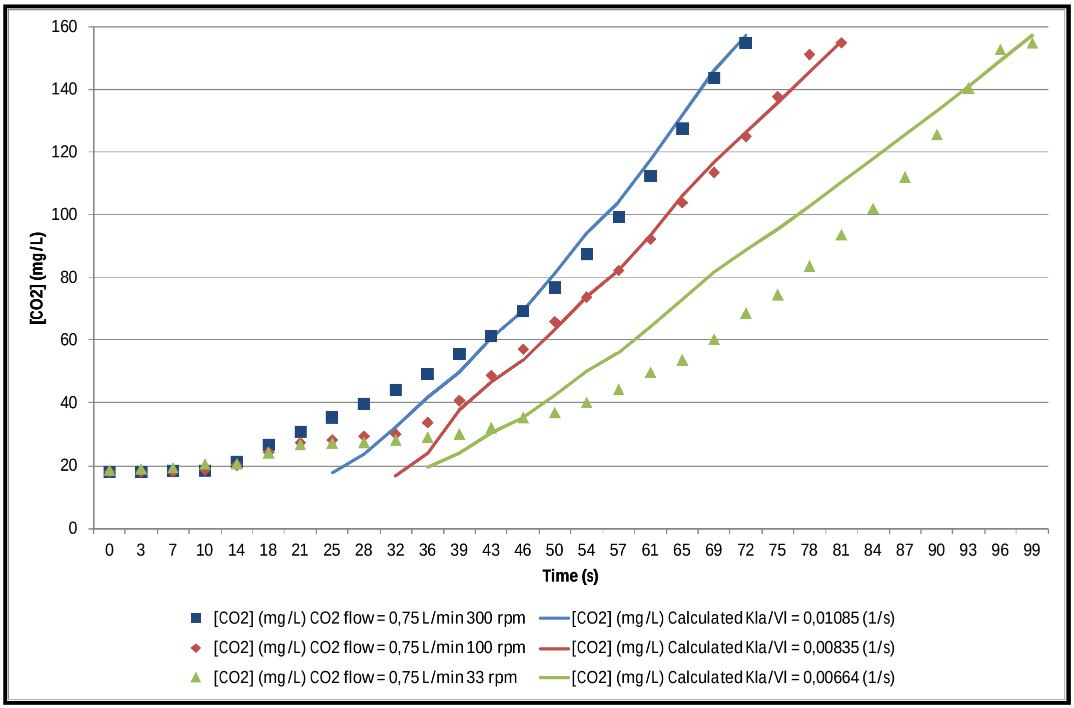

Figure 3.55: Time evolution of CO_2 concentration

c. Experimental study of NH_3 – water – CO_2 absorption system

In this chapter, the CO_2 (g) absorption in aqueous ammonia solution was studied in the stirred tank unit. The capture of CO_2 in ammonia solutions, the influence of different parameters and the application of this system to the regeneration of hydrometallurgical liquors is also analyzed. After study the CO_2 injection in the stirred tank and the influence of the operating conditions in this reactor, the effect of the variables in the NH_3 – water – CO_2 absorption system must be measured.

c.1. Influence of the absorbent concentration

The influence of the presence of dissolved ammonium salts and the concentration of the liquid at the same conditions has to be studied in these experimental works.

The experiments were carried out at the following conditions:

Temperature: 25°C

Gas flow: 1,00 L/min

Liquid volume: 5,5 L

CO_2 (g) concentration: 100%

Rotation speed: 150 r.p.m

The compositions of the liquid were varied. The initial conditions of the absorbents are showed in the Table 3.45, Table 3.46 and Table 3.47:

Table 3.45: Initial conditions of aqueous ammonia solutions

[NH_4OH] = 0,1 M		**[NH_4OH] = 0,45 M**		**[NH_4OH] = 0,8 M**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	98,66	NH_3	447,147	NH_3	796,193
NH_4^+	1,34001	NH_4^+	2,85273	NH_4^+	3,80667
CO_3^{-2}	-	CO_3^{-2}	-	CO_3^{-2}	-
HCO_3^-	-	HCO_3^-	-	HCO_3^-	-
CO_2	-	CO_2	-	CO_2	-
NH_2COO^-	-	NH_2COO^-	-	NH_2COO^-	-
H^+	7,46263E-09	H^+	3,51E-09	H^+	2,63E-09
OH^-	1,34001	OH^-	2,85273	OH^-	3,80667
pH	11,1271	pH	11,4553	pH	11,5805

Table 3.46: Initial conditions of aqueous ammonium carbonate solutions

[$(NH_4)_2CO_3$] = 0,1 M		**[$(NH_4)_2CO_3$] = 0,45 M**		**[$(NH_4)_2CO_3$] = 0,8 M**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	80,5839	NH_3	273,045	NH_3	411,505
NH_4^+	105,129	NH_4^+	463,092	NH_4^+	816,578
CO_3^{-2}	5,24263	CO_3^{-2}	13,6488	CO_3^{-2}	17,5684
HCO_3^-	80,3429	HCO_3^-	271,921	HCO_3^-	409,514
CO_2	0,12755	CO_2	0,567069	CO_2	0,999715

NH_2COO^-	14,2877	NH_2COO^-	163,863	NH_2COO^-	371,918
H^+	7,09E-07	H^+	9,38E-07	H^+	1,09E-07
OH^-	0,0245426	OH^-	0,010731	OH^-	0,009172
pH	9,14	pH	9,02778	pH	8,96372

Table 3.47: Initial conditions of aqueous ammonium bicarbonate solutions

$[NH_4HCO_3]$ = 0,1 M		**$[NH_4HCO_3]$ = 0,45 M**		**$[NH_4HCO_3]$ = 0,8 M**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	2,95479	NH_3	10,4998	NH_3	15,9033
NH_4^+	96,4237	NH_4^+	429,805	NH_4^+	758,467
CO_3^{-2}	0,248623	CO_3^{-2}	0,87007	CO_3^{-2}	1,30345
HCO_3^-	95,3044	HCO_3^-	418,37	HCO_3^-	730,229
CO_2	3,82545	CO_2	21,0651	CO_2	42,8371
NH_2COO^-	0,621501	NH_2COO^-	9,69489	NH_2COO^-	25,63
H^+	1,79302E-05	H^+	2,24916E-05	H^+	2,62046E-05
OH^-	0,000557718	OH^-	0,000444611	OH^-	0,000381613
pH	7,75	pH	7,64798	pH	7,58162

After carrying out the different experimental tests, these are the obtained results:

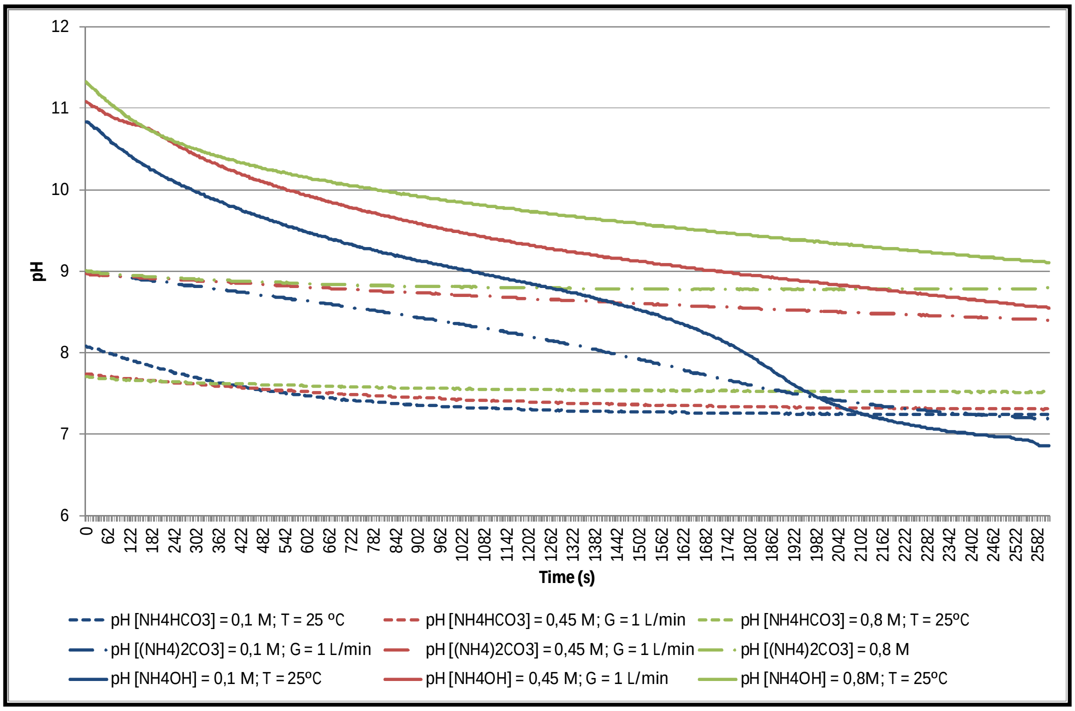

Figure 3.56: Time evolution of the pH

The time evolution of the pH can be seen in Figure 3.56. The influence of the absorbents and their concentrations variations in the CO_2 absorption process was studied.

c.2. Influence of CO_2 (g) flow

The influence of the CO_2(g) flow when ammonium salts are dissolved and with different ammonium concentration in the liquid at the same conditions has to be studied in these experimental works.

The experiments were carried out in the following conditions:

Temperature: 25ºC
Liquid volume: 5,5 L
CO_2 (g) concentration: 100%
Rotation speed: 150 r.p.m

The initial conditions of the absorbents are showed in the preceding Tables. The obtained result could be observed in the following graph, different initial NH_4OH concentration in the liquor:

Aqueous ammonia liquor:

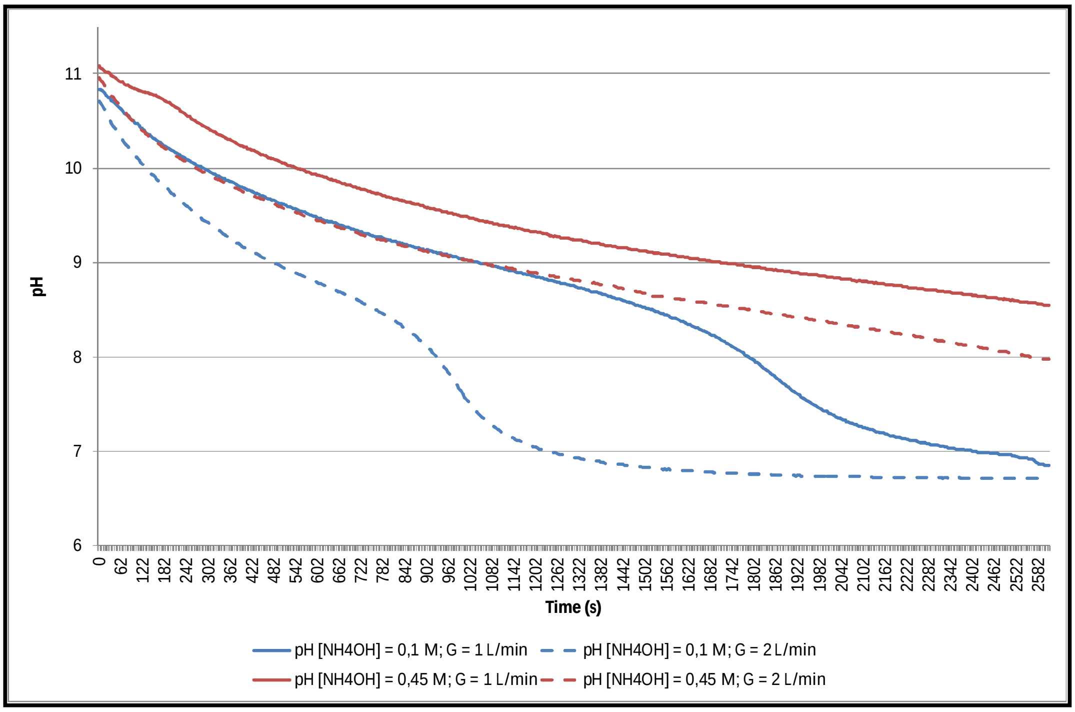

Figure 3.57: Time evolution of the pH

Aqueous ammonium carbonate liquor:

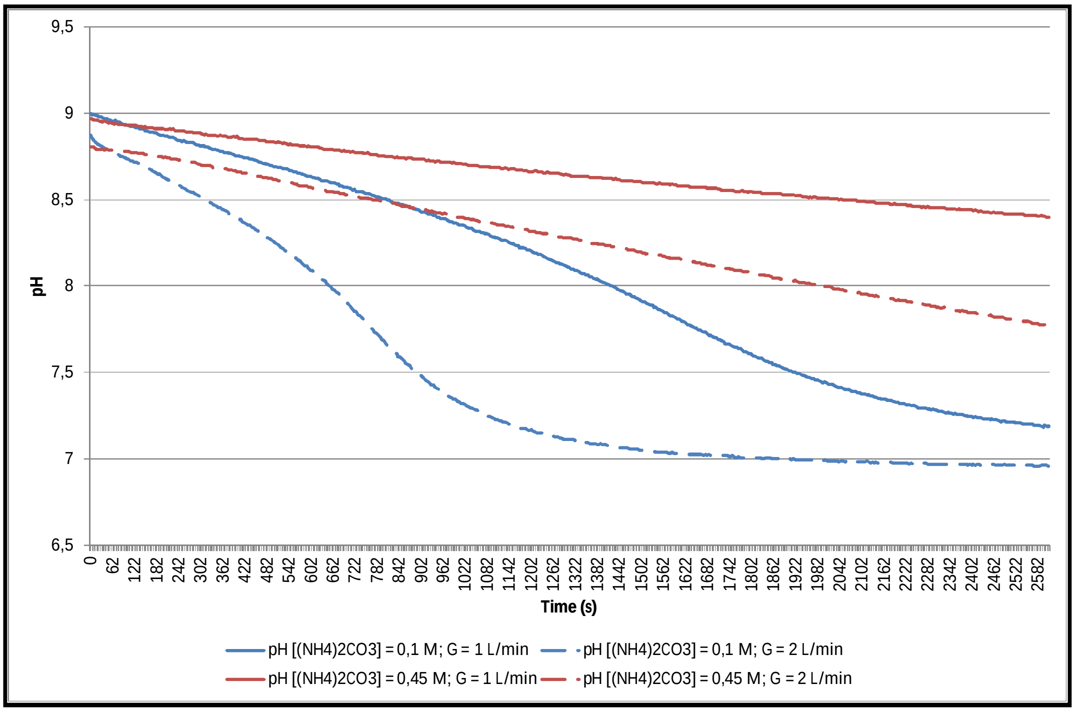

Figure 3.58: Time evolution of the pH

Aqueous ammonium bicarbonate liquor:

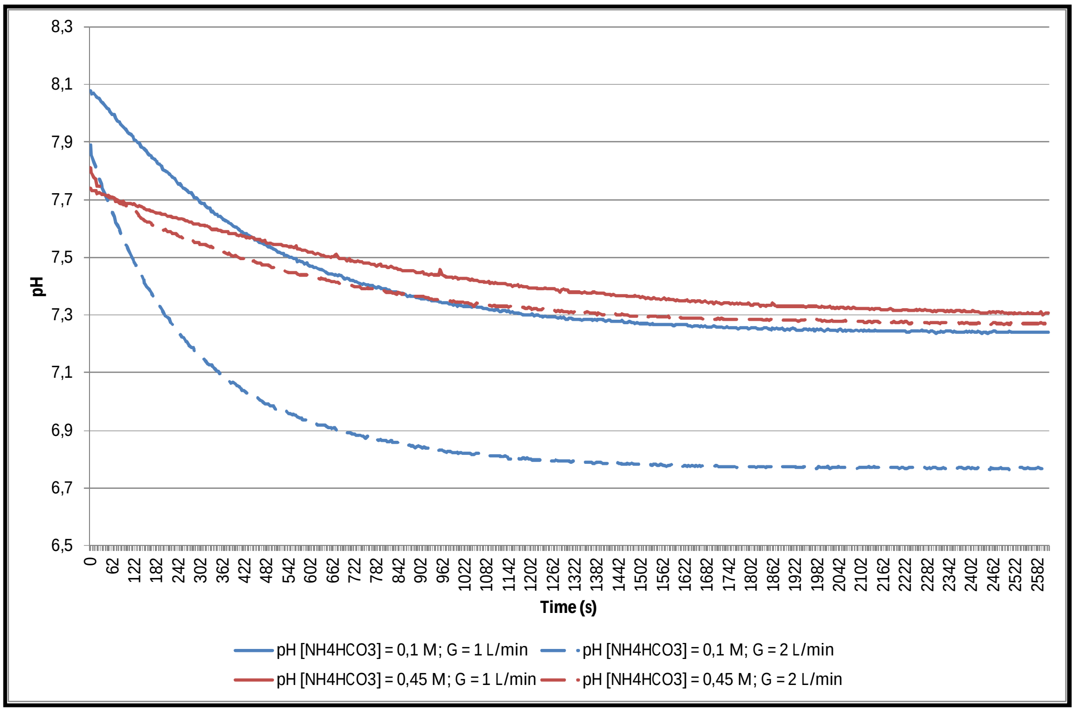

Figure 3.59: Time evolution of the pH

In the three studied cases, the time evolution of the pH was shown. The influence of flow rate of injected CO_2 in the absorption process was studied. Both of the pH profile evolutions are maintained increasing the kinetic of the CO_2 absorption reactions.

c.3. Influence of the temperature

The temperature is another important parameter in absorption processes, and it was analyzed in these experiments. These ones were carried out to compare the effect of temperature using the following conditions:

Gas flow: 1,00 L/min

Liquid volume: 5,5 L

CO_2 (g) concentration: 100%

Rotation speed: 150 r.p.m

The concentrations of the liquid were varied. The initial conditions of the absorbents are showed in the Table 3.48, Table, Table 3.49 and Table 3.50:

Table 3.48: Initial conditions of 0,8 M aqueous ammonia solution

[NH_4OH] = 0,8 M (T = 15ºC)		**[NH_4OH] = 0,8 M (T = 25ºC)**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	792.966	NH_3	796,193
NH_4^+	7,03387	NH_4^+	3,80667
CO_3^{-2}	-	CO_3^{-2}	-
HCO_3^-	-	HCO_3^-	-
CO_2	-	CO_2	-
NH_2COO^-	-	NH_2COO^-	-
H^+	1.4218E-09	H^+	2,63E-09
OH^-	7,03387	OH^-	3,80667
pH	11,8472	pH	11,5805

Table 3.49: Initial conditions of 0,1 M aqueous ammonia solutions

[NH_4OH] = 0,1 M (T = 15ºC)		**[NH_4OH] = 0,1 M (T = 25ºC)**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	97,5331	NH_3	98,66
NH_4^+	2,46685	NH_4^+	1,34001
CO_3^{-2}	-	CO_3^{-2}	-
HCO_3^-	-	HCO_3^-	-
CO_2	-	CO_2	-
NH_2COO^-	-	NH_2COO^-	-
H^+	4,05376E-09	H^+	7,46263E-09
OH^-	2,46685	OH^-	1,34001
pH	11,3921	pH	11,1271

Table 3.50: Initial conditions of 0,8 M aqueous ammonium bicarbonate solution

[NH_4HCO_3] = 0,8 M **(T = 15°C)**		**[NH_4HCO_3] = 0,8 M** **(T = 25°C)**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	7,63522	NH_3	15,9033
NH_4^+	770,466	NH_4^+	758,467
CO_3^{-2}	3,81838	CO_3^{-2}	1,30345
HCO_3^-	740,931	HCO_3^-	730,229
CO_2	33,3527	CO_2	42,8371
NH_2COO^-	21,8985	NH_2COO^-	25,63
H^+	0,0000161733	H^+	2,62046E-05
OH^-	0,000618304	OH^-	0,000381613
pH	7,7912	pH	7,58162

Table 3.51: Initial conditions of 0,1 M aqueous ammonium bicarbonate solution

[NH_4HCO_3] = 0,1 M **(T = 15°C)**		**[NH_4HCO_3] = 0,1 M** **(T = 25°C)**	
Species	Concentration (mol/m3)	Species	Concentration (mol/m3)
NH_3	1,49249	NH_3	2,95479
NH_4^+	97,9536	NH_4^+	96,4237
CO_3^{-2}	0,759715	CO_3^{-2}	0,248623
HCO_3^-	95,8793	HCO_3^-	95,3044
CO_2	2,80707	CO_2	3,82545
NH_2COO^-	0,553926	NH_2COO^-	0,621501
H^+	0,000010519	H^+	1,79302E-05
OH^-	0,000950661	OH^-	0,000557718
pH	7,97803	pH	7,75

After carrying out the different experimental tests, these are the obtained results:

Aqueous ammonia liquor:

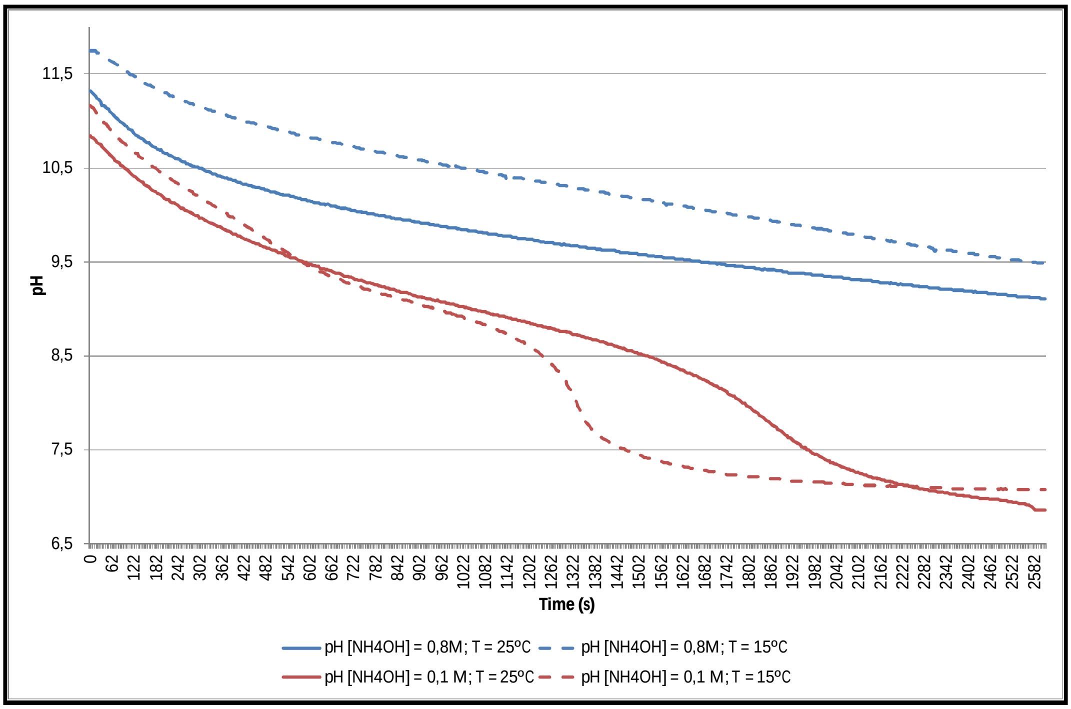

Figure 3.60: Time evolution of the pH

Aqueous ammonium bicarbonate liquor:

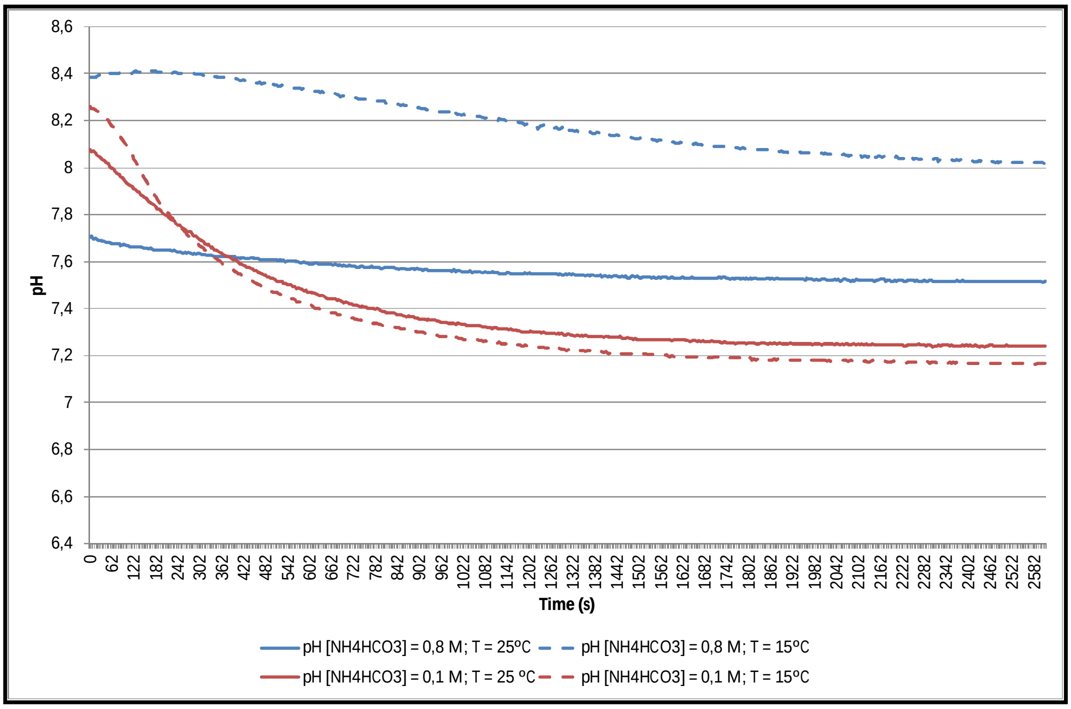

Figure 3.61: Time evolution of the pH

In the two studied cases, the time evolution of the pH was shown. The influence of temperature in the CO_2 absorption process was studied. Both of the pH profile evolutions are also displayed at different liquor concentration, so the effect of the temperature depending on the concentration of the absorbent solutions and the influence in the aqueous reactions were analysed.

d. Comparison between the mathematical model and the experimental data

In order to validate the proposed mathematical model the simulations were checked with the experimental results.

The time evolution of the process was simulated with COMSOL Reaction Engineering Lab software for solving the equilibrium rate equations described in the chapter 3.6.2. (Modelling of the absorption system in liquor regeneration stages). The equations of the CO_2 and NH_3 absorption, taking into account the enhancement factors (E_{CO2} and E_{NH3}) and the volumetric mass transfer coefficients referred to the liquid ($k_L.a$) in the stirred tank in order to close the mathematical model were added to the "DYNAMIC EQUATION", to simulate the carried out experimental tests results.

$$\mathbf{r_{GLCO2} = k_{GL}([CO_2]_{eq}^{G} - [CO_2])}$$

$$\mathbf{r_{GLNH3} = k_{GL}([NH_3]_{eq}^{G} - [NH_3])}$$

When:

$k_L.a = 0,00019498\ s^{-1}$

$[CO_2]_{int} = K_{CO2}.\ P_{CO2}/(8,314.T_{abs})$

$P_{CO2} = 0,98*101.325$ Pa

$[NH_3]_{int} = K_{NH3}.\ P_{NH3}/(8,314.T_{abs})$

$P_{NH3} = 0*101.325$ Pa

After completing the equation system, the values of enhancement factors were estimated through the fitting of the experimental and the calculated data, obtaining the following time evolution graph for whole species in the Figure 3.62:

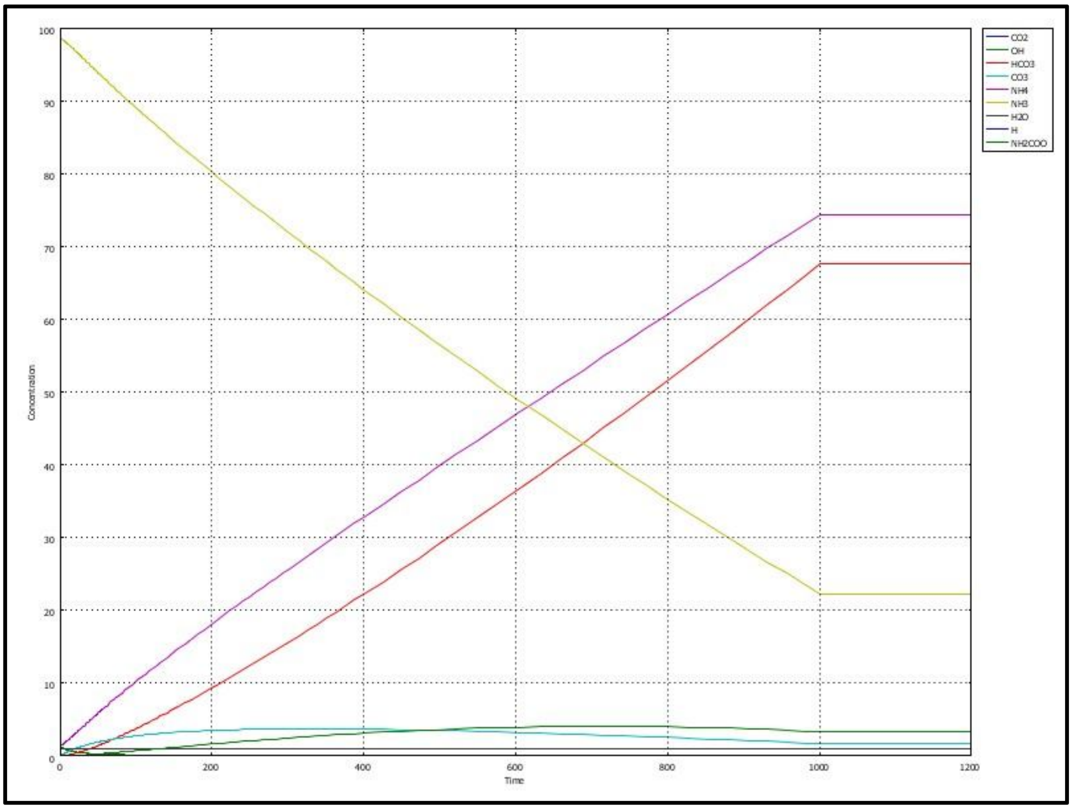

Figure 3.62: Simulation of the time evolution of the system

Calculated parameters: **E_{CO2} = 11,38**

E_{NH3} = 0

The pH profiles in the time interval (until the ammonia has been depleted) resulting after the fitting of the experimental and the calculated data are represented in the Figure 6.63:

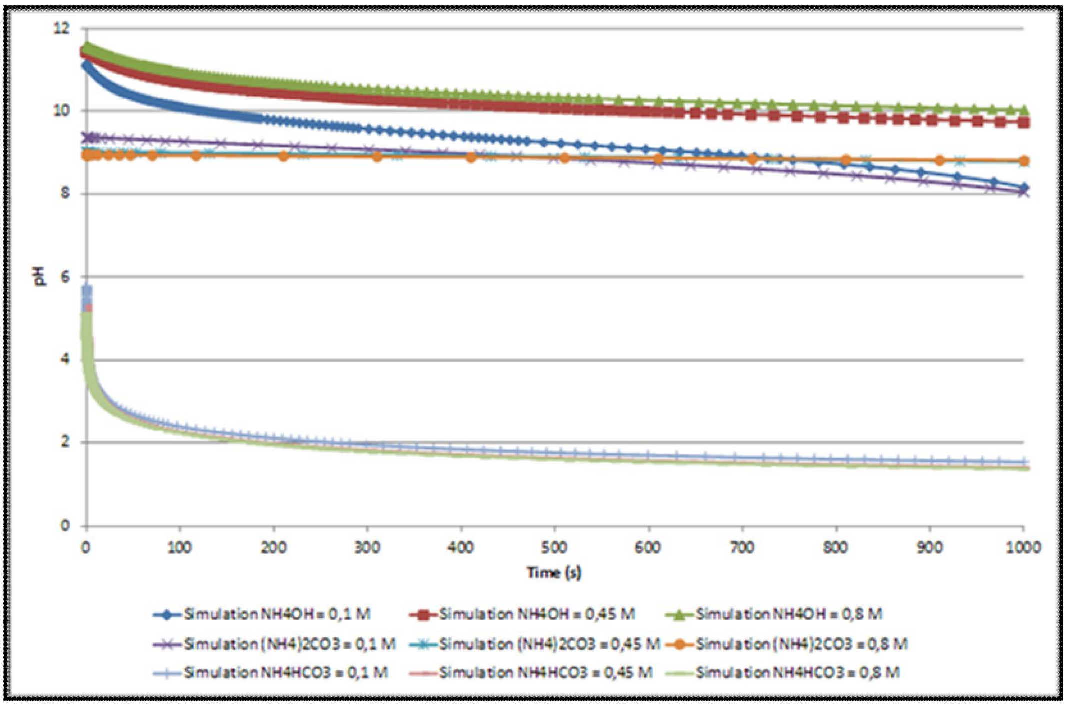

Figure 3.63: Experimental and simulation time evolution of the pH

The time evolution of the pH is compared separately, in accordance with the composition of the used absorption liquid.

<u>Aqueous ammonia liquor:</u>

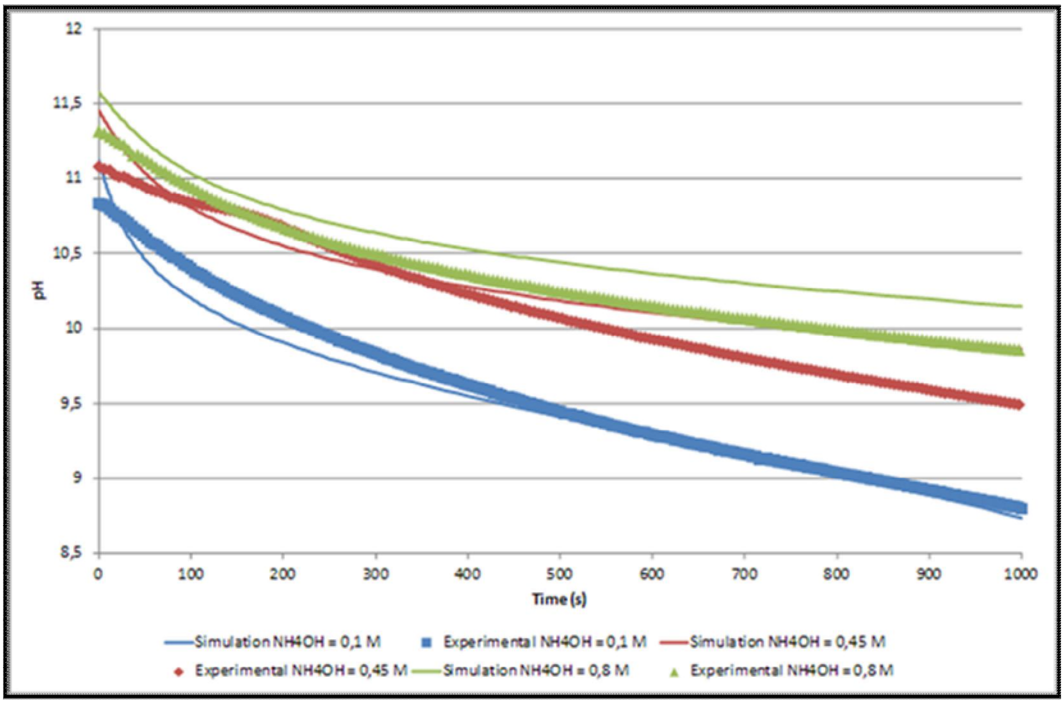

Figure 3.64: Experimental and simulation time evolution of the pH

Aqueous ammonium carbonate liquor:

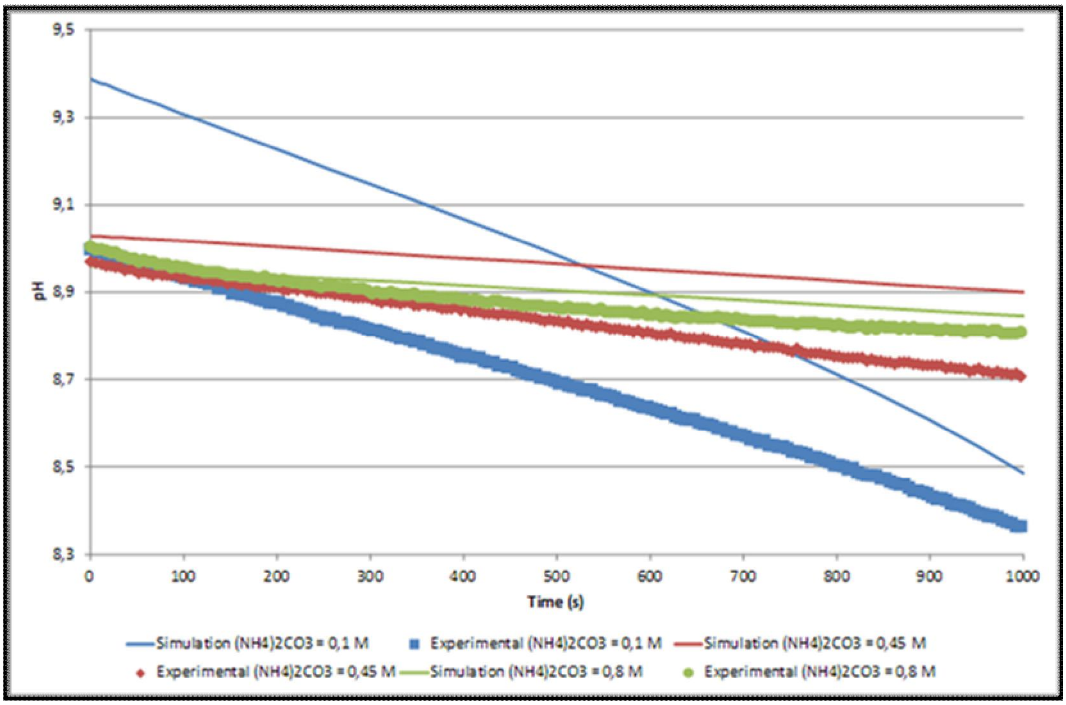

Figure 3.65: Experimental and simulation time evolution of the pH

Aqueous ammonium bicarbonate liquor:

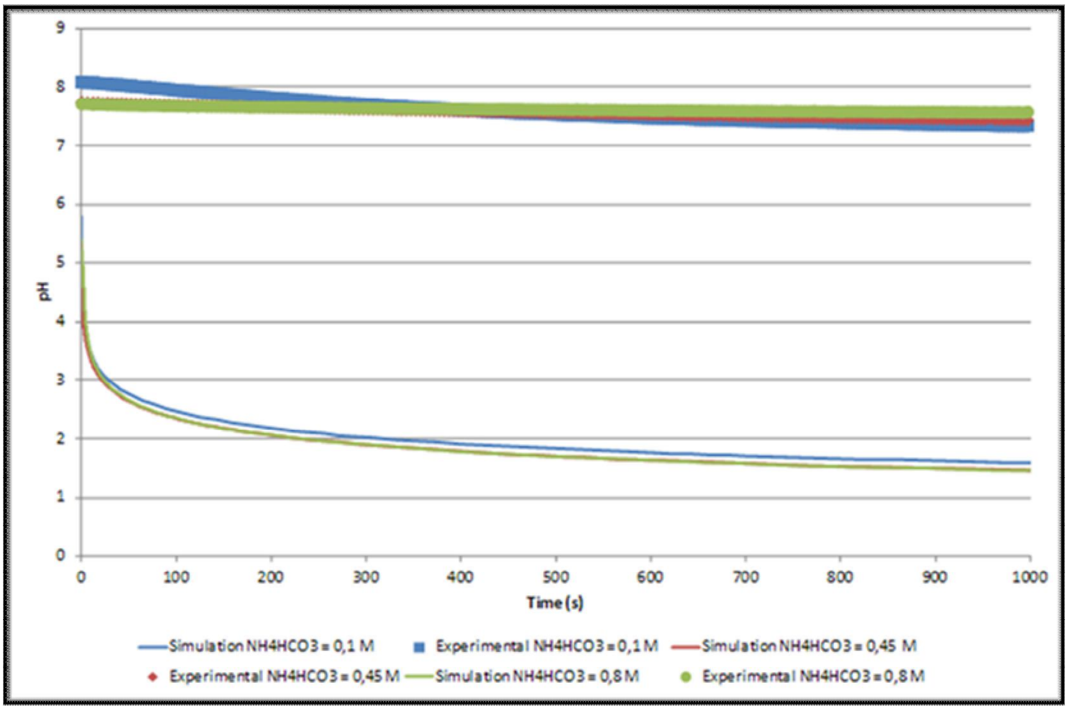

Figure 3.66: Experimental and simulation time evolution of the pH

The time evolution of the pH measured in the stirred tank, using different absorption liquors, it was compared with the simulated pH time evolution. These results were plotted in the previous graphs in order to validate the mathematical model.

d.1. Improvement of the mathematical model

After the comparison between the mathematical model and the experimental results can be concluded that the model has less goodness of fit (when the initial conditions are close to the equilibrium conditions). Therefore, the mathematical model was improved, assuming that the absorption system is governed by the equilibrium equations. Hence, the kinetic equations responses instantly and for this reason the time evolution of the process was simulated with COMSOL Reaction Engineering Lab software for solving this new model based in some assumptions. One of these is the assumption of equilibrium instantaneously reached, therefore meaning that the reaction rate are infinite.

The pH profiles in the time interval (until the ammonia has been depleted) resulting after the fitting of the experimental and the calculated data are represented in the Figure 3.67, Figure 3.68 and Figure 3.69:

Aqueous ammonia liquor:

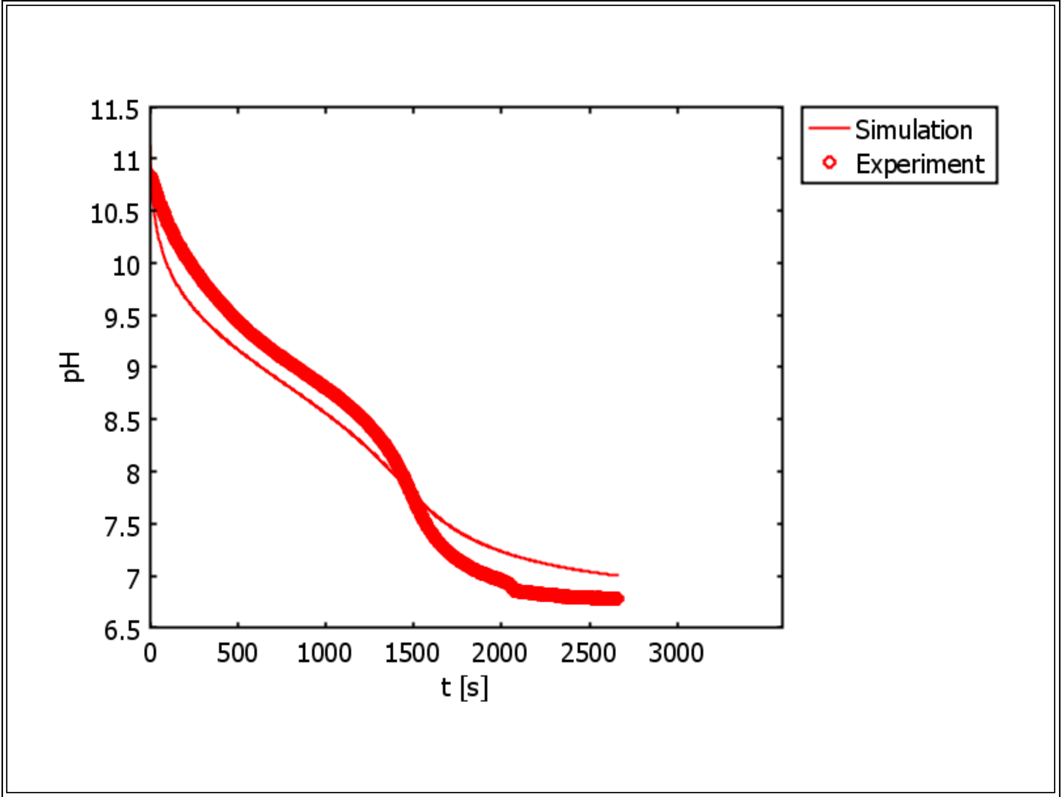

Figure 3.67: Experimental and simulation time evolution of the pH

Aqueous ammonium carbonate liquor:

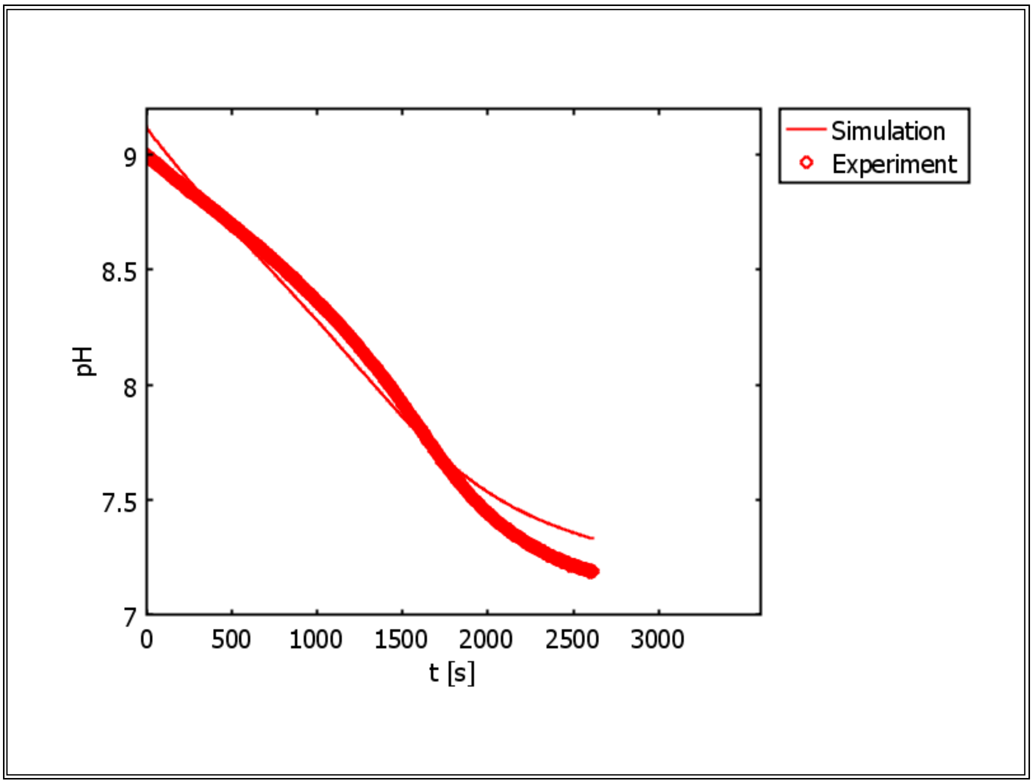

Figure3.68: Experimental and simulation time evolution of the pH

Aqueous ammonium bicarbonate liquor:

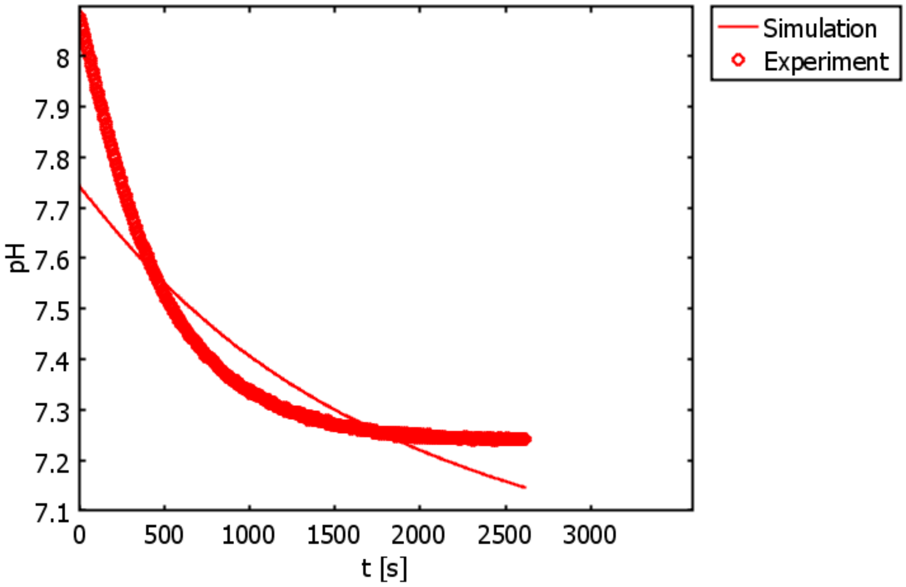

Figure 3.69: Experimental and simulation time evolution of the pH

In these graphs are represented the obtained results by applying the improvements in the mathematical model after having fitted the value of the total gas-liquid interfacial area. The time evolution of the pH measured in the stirred tank, using different absorption liquors only at the lowest concentration which were used in the experimental work, was compared with the simulated pH time evolution.

3.4. CONCLUSIONS

3.4.1. CONCLUSIONS OF THE AMMONIACAL LEACHING STAGE

The conclusions after the in-depth study about the leaching stage are:

- The directly relation between ammonia liquid quantity and the zinc recovery yield could be concluded. But, only it possible in a specific range of pH (9,5 - 12,5). Because the ammonia zinc complex have their highest solubility value under these conditions.
- The total carbonates concentration generates a buffer effect in the liquor, which provides for the maintenance of pH inside the optimal limit. A larger quantity of carbonates permits a higher ammonia concentration in the leaching solution, increase the zinc recovery.
- The temperature has an important influence in the ammonia liquor behaviour. As can be noted, higher temperature increases the zinc recovery, but reduces the amount lost of ammonia to evaporation (lower pH). The optimal temperature to obtain the best zinc recovery with the lowest ammonia losses is 25ºC.
- The necessary time to reach the maximum zinc recovery is 60 minutes.
- The simultaneous absorption of ammonia during the leaching operation could be possible. But, the optimal temperatures (around 15ºC) to increase the ammonia recovery by absorption are harmful for the leaching process. And the absorption liquors must be highly carbonated to maintain the necessary range of pH. So, the exhausted liquor regeneration stage must to be a separate process.

3.4.2. CONCLUSIONS OF THE AMMONIACAL OXIDATION STAGE

The conclusions after this in-depth study about the oxidation stage are:

- The iron removal from the leaching liquor with air has to be carried out between 60 ºC and 80 ºC. The efficiency of the process below 60 ºC is insufficient. On the other hand, an undesirable precipitation of the Zn^{2+} takes place when the temperature is over 80 ºC.

- At 60 ºC the iron removal yield is increased with the air flow until 1,25 L/min, over this point the oxidation is maintained (65,89% of removal). At 80 ºC the purification stage has the same behaviour, but the removal is increased until the critical point (78,15 % removal) at 2,75 L/min. These air flow rates are dependent of the gas-liquid facility used.
- The pH decrease can be associated with ammonia losses. So, with the buffer effect generated in the liquor by carbonates, these losses are more affected by the air flow stripping than by an increase of the process temperature.
- The economy of the process and its environmental impact are affected by ammonia losses, being this an important consideration in this research. Therefore, the oxidation stage has been optimized at 80 ºC and 2,25 L/min of air flow. At these operation conditions the process reach enough iron removal (76,26 %) and the ammonia losses, remain within acceptable limits. Using the studied optimal conditions for the oxidation stage (80ºC and 2,25 L/min air flow), the kinetic is optimized so the operation is finished after 70 minutes.

3.4.3. CONCLUSIONS OF THE AMMONIACAL CEMENTATION STAGE

The conclusions reached after the in-depth study about the cementation stage are:

- The purification stage through cementation is an effective process in order to obtain the required impurities concentration in the liquor. This is necessary to reach the target quality of the final product.
- The optimal zinc dust concentration to minimize the impurities concentration in the liquor is 1,33 g/L at 25 ºC. These removal yields are higher than the specification of the final product, so it is not necessary to operate at temperatures higher than the room one.

- As the difference of reduction potential between an ionic impurity and the Zn^{2+} one decreases, higher zinc dust must be added to eliminate this metallic ion by cementation.
- After the kinetic study, the optimized time to get an acceptable removal of all impurities in the cementation step is 45 minutes at room temperature.

3.4.4. CONCLUSIONS OF THE PRECIPITATION STAGE

The conclusions after the in-depth study about the cementation stage are:

- The recovery of dissolved zinc by carbonation through CO_2 injection increases with increasing the gas flow rate. After experimental work it can be conclude that the optimized CO_2 flow is 6 L/min for the experimental facilities used.
- After the kinetic study of the precipitation stage it can concluded that 40 minutes is the optimized time in order to obtain the maximum recovery yield (around 90 %).
- The exhausted liquor after all these hydrometallurgical stages contains 7,14 g/L of dissolved zinc and 43,5 g/L of ammonia (aq.), therefore the design of an hydrometallurgical stage to recover them must be studied.

3.4.5. CONCLUSIONS OF THE CALCINATION STAGE

The conclusions after this in-depth study about the calcination stage are:

- The TGA analysis indicates that the free water removal takes place while heating until 100 ºC (18,06 % of weight loss). The carbonates and absorbed water are removed between 100 ºC and 300 ºC (76,15 %

of weight loss). The zinc oxide losses the 5,79 % of its weight before reaching 600ºC. This reduction is associated to the removal of some impurities (chlorides, fluorides, sulphur compounds...).

- 600 ºC is the optimal temperature in order to obtain the required quality of zinc oxide with a minimum energetic expenditure.
- The kinetic of the calcination improves with temperature, but the energetic spending increases. Therefore, the optimized conditions for the calcination stage are 600ºC and 45 minutes in order to obtain the target product.

3.4.6. CONCLUSIONS OF THE AMMONIA RECOVERY STAGE

3.4.6.1. Conclusions of ammonia balance

The conclusions after the in-depth study about the ammonia balance are:

- 80 % of the required ammonia to obtain high purity zinc oxide can be recovered (2,21 mg / g WO).
- 44 % of the recoverable ammonia (1,22 mg / g WO) appears in the exhausted liquor. So, the need of an ammonia recovery stage has been confirmed, where the ammonia must to be recovered from the liquid phase obtaining a gaseous stream with optimal conditions to regenerate the hydrometallurgical liquor.

20 % of required ammonia (0,55 mg / g WO) seems to be unrecyclable ammonia losses, which must be treated to avoid a negative environmental impact of the production process. The treatment to prevent ammonia emissions could be carried out through acid absorption.

3.4.6.2. Conclusions of ammonia recovery stage

The conclusions after the in-depth study about the ammonia recovery stage are:

- A sodium hydroxide is the chosen alkaline solution to increase the pH of the exhausted liquor over 11,5. This liquor can be previously used to treat the solid residues generated in the main processes to recover some zinc, being optimized at 6,5 M of NaOH concentration.
- The mixing ratio to maintain the pH of the exhausted liquor above 11,5 with a caustic soda solution of 6,5 M was optimized and it is 1 volume of exhausted liquor per 1/2 volume of caustic solution.
- The optimal temperature of the ammonia recovery process was fixed at 60 ºC. This temperature (at least) is necessary for reaching the maximum ammonia recovery in this step. On the other hand, 30 L/min is the optimal air flow in order to obtain the target objective of the process in the absorber reactor used (geometry of the designed absorption system).
- The optimal ammonia recovery yield at the studied conditions is 98,4 % and the zinc recovery yield is 86,3 %, when the optimal time to complete the process is 100 minutes.

The technical viability of ammonia recovery stage was demonstrated and its adequacy to the liquor regeneration stage, modifying the air flow rate to overcome the head loss of the system. It is really important to control the flow rate to overcome the pressure drop, but the flow which causes the ammonia stripping in the absorption must be avoided.

3.4.7. CONCLUSIONS OF EXHAUSTED LIQUOR REGENERATION STAGE

3.4.7.1. Conclusions after experimental study of water – CO_2 absorption system

The following conclusions were obtained after the experiments with stirred tank:

- High CO_2 flows involve important increases in the absorption velocity in the aqueous solution.
- The stirring has some direct influence in the liquid – gas contact. Therefore, the absorption velocity increases when the rotation speed is higher.
- The calculated ($k_L.a$) for the CO_2 absorption in the stirred tank pilot plant with 1 L/min gas flow is 0,00019498 s^{-1} (at the used conditions). This value is slightly below the order of magnitude for mass – transfer parameters in industrial reactors, 0,005 – 0,8 s^{-1} for mechanically stirred tanks (Trambouze, P. And Euzen, J.P., 2004).

The calculated ($k_L.a$) demonstrates that the flow rate has an important influence on the absorption process. It was also checked that the stirring speed has a lower influence on the mass transport.

3.4.7.2. Conclusions after experimental study of NH3 – water – CO2 absorption system

After the different experiments in order to analyze the NH_3 – Water – CO_2 absorption system with a pilot plant and the comparison between experimental data and the mathematical model, the following conclusions were extracted:

- The CO_2 capture, measured as the pH decreasing, is higher when the NH_3 concentration in the liquor is bigger. This process requires a high ammonia content and a pH over 8,5.
- Higher concentrations of NH_3 in the liquor generate a greater formation of carbonates and consequently the target buffer effect in the solution to be regenerated.
- The obtained results at different temperatures show that their influence in the process changes with the absorption liquid concentration. This fact, however, indicates that the reactions in the CO_2

(g) capture process in ammonia liquors are diffusion-controlled or diffusion-limited .

- The mathematical model developed fits properly until the NH_3 concentration is depleted. During the chemical reaction regime, the model simulates the CO_2 absorption process. When ammonium bicarbonate aqueous solutions are used as absorbent, the adjustment of the model with experimental results is not correct, because the initial concentrations are too close to the equilibrium conditions.
- The mathematical model has been improved in order to solve the mentioned fitting problems, obtaining a higher goodness of fit. Therefore, can be concluded that the absorption system is governed by the equilibrium reactions, considering instantaneous the kinetic reactions.
- The calculated enhancement factor (E) is 11,38. Therefore, the reaction when dissolved NH_3 exists in the absorption liquor is really fast. At this fast reaction regime, E = Ha, and all the chemical reaction take place inside the liquid film.
- The designed mathematical model could be an interesting tool to study the influence of the operation parameters in this hydrometallurgical liquors regeneration stage. But only it was verified when the absorption process satisfied the mentioned conditions (until the NH_3 concentration is depleted).

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CHAPTER 4

4. THE PURIFICATION OF WAELZ OXIDE IN ORDER TO USE AS THE MAIN SOURCE IN THE ELECTROLYTIC ZINC PRODUCTION PROCESS

In this part of the thesis, an in-depth study about the purification of Waelz oxide in order to use it as an acceptable source for the electrolytic zinc production process will be presented. A careful consideration to remove the halogens (fluorine and chlorine concentration) is crucial for this purpose.

4.1. INTRODUCTION

Nowadays, the Waelz oxide is useful as one of the raw materials for metallic zinc production in the Imperial Smelting Furnace, but some impurities limit its use in the leaching stage of the electrolytic process. The most damaging substances which the Waelz oxide contains are the fluorides, because they cause the corrosion of the aluminium cathodes. The accepted fluorine concentration in the liquor to be feed to the cells must be controlled to be less than 50 mg/L (de Goicoechea y Gandiaga, N. Et al., 1999). The halogens quantity in the zinc concentrates degrade the product value (Gouzhu, Y. Et al., 1999), specifically a high fluorine concentration is more detrimental than other impurities, for instance cobalt, nickel or cooper (Garcia – Carcedo, F. Et al., 2000).

Therefore, in this research the different hydrometallurgical processes in order to remove fluorides from Waelz oxide have been studied. So far, there are different strategies to purify the Waelz oxide:

- **Waelz process modifications:** the use of some gas injection in the furnace such as hydrogen (Antrekowich, J., 2004), CO_2 (Stallone, K. B., Et al, 2003) or the combining of roasting and leaching with sulfuric acid in the kiln (Lan, Y. Et al., 2005).
- **Leaching process implementation:** the double leaching with sodium carbonate (Dañobeitia, I. Et al., 1996) and the leaching with aluminium salts at pH = 3 – 4,2 (Jomoto, K. Et al., 1995).

4.2. EXPERIMENTAL

All experiments were conducted with Waelz Oxide (WO), kindly supplied by BEFESA ZINC S.A. – ASER. The experimental methods were described for each designed and studied stage.

All experiments were carried out in 2 litter glass reactor with mechanic stirring. The reactor works in a thermostatic bath and it is operated closed in order to avoid the water losses by evaporation.

An Orion Star A329 Multiparameter meter was used as pH and temperature controller. The pH control of the leaching, precipitation and washing stages was carried out automatically by the acid/alkali addition through a peristaltic pump of the Multiparameter.

A Millipore ASME-MU High pressure filter was used to solid/liquid separation so as to take the samples which were analyzed.

4.3. RESULTS AND DISCUSSION

4.3.1. SELECTIVE REMOVAL OF FLUORINE BY LEACHING

In this chapter a preliminary study of the fluorine removal from Waelz oxide will be presented. The selective removal of fluorine by leaching without significant zinc losses has been researched, because this possibility should be the best and the easiest solution in order to obtain the target product.

So, the initial experiments were carried out to analyze the fluorine solubility from Waelz oxide by leaching. The different hydrometallurgical liquors and their influence of the main operation parameters were tested taking into account the existing data or studies.

4.3.1.1. Fluorine removal by leaching with aqueous sodium salts solutions

The Waelz oxide was leached with different aqueous sodium salts solutions, at different pH values in order to study the yield of fluorine removal and their solubility using the following operating conditions that appear in Table 4.1:

Table 4.1: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	25
Water volume	L	0,250
Aqueous sodium compounds concentration	g/L	50
pH (modify with NaOH (aq))		Changes every experiment
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The results of these experimental tests are following the ones:

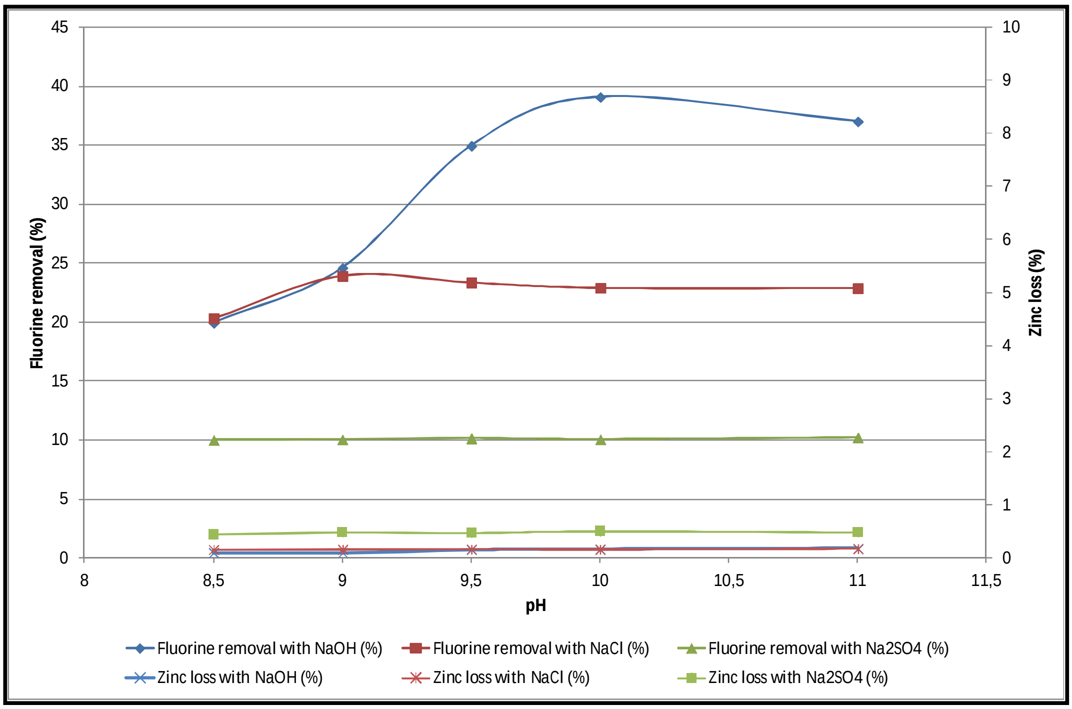


Figure 4.1: Fluorine removal and zinc loss as function of the pH

After these results it can be concluded that the highest fluorine removal is obtained with NaOH liquor, but it is lower than the target objective (the accepted fluorine concentration in the liquor to be feed to the cells must be controlled to be less than 50 mg/L after the leaching of the obtained new product). On the other hand, the zinc losses are very small, and this virtue is an important conclusion. Therefore, the liquor of aqueous NaOH and aqueous sodium carbonate (used industrially) were chosen in order to analyze the influence of the operating conditions to improve the results at 25ºC and 1 bar.

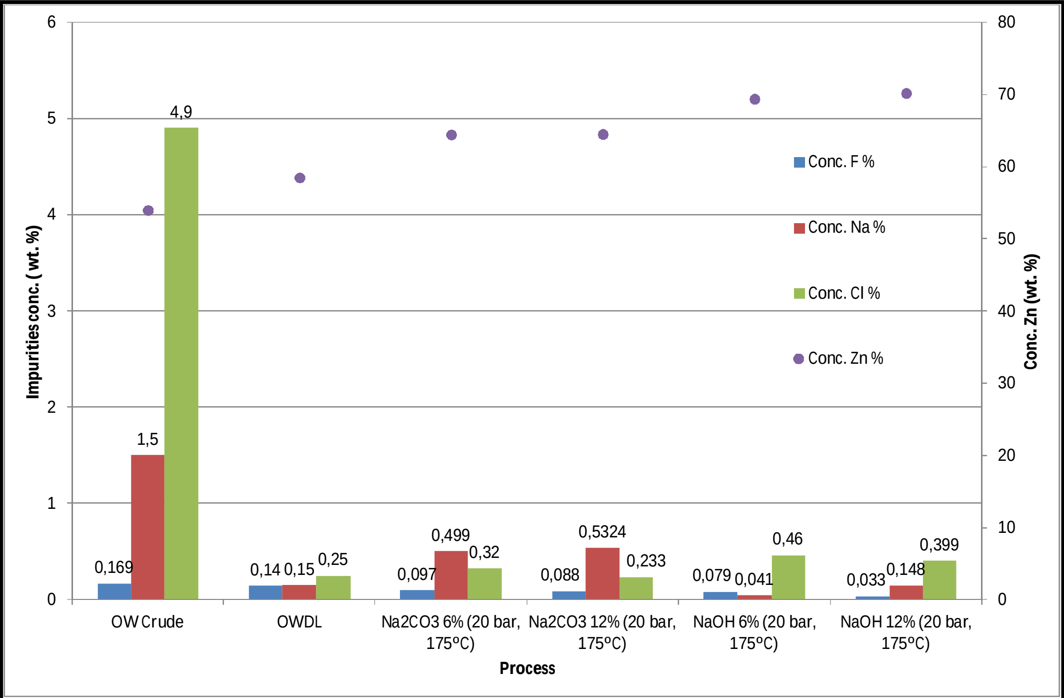


Figure 4.2: The zinc, sodium, chloride, and fluorine concentration as function of the leaching conditions

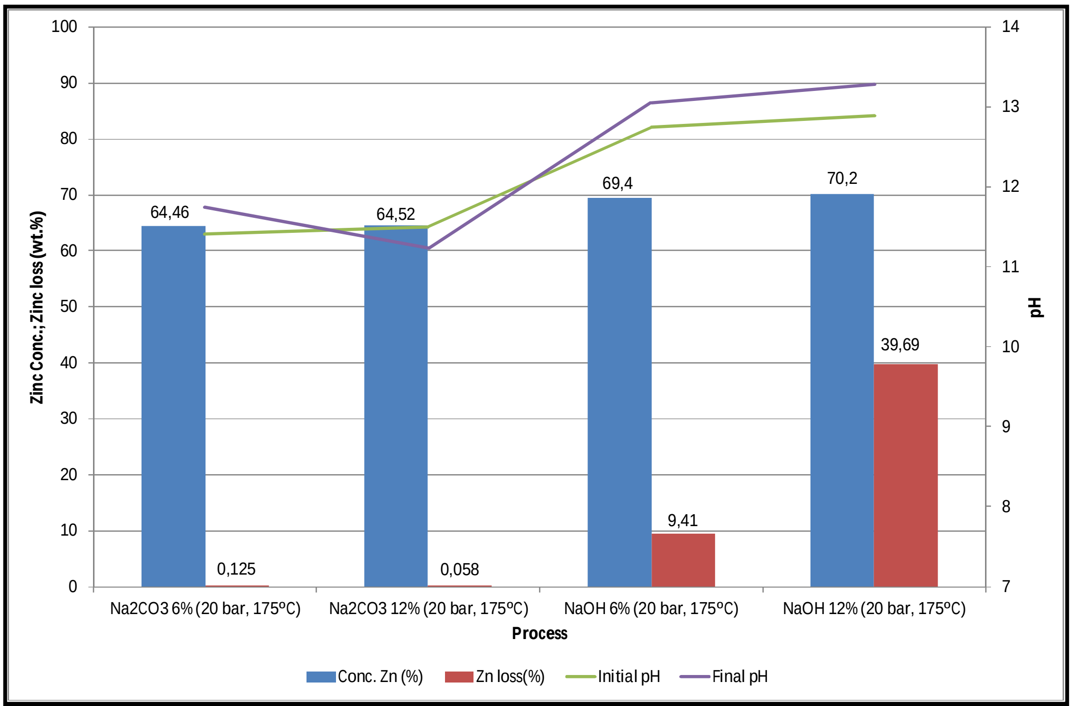


Figure 4.3: The zinc concentration, zinc loss and pH variation as function of the leaching conditions

The Figure 4.2 and Figure 4.3 show the alkaline leaching effects in the Waelz oxide hydrometallurgical treatment under pressure. In the Figure 4.2 the evolution of the final products concentration leaching at 175 ºC and 20 bar when the concentration of the liquor is modified has been studied. On the other hand, the Figure 4.3 shows the zinc concentration in the obtained product, taking into account the zinc loss by leaching under pressure.

4.3.1.2. Fluorine removal by leaching with aqueous aluminium salts solutions

Waelz oxide was leached with different aqueous aluminium salts solutions, at different pH values in order to study the yield of fluorine removal and their solubility at the following operating conditions that appear in Table 4.2:

Table 4.2: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	25
Water volume	L	0,250
Aqueous aluminium salt concentration	g/L	50
pH (modify with H_2SO_4 (aq) or HCl (aq) or NaOH (aq))		Changes every experiment
Ratio S/L		0,15
Stirring speed	r.p.m	700
Time	min	90

The results with different aqueous aluminium salts liquors of these experimental tests are the following ones:

Aluminium sulphate aqueous solution:

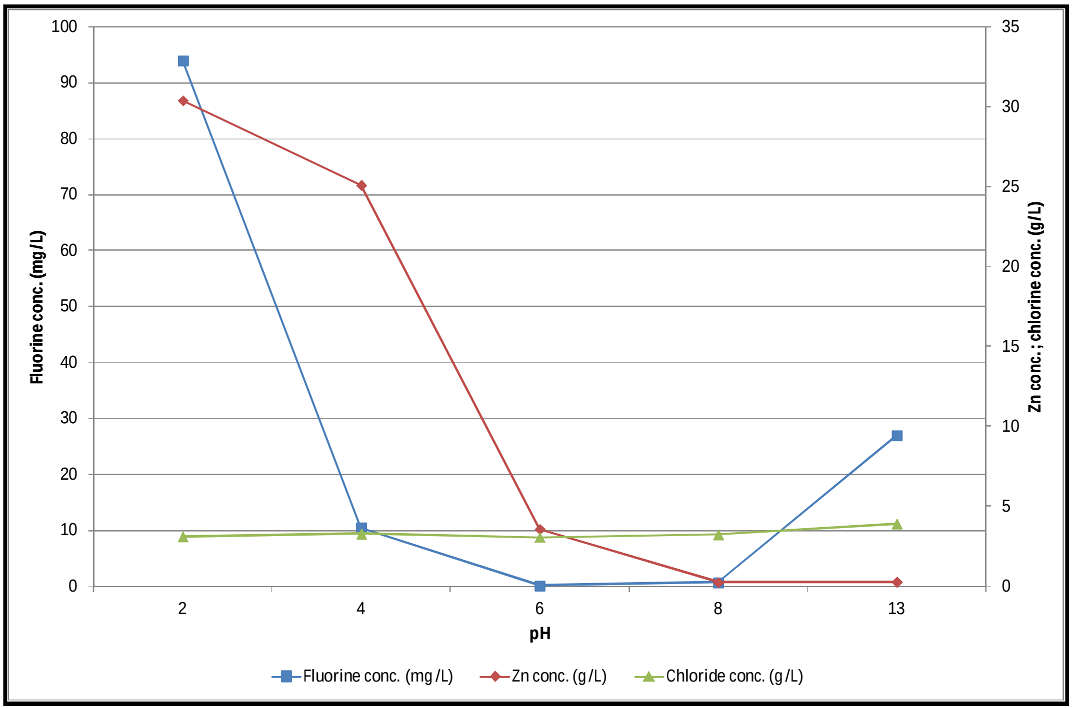


Figure 4.4: The zinc, fluorine and chloride concentration as function of the pH

Aluminium chloride aqueous solution:

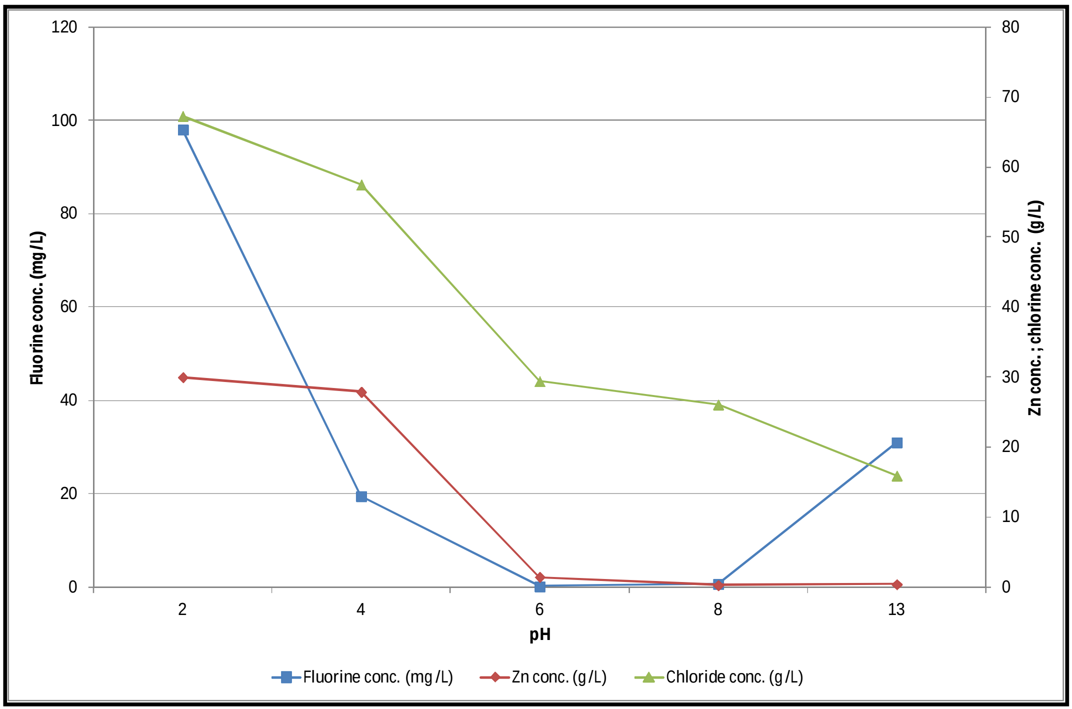


Figure 4.5: The zinc, fluorine and chloride concentration as function of the pH

Both graphs represent the fluorine, zinc and chloride concentrations in the liquor after leaching at the specified pH. Therefore, the influence of the pH in the solubility of these compounds can be noticed as very important.

In the Figure 4.4 and Figure 4.5 the relation between zinc or fluorine solubility and pH was shown. So, the influence of the pH in the aluminium and the fluorine solubility will be an important parameter:

Aluminium sulphate aqueous solution:

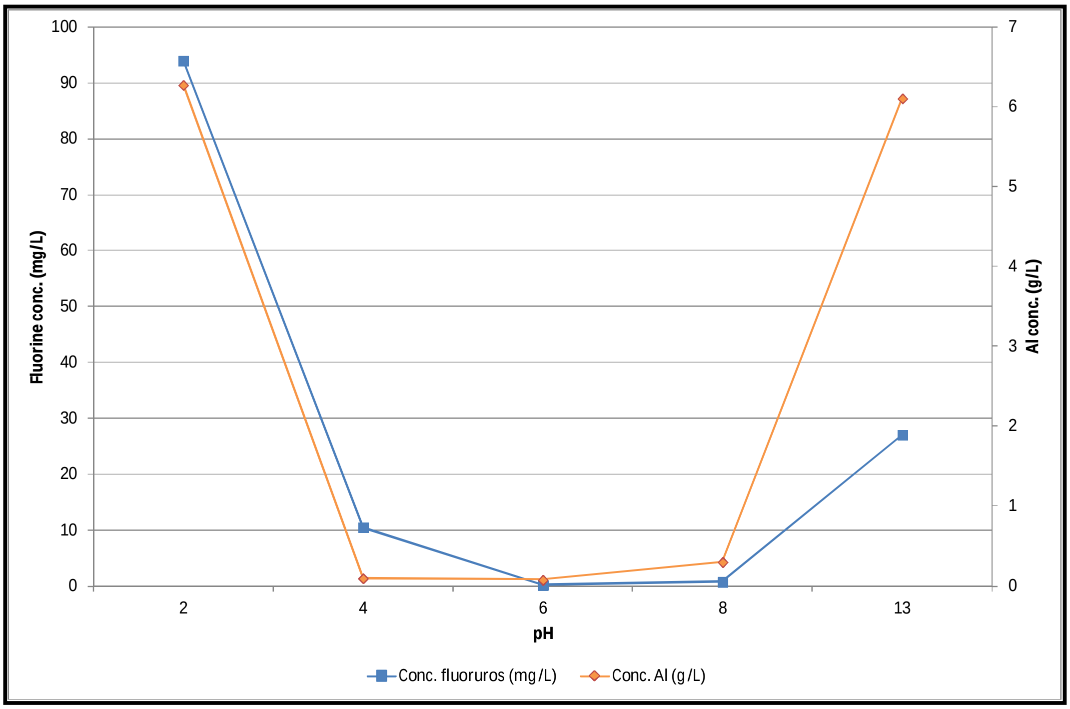


Figure 4.6: The fluorine and aluminium concentration as function of the pH

Aluminium chloride aqueous solution:

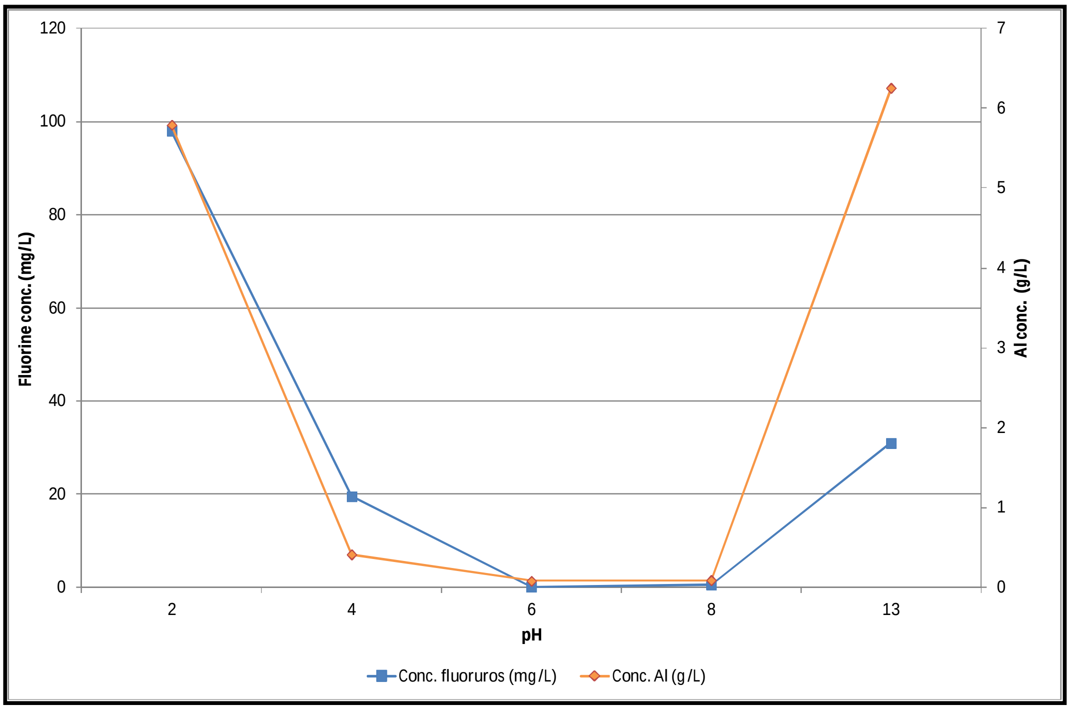


Figure 4.7: The fluorine and aluminium concentration as function of the pH

4.3.2. THE STUDY OF A METHODOLOGY IN ORDER TO FLUORINE REMOVAL BY THE SELECTIVE PRECIPITATION IN ALUMINIUM PRESENCE

From the preliminary study about fluorine solubility as a function of the pH and Al^{3+} (aq) concentration, a difference between Zn^{2+} and F^{-} solubilities has was measured within some pH ranges. Hence, a methodology of fluorine removal by selective precipitation was tested.

Therefore, the designed procedure consists of zinc and fluorine leaching with the formation of soluble aluminium – fluorine complex ions. After this step, the pH was modified in order to precipitate the aluminium – fluorine compounds without solved zinc losses.

4.3.2.1. Technical considerations of the fluorine selective precipitation in aluminium presence

The pH has some influence on the solubility of many species. Thus, this property is used in the chemical industry in order to separate them. Fractional precipitation takes advantage of the different solubilities of ions. The pH variations affect the solubility of slightly soluble compounds containing anions that are conjugate bases of weak acids, such as F^-, NO_2^-, OH^-, SO_3^{2-}, and PO_4^{3-}, but not the one of those containing anions which are conjugate bases of strong acids, such as SO_4^{2-}, Cl^-, Br^-.

Consider the following equilibrium reaction involving metal solubility:

$$\mathbf{MA_x\ (s) \leftrightarrow M^{x+} + x\ A^-}$$

$$\mathbf{K_{sp} = [M^{x+}]\ [A^-]^x}$$

These equations indicate that the equilibrium concentration (in precipitation processes this is referred to as residual concentration) of the metal in solution is solely dependent upon the concentration of A^-. When A^- is a hydroxide ion the residual metal concentration is a function of pH such that (Edzwald, J., 2010):

$$\mathbf{\log[M^{x+}] = \log K_{sp} - x\ \log K_w - x\ pH}$$

Thus, the designed methodology, in order to remove the fluorine from the leached Waelz oxide, uses the formation of complex ions adding soluble aluminium salts. Once the AlF_n^{3-n} complexes are formed, the pH of the solution is modified for the purpose of decreasing the solubility of these complex ions. The main chemical reactions in the complexes formation by aluminium salts addition into the leaching liquor are the following ones (Steel, K. M. Et al., 2008):

$\mathbf{Al^{3+} + F^- \Leftrightarrow n\ H^+ + AlF(OH)_n^{2-n}}$

$Al^{3+} + F^- \Leftrightarrow H^+ + AlF(OH)^+$

$Al^{3+} + F^- \Leftrightarrow 2\ H^+ + AlF(OH)_2$

$Al^{3+} + F^- \Leftrightarrow 3\ H^+ + AlF(OH)_3^-$

Therefore, the goal of this study was to find the pH value that makes the K_{sp} of the aluminium fluorine complexes (after the complexes have been formed through the described reactions) far less soluble than Zn^{2+} ions, so the fluorine can be selectively removed with this method.

4.3.2.2. Optimization of the selective precipitation of fluorine compounds

The designed experimental work in order to study the selective precipitation of fluorine compounds was carried out using the obtained leaching liquor in the previous chapter with sulphuric acid and aluminium sulphate at pH = 2. The characterization of this solution is the following one that appears in the Table 4.3 and the Table 4.4:

LEACHING LIQUOR at pH=2 with 50 g/L $Al_2(SO_4)_3$

Table 4.3: Metallic composition

Element	**Concentration (mg / L)**	**Leaching stage recovery (%)**
Cu	2,9	1,2988
Zn	30.400	**98,3309**
Ni	0,3	0,6550

Cr	1,4	4,8907
Mn	14,9	5,2051
Fe	72,3	4,5101
Cd	45,2	39,4747
Sn	0	0
Pb	9,1	0,1766
Al	6.274	

Table 4.4: Other composition parameters

Parameter	**Quantity**
pH	2
Fluorine concentration (ppm)	94
Chlorides concentration (ppm)	3112

Hence, the study of the precipitation effectiveness in the fluorine removal has been carried out under the following conditions that appear in Table 4.5:

Table 4.5: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	20
Liquor volume	L	0,235
Initial pH		2
Precipitation pH		Changes in every experiment

Stirring speed	r.p.m	700
Time	min	40

The obtained results of these experimental tests are the following ones:

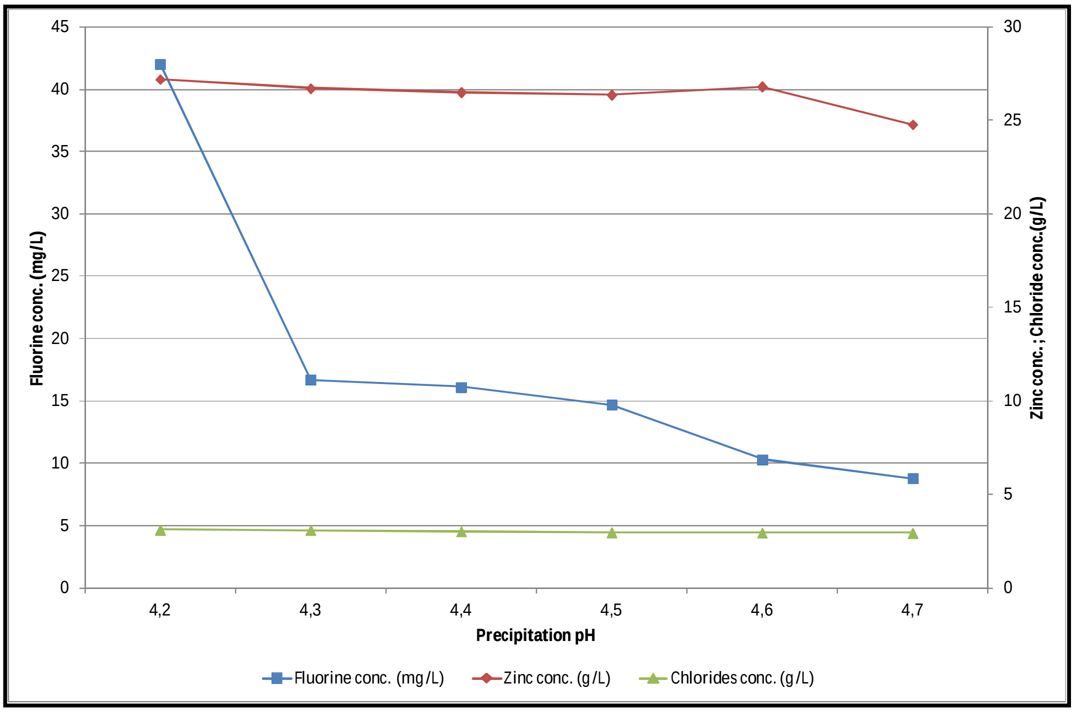


Figure 4.8: The fluorine, zinc and chloride concentration as function of the pH

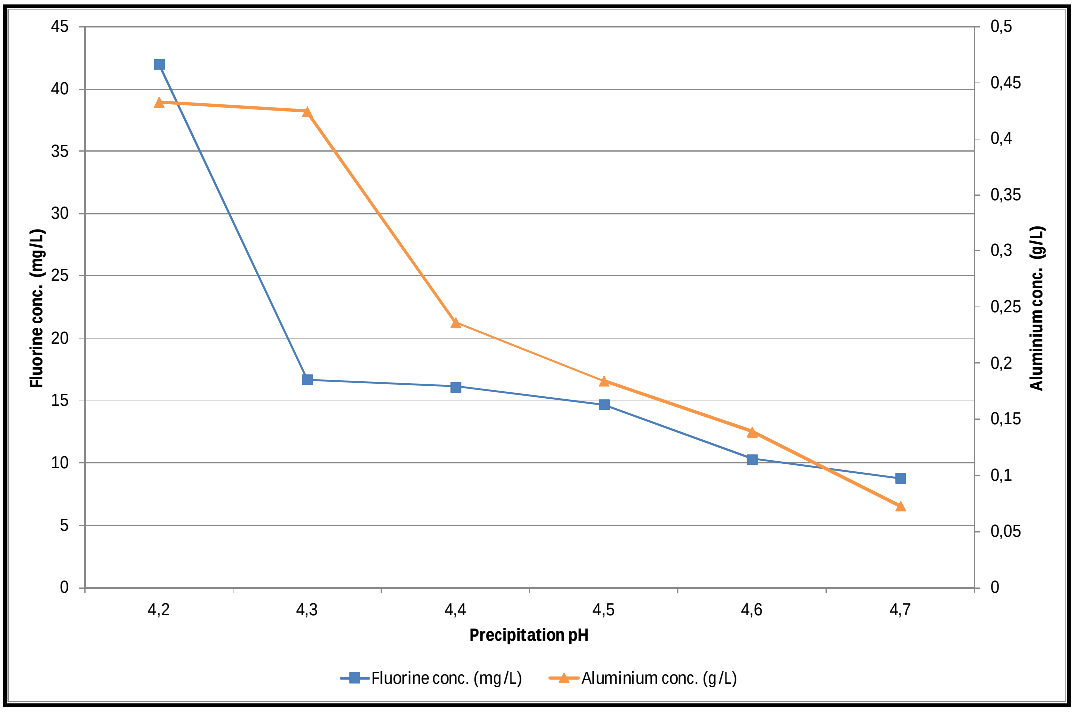


Figure 4.9: The fluorine and aluminium concentration as function of the pH

Both figures (Figure 4.8 and 4.9) represent the fluorine, zinc, chloride and aluminium concentrations in the liquor after the precipitation step with NaOH (aq) at the specified pH. Therefore, the influence of the pH in the solubility of these compounds can be clearly noticed.

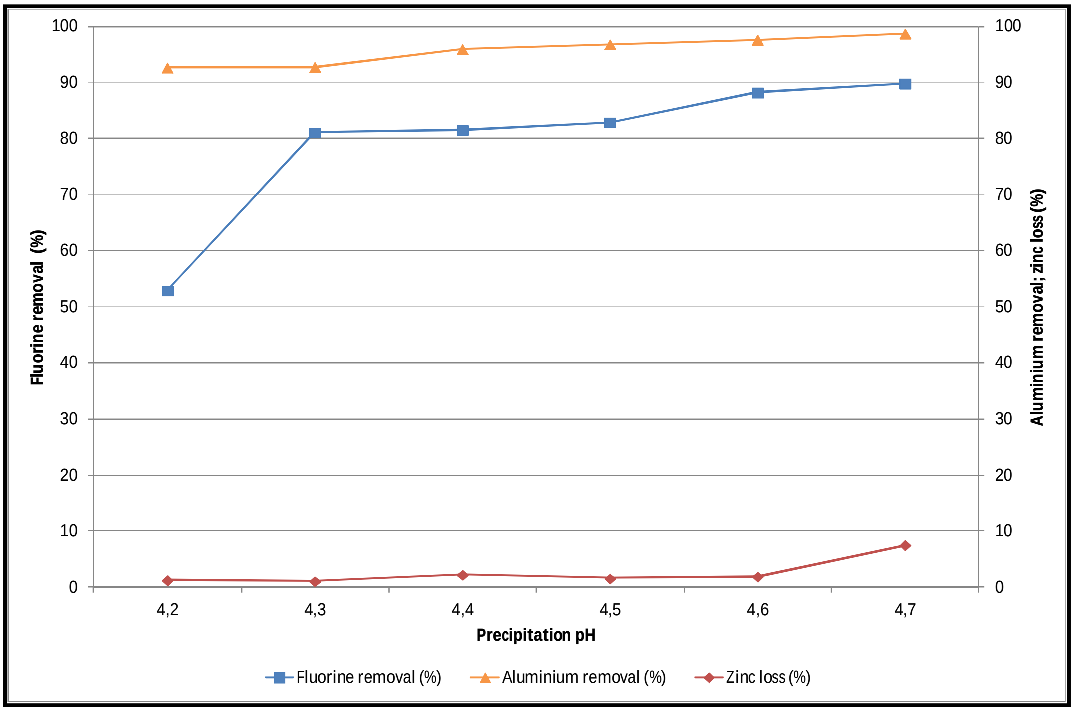


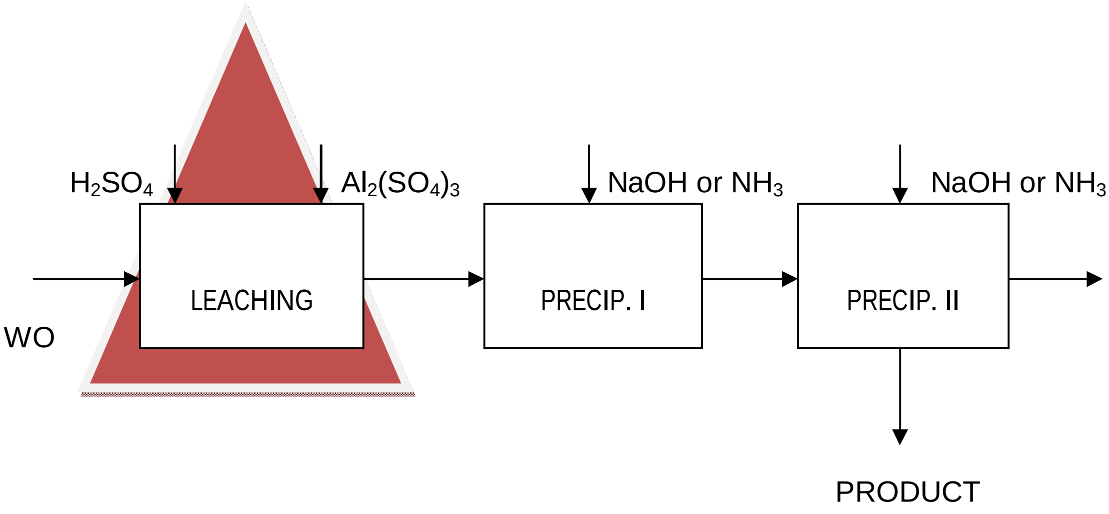
Figure 4.10: The zinc loss, fluorine and aluminium removal as function of the pH

Figure 4.10 shows the evolution of the fluorine removal, the aluminium removal and zinc loss when the pH of the solution was modified in this precipitation stage.

4.3.3. DESIGN AND OPTIMIZATION OF HYDROMETALLURGICAL PROCESSES IN ORDER TO REMOVE THE FLUORINE FROM WAELZ OXIDE

After the study of the obtained data in the preliminary research of the fluorine removal by leaching, a hydrometallurgical methodology was designed and optimized. The high solubilities of fluorine and zinc at low pH, the different solubility between zinc and fluorine due to aluminium presence within a specific range of pH and the washing effect of sodium hydroxide and sodium carbonate aqueous solutions were been taken into account.

4.3.3.1. Leaching stage with sulphuric acid and aqueous aluminium sulphate liquor



The first step of the designed hydrometallurgical process is the leaching stage. The solid zinc contained in the Waelz oxide is solved in aqueous phase using a sulphuric acid and adding aluminium sulphate. The goal of this initial process is to find the best operating conditions in order to reach the highest solubility of the zinc and fluorides.

a. Technical considerations of sulphuric leaching in the presence of aluminium

Leaching is a liquid-solid operation. The two phases are in intimate contact, the solute(s) can diffuse from the solid to the liquid phase, which causes a separation of the components originally in the solid. In the metals processing industry, leaching is used to remove the metals from their ores, which contains many undesirable constituents, as solute salts.

Raw material

(ZnO (s), ZnS (s), Zn_2SO_4 (s), ...)

\+

Solvent

(Acids (l), alkalis (l), organics (l), ...)

=

Leaching liquor

(Zn^{2+} (aq), $cations^{n+}$ (aq), $anions^{n-}$ (aq), complex (aq), ...)

\+

Solid waste

(Non-soluble solids)

The leaching stage is conditioned by the size of the solid, the solid/liquid ratio, the temperature, the solubility of the target product in the used solvent and the stirring speed, among other operation parameters.

a.1. The main chemical reactions of sulphuric leaching in the presence of aluminium

The optimization of a leaching stage is the result of the experimental study of operating variables, which have a direct impact on these chemical reactions (Bell, R. P. Et al., 1956; Hem, J. D., 1968 and McTingue, P. Et al., 1985):

<u>Leaching liquor equilibrium reactions:</u>

$H_2SO_4 \Leftrightarrow H^+ + HSO_4^-$

$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-}$

$H_2O \Leftrightarrow H^+ + OH^-$

$Al^{3+} + SO_4^{2-} \Leftrightarrow AlSO_4^+$

$AlSO_4 + SO_4^{2-} \Leftrightarrow Al(SO_4)_2^-$

$Al^{3+} + n\,H_2O \Leftrightarrow Al(OH)_n^{(3-n)+} + n\,H^+$ n = 1 and 4

Leaching of zinc oxide reactions in used leaching liquor:

$ZnO + H_2O \Leftrightarrow Zn(OH)_2$ (Surface hydroxylation)

$Zn(OH)_2 + 2H^+ \Leftrightarrow Zn^{+2} + 2H_2O$ (Surface protonation)

Zinc, aluminium and fluorine equilibrium reactions:

$AlF_{n-1}^{4-n} + F^- \Leftrightarrow AlF_n^{3-n}$ n = 1 – 6

$Al^{3+} + 2\,F^- \Leftrightarrow H^+ + AlF(OH)$

$Al^{3+} + 2\,F^- \Leftrightarrow 2\,H^+ + AlF(OH)_2^-$

$Al^{3+} + 3\,F^- \Leftrightarrow 2\,H^+ + AlF_3(OH)^-$

$HF \Leftrightarrow H^+ + F^-$

$n\,HF + F^- \Leftrightarrow H_nF_{n+1}^-$ n = 1 – 4

$Zn^{2+} + n\,OH^- \Leftrightarrow Zn(OH)_n^{(2-n)+}$ n = 1, 3 and 4

Zinc, aluminium and fluorine solubility equilibrium reaction:

$Zn(SO_4) \Leftrightarrow Zn^{2+} + SO_4^{2-}$

$Zn(OH)_2 \Leftrightarrow Zn^{2+} + 2\,OH^-$

$Al_2(SO_4)_3 \Leftrightarrow 2\,Al^{3+} + 3\,SO_4^{2-}$

$Al(OH)_3 \Leftrightarrow Al^{3+} + 3\,OH^-$

b. Optimization of the sulfuric leaching stage

In this chapter the operation parameters of leaching liquor studied are presented and discussed. The highest solubility of zinc and the lowest reactants consumption have been the main goal of this experimental work. Several parameters were studied:

b.1. Optimization of solid / liquid ratio

The yield of zinc recovery in the leaching stage was studied, because the processing capacity of the designed methodology depends on this parameter. The dissolved fluorine and chlorine were measured during this experimental work. Hence, the study of the solid/liquid ration in the leaching step was carried out under the following conditions that appear in Table 4.6:

Table 4.6: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	20
Time	minutes	100
pH_0 (water+ lix.)		2,90
pH		2,00
Ratio S/L		Studied parameter
Composition:		
$Al_2(SO_4)_3$ (18-hydrate)	g	50
	Concentration (g/L)	100
H_2O	mL	500
Waelz oxide	g	Changes for each experiment

The obtained results of these experimental tests are the following ones:

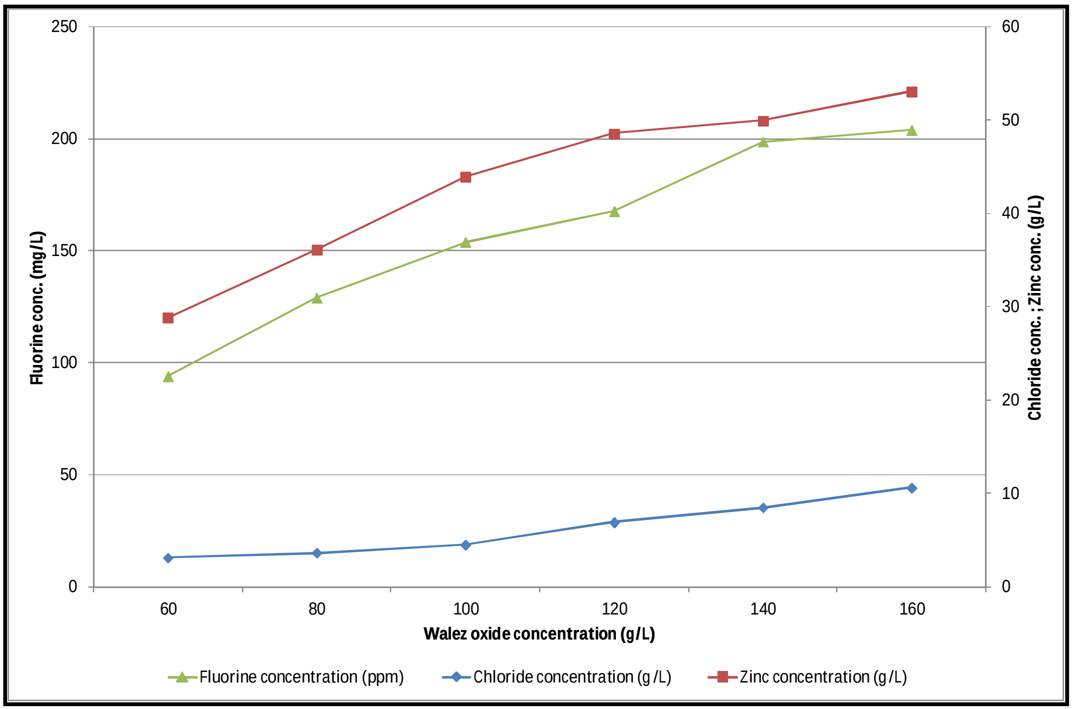


Figure 4.11: The zinc, fluorine and chloride concentration as function of the processed WO

Figure 4.11 represents the fluorine, the zinc and the chloride concentration in the liquor after the leaching changing the S/L ratio in the process at the aforementioned conditions.

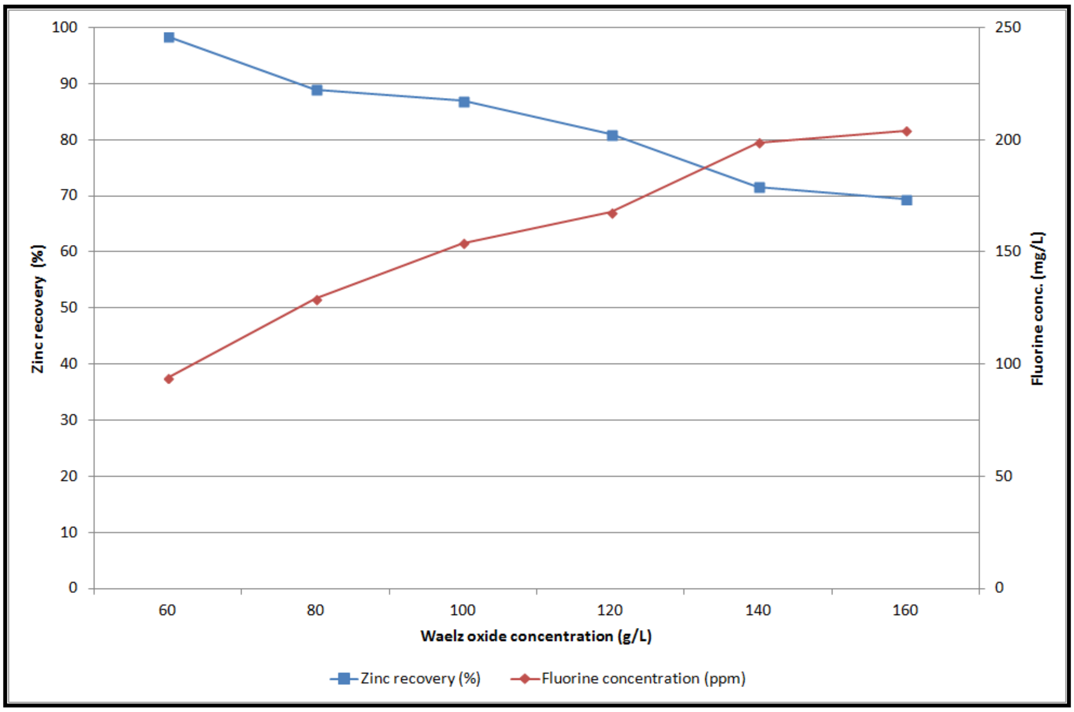


Figure 4.12: The zinc recovery and fluorine concentration as function of the processed WO

Figure 4.12 shows the zinc recovery and the fluorine concentration in the solution as a function of the Waelz oxide processed in the leaching stage.

b.2. Optimization of solid / liquid ratio at 60ºC

After the study of the influence of solid / liquid ratio in the zinc recovery by sulphuric leaching, the obtained data were compared to the results of similar experiments at 60ºC. The sulphuric acid concentration of the used leaching liquor at this temperature (60 ºC) is capable to solve all zinc, present as ZnO, in the raw material (Ballester, A. Et al, 2000). Therefore, the effect of the temperature in the leaching stage and the optimization of it were been carried out. Hence, the study of the solubilization effectiveness in this stage was carried out under the following conditions that appear in Table 4.7:

Table 4.7: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	60
Time	minutes	100
pH_0 (water+ lix.)		2,90
pH		2,00
Ratio S/L		Studied parameter
Composition:		
$Al_2(SO_4)_3$ (18-hydrate)	g	50
	Concentration (g/L)	100
H_2O	mL	500
Waelz oxide	g	Changes every experiment

The obtained results of these experimental tests are the following ones:

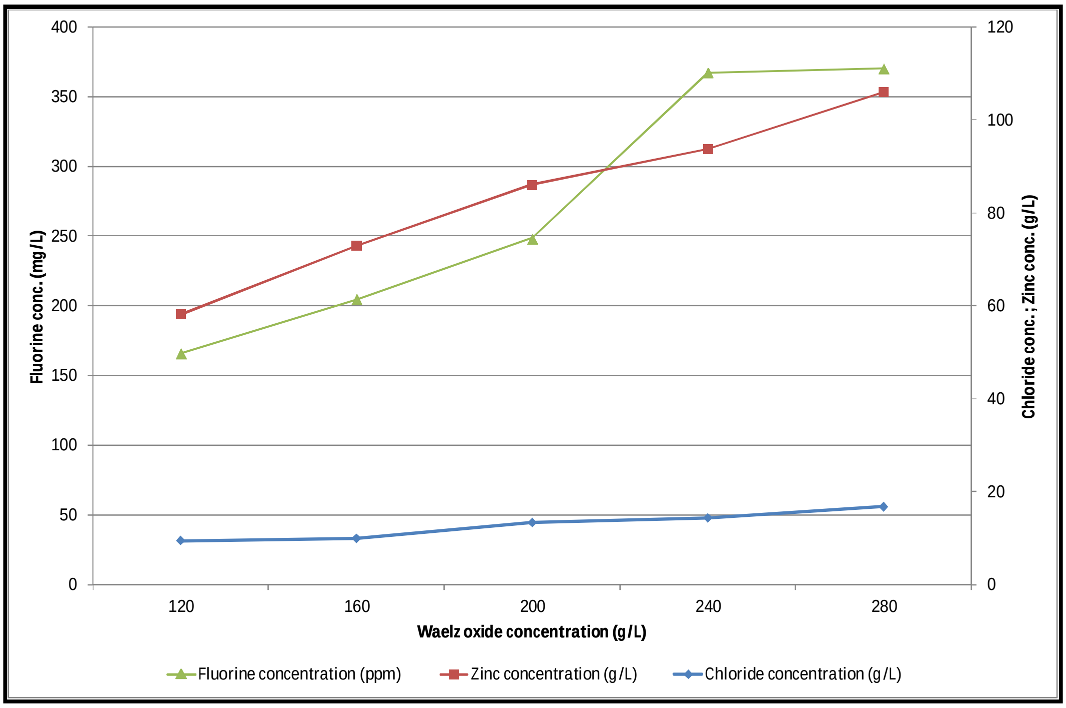


Figure 4.13: The zinc, fluorine and chloride concentration as function of the processed WO

Figure 4.13 represents the fluorine, the zinc and the chloride concentration in the liquor after the leaching changing the S/L ratio in the process at 60ºC in order to compare the influence of solid/liquid ration as a function of temperature.

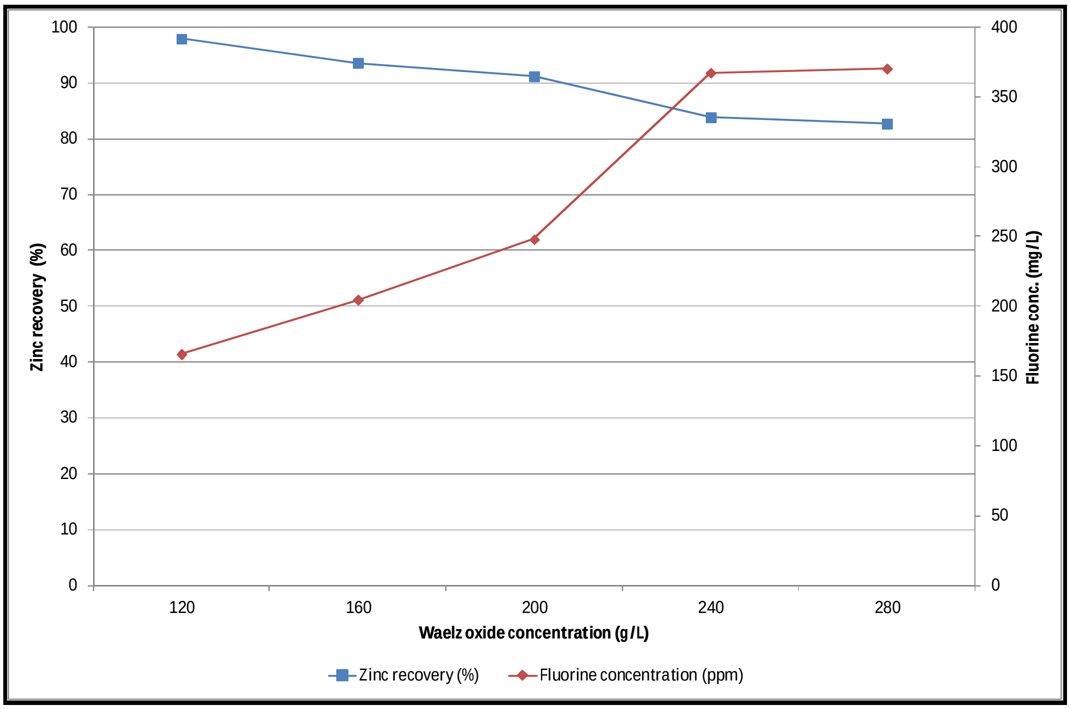


Figure 4.14: The zinc recovery and fluorine concentration as function of the processed WO

Figure 4.14 shows the zinc recovery and the fluorine concentration in the solution as a function of the Waelz oxide processed in the leaching stage at 60ºC.

c. Characterization of leaching liquor

The characterization of the obtained liquor at the optimal leaching conditions is shown in the Table 4.8 and 4.9:

LEACHING LIQUOR AT pH = 2,0 and 60°C

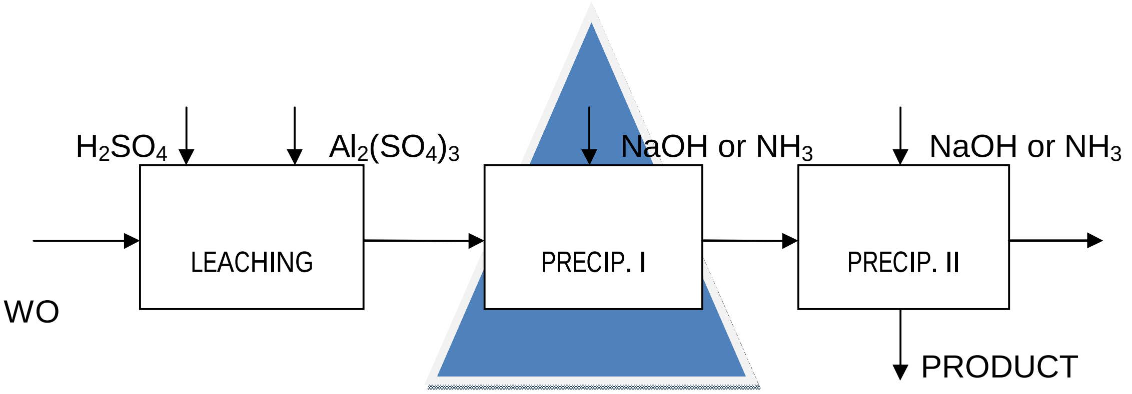
Table 4.8: Metallic composition

Element	Concentration (mg / L)	Recovery (%)
Cu	0,7	0,10
Zn	**86.730**	**91,23**
Ni	1,2	0,85
Cr	2,8	3,18
Mn	0,9	0,10
Fe	10,6	0,21
Cd	1,4	0,40
Sn	20,3	7,69
Pb	8,7	0,05

Table 4.9: Other composition parameter

Parameter	Quantity
pH	2,0
Fluorine concentration (ppm)	248
Chloride concentration (ppm)	13.300

4.3.3.2. Precipitation stage in order to remove the solved fluorine



The second step of the designed hydrometallurgical process is a precipitation of the solved fluorine. After the leaching stage with sulphuric acid and aluminium sulphate, the solved fluoride must be removed by precipitation, maintaining the solved zinc in the liquor. The goal of this stage was to find the best operation conditions in order to reach the highest fluorine removal with the lowest possible zinc loss.

a. Technical considerations of the precipitation stage in order to remove the solved fluorine.

This step has been designed based on the studied methodology to remove fluorine by the selective precipitation in aluminium ions presence. Thus, the technical considerations have been described in the Chapter 4.2.1.

a.1. Optimization of the aluminium / fluorine ratio.

In this chapter the operation parameters of the selective precipitation stage study are presented. The removal was carried out through insolubilisation of the aluminium and fluorine complexes when the pH of the liquor is increased. The optimal pH has been selected at 4,6 in the preliminary study (Chapter 4.2.1.), because at this point the fluorine removal is maximum (> 88 %) with the lowest zinc loss (< 2%).

Therefore, the optimal Al/F ratio was been study. The leaching stage was carried out under the selected conditions in the previous chapters, but modifying the $Al_2(SO_4)_3$ dosage. Hence, the study of influence of the aluminium concentration in the fluorine removal in this stage was carried out under the following conditions that appear in the Table 4.9 and the Table 4.10:

LEACHING STAGE

Table 4.9: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	60
Time	minutes	100
pH_0 (water + lix.)		2,90
pH		2,00
Ratio S/L		0,2
Composition:		
$Al_2(SO_4)_3$ (18-hydrate)	g	Studied parameter
	Concentration (g/L)	Studied parameter
H_2O	mL	500
Waelz oxide	g	100

PRECIPITATION I

Table 4.10: Experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	20

Time	minutes	30
pH_0(Leaching liquor)		2,00
pH		4,60
Volume	mL	570
Composition	mg/L	Fixed in the Chapter 4.1.3.4

The obtained results of these experimental tests are the following ones:

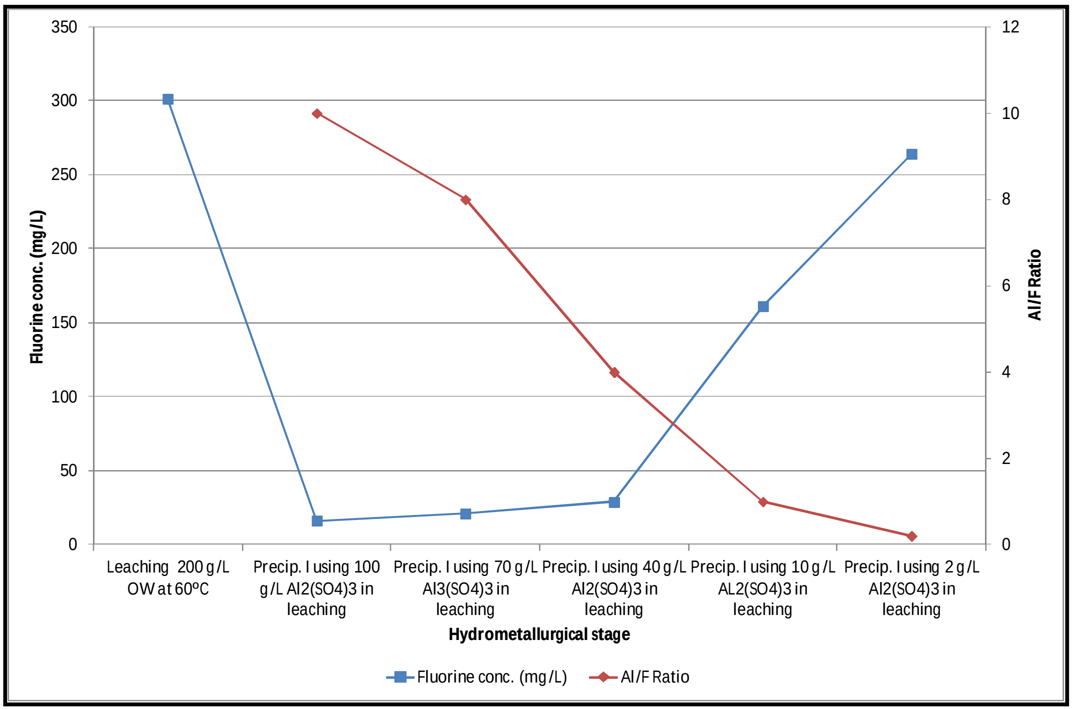


Figure 4.15: The relation between fluorine concentration and Al/F ratio

Figure 4.15 represents the fluorine concentration in the liquor in different stage as a function of the aluminium sulphate concentration in the leaching stage and the evolution of this fluorine since the leaching stage. Hence, the Al/F has been represented taking into account this aluminium sulphate dosage in the leaching stage and can be observed the influence of this parameter in the contraction of the fluorine concentration.

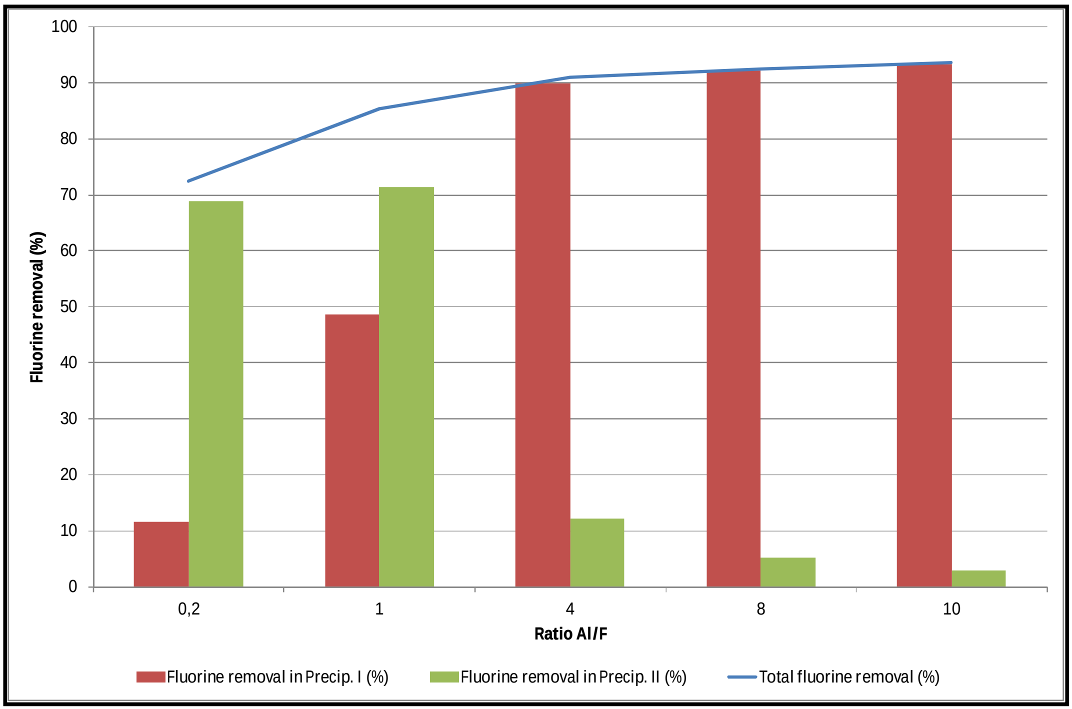
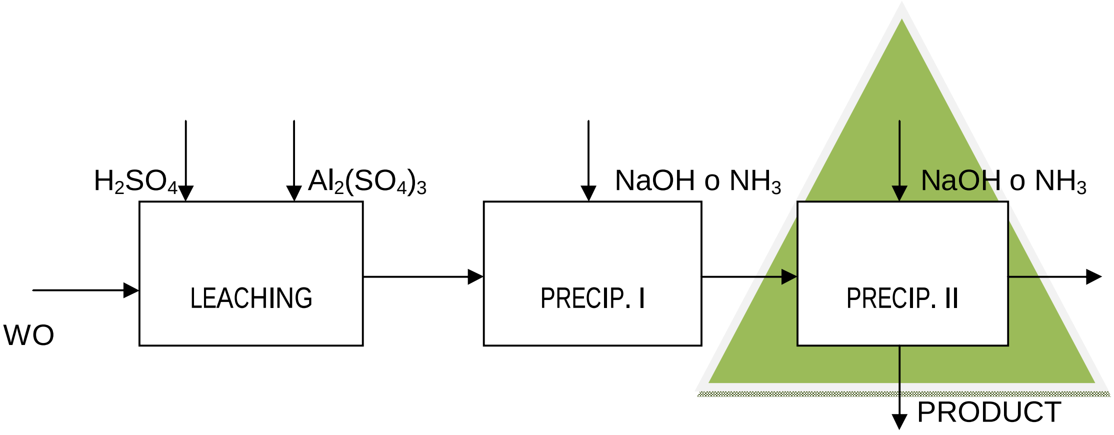


Figure 4.16: The fluorine removal as function of Al/F ratio

Figure 4.16 shows the evolution of the fluorine removal as a function of the Al/F ratio used in the leaching stage. The fluorine removal was studied after the two designed precipitation stages, the first one (Precip. I) is the selective precipitation stage at pH = 4,6 and the second one (Precip. II) is the zinc recovery stage at pH > 4,6 (this pH will be optimized in the next chapter).

4.3.3.3. Precipitation stage in order to recover the zinc content



The final step of the designed hydrometallurgical process is a precipitation of the solved zinc. After the leaching stage and the selective precipitation stages, the solved zinc in the liquor must be recovered by insolubilisation of solved zinc increasing the pH of the liquor. The goal of this stage is to find the best operation conditions in order to reach the highest zinc recovery. At this chapter, the study about the influence of different reagents in order to increase the pH in both precipitation steps is presented. On the other hand, the obtained quality is discussed as a function of the used raw material (Waelz oxide or Double leached Waelz oxide).

a. Technical consideration of precipitation stage in order to recovery the zinc content

Precipitation from aqueous solutions may be of the following kinds (Rosenqvist, T., 2004):

- Precipitation of hydroxides by change in pH without changes in oxygen potential.
- Precipitation of insoluble compounds or salts by addition of certain chemicals or by cooling.
- Precipitation by reduction or oxidation.

In this case, the pH affects the concentrations of ions in the solubility equilibrium. The magnitude of this effect can be estimated from the solubility product, in this case:

$$\mathbf{Zn(OH)_2\ (s) \Leftrightarrow Zn^{2+}\ (aq) + 2\ OH^-\ (aq)}$$

$$\mathbf{K_{sp}\ (25°C) = [Zn^{2+}].[OH^-]^2}$$

The precipitation occurs if $[Zn^{2+}].[OH^{-}]^2 > K_{sp}$, therefore $\mathbf{log[Zn^{2+}] = logK_{sp} -2(pH - pK_w)}$ quantifies the influence of the pH on the zinc recovery by precipitation.

b. Optimization of the precipitation stage in order to recovery the zinc content

The influence of some variables on the solved zinc precipitation stage is discussed. The recovery has been carried out through insolubilisation of the zinc when the pH of the liquor is increased over 6,5. For this reason, the experiments were carried out at pH = 7 and pH = 9, changing the processed raw material and the used reagents in order to increase the pH (NaOH and NH_3). Hence, this study was carried out under the following conditions that appear in Table 4.11:

PRECIPITATION II

Table 4.11: Experimental conditions

Parameter	Units	Quantity
Temperature	ºC	20
Time	minutes	30
pH_0(liquor from prep.I)		4,60
pH		Studied parameter
Volume	mL	605
Composition	mg/L	Obtained liquor after the optimized leaching and precipitation I.

The results of these experimental tests are the following ones:

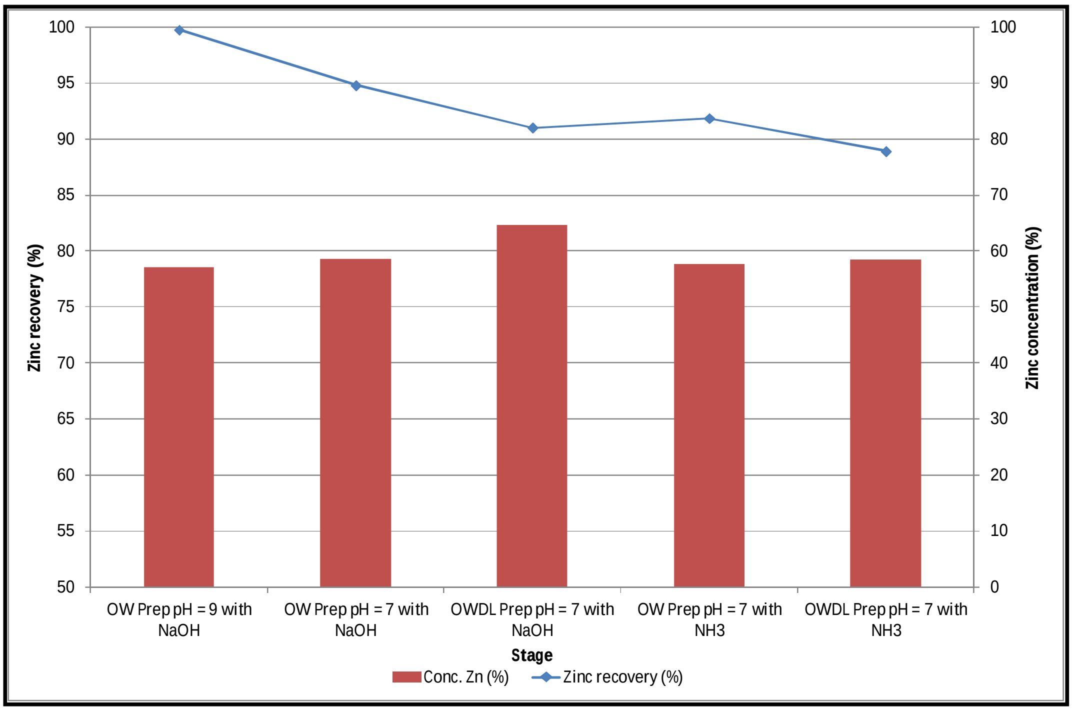


Figure 4.17: The zinc recovery in the precipitation II and zinc concentration in the obtained product as function of the used raw material and pH in the precipitation stage

In the Figure 4.17 the zinc recovery after the precipitation II has been shown, taking into account the final pH, the used reagent in order to modify the pH and the processed raw material.

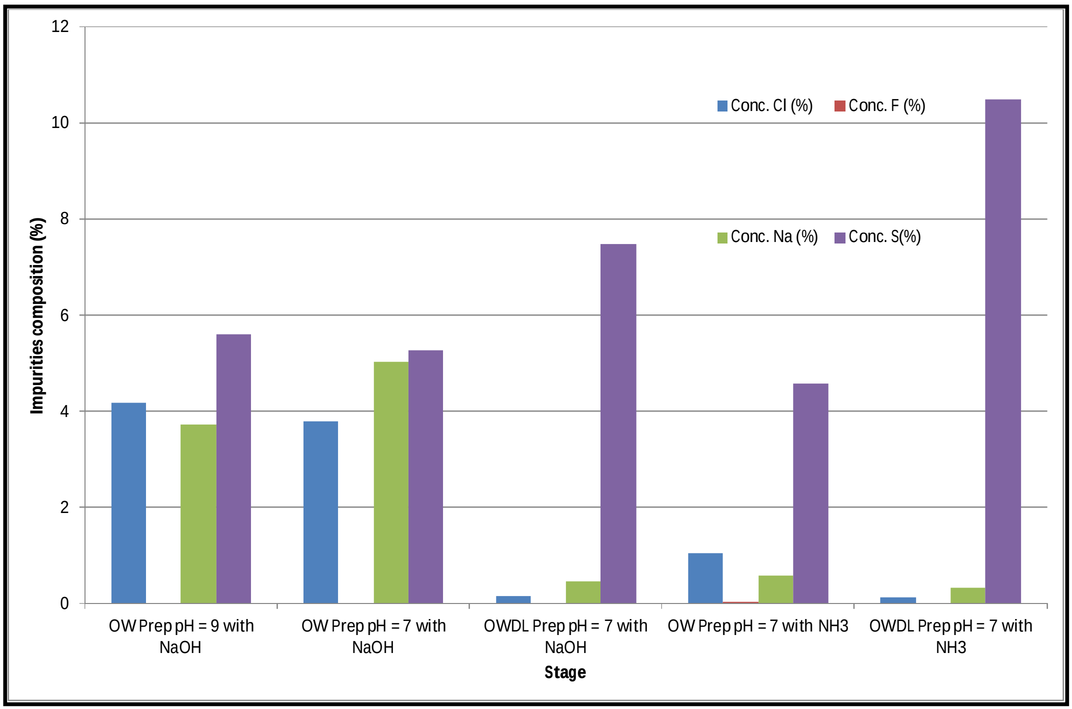


Figure 4.18: The chloride, fluorine, sodium and sulphur concentration in the obtained product as function of the used raw material and pH in the precipitation stage

Figure 4.18 represents the impurities concentration in the final product as a function of the final pH, the used reagent in order to modify the pH and the processed raw material during the designed hydrometallurgical process.

c. Characterization of the obtained products

The characterization of the obtained products at the optimal processes conditions is indicated in the following Tables:

Initial Waelz oxide

Table 4.12: Composition of initial Waelz oxide

Element	Concentration (% weight)
Cu	0,39

Zn	**54**
Ni	0,08
Cr	0,05
Mn	0,5
Fe	**2,8**
Cd	0,2
Sn	0,15
Pb	**9**
Na	**1,1**
S	**1,0**
Cl	**4,98**
F	**0,165**

Precipitated product with NaOH at pH = 9 from WO

Table 4.13: Composition of precipitated product with NaOH at pH = 9 from WO

Element	**Concentration (% weight)**
Cu	0,006
Zn	**57,10**
Ni	0,005
Cr	0,001
Mn	0,0224

Fe	**0,1158**
Cd	0,0756
Sn	0,001
Pb	**0,0202**
Na	**3,72**
S	**5,76**
Cl	**4,18**
F	**0,018**

Precipitated product with NaOH at pH = 7 from WO

Table 4.14: Composition of precipitated product with NaOH at pH = 7 from WO

Element	**Concentration (% weight)**
Cu	0,005
Zn	**58,65**
Ni	0,0143
Cr	0
Mn	0,0527
Fe	**0,1181**
Cd	0,0656
Sn	0,001
Pb	**0,0102**

Na	**5,2**
S	**5,28**
Cl	**3,12**
F	**0,014**

Precipitated product with NaOH at pH = 7 from DLWO

Table 4.15: Composition of precipitated product with NaOH at pH = 7 from DLWO

Element	**Concentration (% weigth)**
Cu	0,001
Zn	**64,64**
Ni	0,0141
Cr	0
Mn	0,0534
Fe	**0,0947**
Cd	0,0465
Sn	0,001
Pb	**0,0104**
Na	**0,463**
S	**7,48**
Cl	**0,2**
F	**0,013**

Precipitated product with NH_3 at pH = 7 from WO

Table 4.16: Composition of precipitated product with NH_3 at pH = 7 from WO

Element	**Concentration (% weight)**
Cu	0,0025
Zn	**57,60**
Ni	0,001
Cr	0
Mn	0,0042
Fe	**0,1154**
Cd	0,0127
Sn	0,001
Pb	**0,0183**
Na	**0,58**
S	**4,58**
Cl	**1,05**
F	**0,011**

Precipitated product with NH_3 at pH = 7 from DLWO

Table 4.17: Composition of precipitated product with NH_3 at pH = 7 from DLWO

Element	**Concentration (% weight)**
Cu	0,0005

Zn	**64,16**
Ni	0,001
Cr	0
Mn	0,0022
Fe	**0,0954**
Cd	0,0147
Sn	0,001
Pb	**0,0133**
Na	**0,34**
S	**10,48**
Cl	**0,2**
F	**0,016**

These Tables show the quantitative analyses of the obtained product depending on the used liquors in order to increase the pH in the Precipitation I and Precipitation II and the processed raw material. Therefore, the need for further washing stage were concluded taking into account these composition results.

4.3.4. DESIGN AND OPTIMIZATION OF WASHING STAGE

After the designed methodology in order to remove the fluorine of the Waelz oxide, the product must be treated by washing, because its chloride content is still so high. In this chapter the design of the washing stage is presented, using the data from the chapter 4.1.1., taking into account the impurities removal capacity of the sodium salts solutions without zinc losses.

4.3.4.1. SIMPLE WASHING WITH WATER

The product from the optimized hydrometallurgical processes was washed with water under the following conditions that appear in Table 4.18:

Table 4.18: Used experimental conditions

Parameter	**Units**	**Quantity**
Temperature	ºC	20
Time	minutes	30
pH_0 (mili-Q)		5,89
Obtained product	g	30,49
Volume Milli-Q	mL	200
Final product	g	25,73

The obtained results of these experimental tests are the following ones:

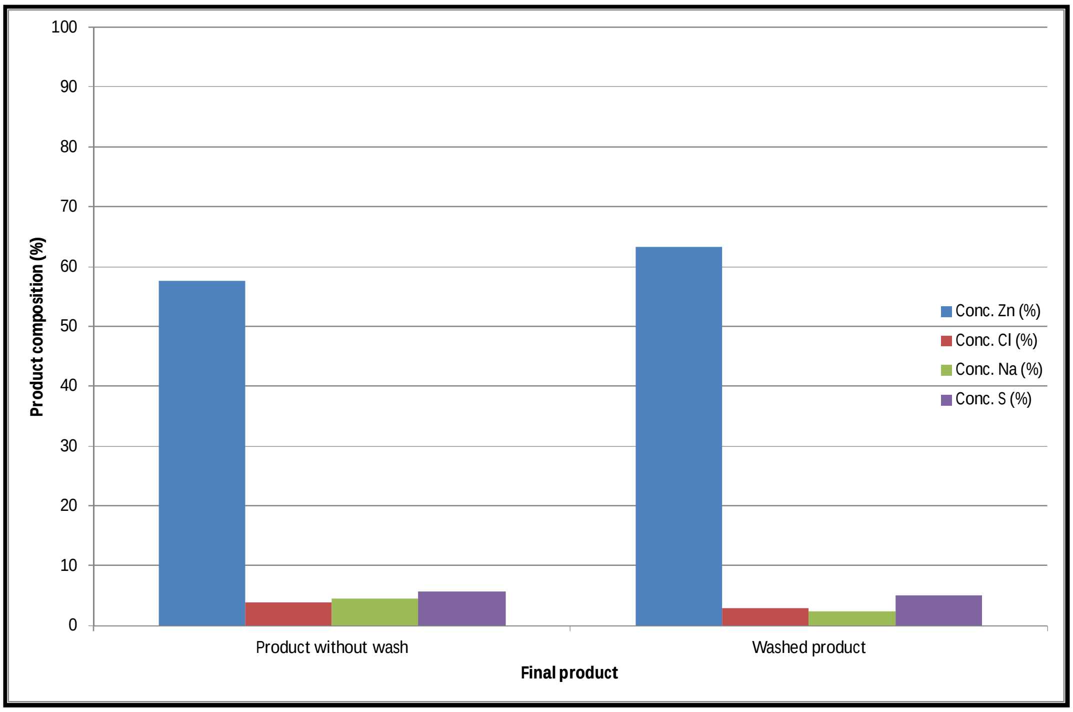


Figure 4.19: The comparison between the chloride, zinc, sodium and sulphur concentration of the product without wash and washed

Figure 4.19 shows the comparison of final product quality before the water washing stage and after. Therefore, the composition of the most important elements has been represented.

4.3.4.2. DOUBLE WASHING WITH SODIUM CARBONATE LIQUOR

The product from the optimized hydrometallurgical processes was washed with sodium carbonate and after with water under following conditions that appear in the Table 4.19 and the Table 4.20:

FIRST WASH

Table 4.19: Used experimental conditions

Parameter	Units	Quantity
Temperature	ºC	70
Time	minutes	45
pH_0 (water)		4,90
pH		9,0
S/L Ratio		0,2
Composition:		
Na_2CO_3 1-hydrate	g	Studied parameter
	Concentration (g/L)	Studied parameter
H_2O	mL	500
Intermediate product	g	100

SECOND WASH

Table 4.20: Used experimental conditions

Parameter	Units	Quantity
Temperature	ºC	20
Time	minutes	45
pH_0 (water)		4,90
S/L Ratio		5
Composition:		
H_2O	mL	500
Product after first wash	g	100

The obtained results of these experimental tests are the following ones:

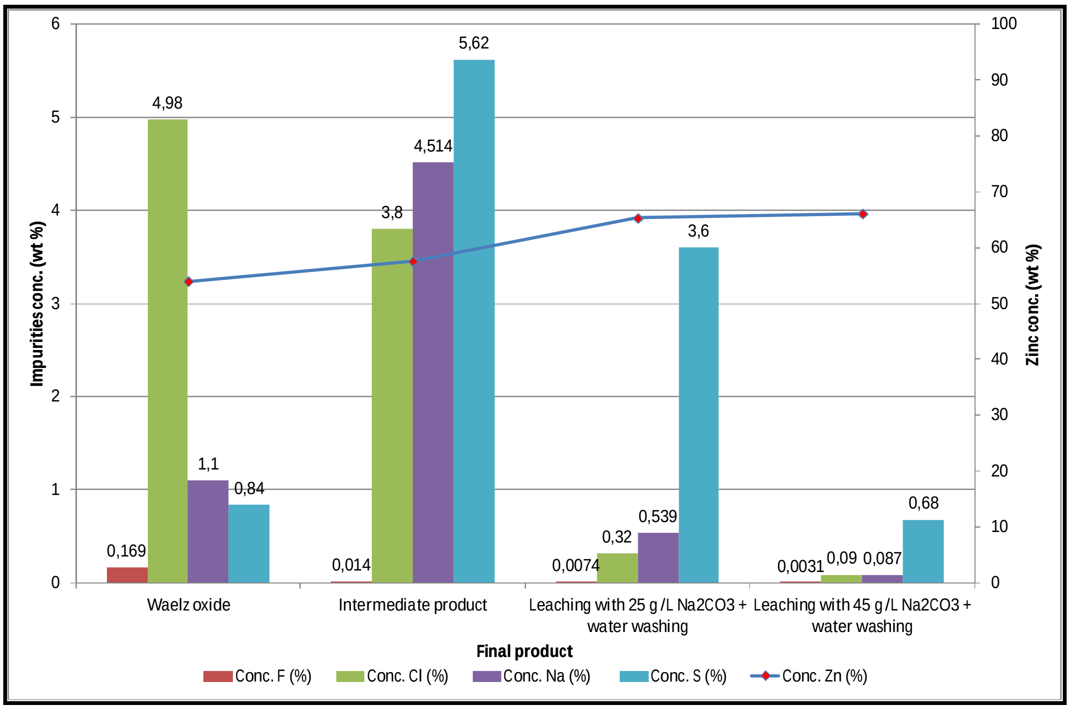


Figure 4.20: The chloride, fluorine, sodium, sulphur and zinc concentration in the obtained product as function of the sodium carbonate dosage

4.3.4.3. Characterization of the final products

The characterization of the final products at the optimal processes conditions is noted in the following Tables:

Product after simple washing with water

Table 4.21: Composition of the product after simple washing with water

Element	Concentration (% weight)
Cu	0,005
Zn	**63,25**
Ni	0,0143
Cr	0

Mn	0,0527
Fe	**0,1181**
Cd	0,0756
Sn	0,001
Pb	**0,0112**
Na	**2,64**
S	**5,19**
Cl	**3,03**
F	**0,0109**

Product after leaching with 25 g/L Na_2CO_3 + water washing

Table 4.22: Composition of the product after leaching with 25 g/L Na_2CO_3 + water washing

Element	**Concentration (% weight)**
Cu	0,0020
Zn	**65,3**
Ni	0,0023
Cr	0,0010
Mn	0,003
Fe	**0,36**
Cd	0,0275
Sn	0
Pb	**0,0186**
Na	**0,539**

S	**3,6**
Cl	**0,32**
F	**0,0074**

Product after leaching with 45 g/L Na_2CO_3 + water washing

Table 4.23: Composition of the product after leaching with 45 g/L Na_2CO_3 + water washing

Element	Concentration (% weight)
Cu	0,0035
Zn	**66,1**
Ni	0,0025
Cr	0,0009
Mn	0,002
Fe	**0,34**
Cd	0,0278
Sn	0
Pb	**0,0189**
Na	**0,087**
S	**0,68**
Cl	**0,09**
F	**0,0031**

These Tables show the quantitative analyses of the obtained product depending on the operation conditions in the washing stage.

4.3.5. FEATURES OF THE OBTAINED PRODUCT

After the study and optimisation of the designed hydrometallurgical processes in order to increase the quality and added value of the Waelz oxide, the improvements of the new product are described:

- Higher zinc content, therefore the economical value of the new product increase with its zinc concentration. Moreover, the contained zinc is totally soluble in sulphuric acid, without solid residue generation.
- The metallic impurities are considerably reduced. Hence, the content of non removable metals through cementation (Ni and Cr) is fitted within the admissible limits for the electrolysis stage. And the content of the other metallic impurities (Cd, Pb, Sn, Cu y Mn) is substantially reduced, so the cost of the purification stages will be decreased.
- The iron content is also reduced (0,34 % in the obtained product). This means that the oxidant consumption, MnO_2 and O_2 injection, during the leaching stage is going to be lower. Thus, the expenditures in the electrolytic zinc obtaining process will be reduced, making more profitable the industrial process.
- The halogens content is really low. The fluorine value is less than 0,005 % wt. and the chlorides concentration is lower than 0,01 % wt. For this reason, the new product can be used as a direct feed to the electrolytic industrial process, because the halogens concentration in the electrolysis liquor will be below than the value which generates corrosion problems in the electrodes.
- The sodium level is appropriated to the industrial process. The adjustment of its concentration is not necessary during the Jarosite process, allowing the use of the new product as the only raw material if necessary.

- Finally, the sulphur content is really low, but this value is not a problem in sulphuric leaching. Therefore, the low sulphur content provides higher zinc content of the new product, increasing its economical value.

4.3.5.1. Quality control and validation of the new product

In this chapter the conclusions about the new product have been endorsed. The experimental simulation of an industrial leaching stage using the new product as raw material has been the method in order to validate the quality of the product. Thus, the experiment was carried out under the following conditions that appear in Table 4.23:

Table 4.24: Used experimental conditions

Parameter	Units	Quantity
Temperature	ºC	65
Time	minutes	60
pH_0 (water)		4,90
pH_f		0,16
Ratio S/L		0,3
Composition:		
H_2SO_4 97%	mL	10
	Concentración (g/L)	150
H_2O	mL	90
New product	g	30

The obtained results of these experimental tests are the following ones:

Table 4.25: Comparison between the composition of the leaching liquor using the new product and the composition of industrial leaching liquor

Element	**Concentration in the liquor (mg / L)**	**Liquor concentration in industrial process (mg / L)**
Cu	48,15	10 – 600 (Ballester, A. Et al, 2000)
Zn	**189.800**	**180.000 – 110.000** (Ballester, A. Et al, 2000)
Ni	4,28	1 – 10 (Ballester, A. Et al, 2000)
Cr	1,32	No data
Mn	31,9	2.500 - 2.000 (Ballester, A. Et al, 2000)
Fe	**743,4** *	**1 – 10** (Ballester, A. Et al, 2000)
Cd	153,2	10 – 500 (Ballester, A. Et al, 2000)
Sn	0	No data
Pb	**28,3**	**No data**
Na	**435,8**	**No data**
Al	**575,2**	**No data**
Cl	**280**	**100 – 400** (Ballester, A. Et al, 2000)
F	**0,41**	**2 – 20** (Ballester, A. Et al, 2000)

*Fe concentration is exceeds the limit, but the leaching stage has been carried out without oxidation with MnO_2 and O_2 during the leaching. For this reason the Mn concentration in the liquor is really low.

Therefore, the applications of the new product have been tested in order to confirm the obtained conclusions during the study of the designed new Waelz oxide purification hydrometallurgical methodology.

4.4. CONCLUSIONS

4.4.1. CONCLUSIONS OF FLUORINE REMOVAL BY LEACHING WITH AQUEOUS SODIUM SALTS SOLUTIONS

The conclusions after the in-depth study about the leaching stage are:

- The fluorine removal is not enough to reach the target product, when sodium compounds aqueous solutions are used to leach. But it should be noted the exceptional chlorine and sodium removals without considerable zinc losses.
- The most efficient sodium compounds in order to remove halogens from Waelz oxide are sodium hydroxide or sodium carbonate. Because the fluorine removal efficiency is higher and there is no addition of chlorides or sulphates as is the case when NaCl (aq) or Na_2SO_4 (aq) are used.
- The increase of the leaching temperature has a positive effect on fluorine removal, because its solubility increases with temperature. The pressure is a parameter that permits the operation at temperatures over 100 ºC maintaining the liquor in liquid phase in order to study the influence of the temperature on the fluorine solubility.

- The zinc loss when the NaOH concentration is high and the absence of this effect when Na_2CO_3 concentration increases, indicates that the pH must be controlled in order to limit this metallic loss.

4.4.2. CONCLUSIONS OF THE FLUORINE REMOVAL BY LEACHING WITH AQUEOUS ALUMINIUM SALTS SOLUTIONS

The conclusions after the in-depth study about the leaching stage are:

- The fluorides in the Waelz oxide are leachable only at high and low pH, being more soluble at the acid range. But the zinc loss is also more pronounced at low pH too.
- The solubilities of aluminium and fluorine follow similar patterns, taking into account that the aluminium is added, but the fluorine has to be solubilised.
- The fluorine solubility (mainly due to aluminium presence) maintains a different pattern than the zinc solubility at pH = 2 – 4 and pH = 8 – 13. Therefore, this characteristic will be useful to solve the problem which motivated this project.
- The chloride solubility seems constant except when HCl (aq) has been added to control the pH.

4.4.3. CONCLUSIONS OF THE SELECTIVE PRECIPITATION OF FLUORINE

The conclusions after the in-depth study about the leaching stage are:

- Fluorine removal when the pH of the leaching liquor is increased can be observed. Therefore this removal occurs within the low solubility range of the formed AlF^{-x} complexes ($4 \geq pH \geq 12$).
- This fluorine removal is greater when the pH increase is higher, but the zinc loss is increased too. In fact, the optimization of the

precipitation pH must be carried out in order to increase the fluorine removal minimizing zinc losses.

- The aluminium precipitation is so high (> 92 %), thus it can be concluded that the fluorine removal occurs because the AlF^{-x} complexes insolubility is reached and it is accompanied by the precipitation of the soluble aluminium surplus as aluminium hydroxide at the selected pH.
- The highest fluorine removal (> 88%) without appreciable zinc loss (< 2%) has been observed at pH = 4,6. Therefore, this is the chosen optimal pH.
- The chlorine removal is insignificant using this hydrometallurgical process.
- The aluminium removal after the pH modification is not completed, so the remaining fluorine concentration in the liquor is as AlF^{-x} complexes. This consideration means that this fluorine will be combined with aluminium in the electrolysis liquors. Hence, the cathodic deposits will be avoided, increasing the value of the target product.

4.4.4. CONCLUSIONS OF THE LEACHING STAGE WITH SULPHURIC ACID AND AQUEOUS ALUMINIUM SULPHATE LIQUOR

The conclusions after the in-depth study about the leaching stage are:

- The zinc, the fluorine and the chloride concentrations increase when the solid/liquid ratio is increased (regardless of used temperature).
- The optimal solid/liquid ratio is 80 g/L at 20 ºC and 200 g/L at 60 ºC, because in both cases, the zinc recovery is higher than 90 %. Therefore, the chosen operation parameters during the leaching stage are 60 ºC and a S/L ratio of 200 g/L in order to maximize the processing capacity of the designed process.

- The fluorine and chloride concentrations increased with the solid/liquid ration too. Thus, the fluorine concentration at optimized condition is 248 mg/L and 13.300 mg/L in the case of the chlorides.

4.4.5. CONCLUSIONS OF THE SELECTIVE PRECIPITATION OF FLUORINE

The conclusions after the in-depth study about the selective precipitation of fluorine are:

- The fluorine removal by selective precipitation at pH = 4,6 increases when the aluminium concentration in the leaching liquor is increased.
- When the Al / F ratio is higher than 4, the fluorine removal shows a minor rise (lower than 2 %). Therefore, the optimal Al/F ratio has been fixed at this value.
- It can be observed that some fluorine is not removed in both precipitation stages, so it will not be present in the final product, being removed too.
- Applying the designed and studied methodology more than the 90 % (91,02 %) of the Waelz oxide contained fluorine can be removed.

4.4.6. CONCLUSIONS OF THE PRECIPITATION STAGE IN ORDER TO RECOVERY THE ZINC CONTENT

The conclusions after the in-depth study about the solved zinc precipitation are:

- The zinc recovery is higher when the final pH is 9, but the zinc concentration in the final product is lower. Therefore, this data indicate that the precipitation of some impurities increases when the final pH is higher. For this reason, pH = 6,5 – 7 is considered as the optimal pH.

- When the pH modifier is aqueous ammonia, 7 has been the used pH in order to precipitate the zinc, because it is leached with ammonia solutions at higher pH, inhibiting the recovery. The zinc recovery is lower than if the used reagent is NaOH (aq), this is due to the formation of soluble zinc complex ions with ammonia. But the quality of the obtained product is better, because the precipitation of impurities (Na, Cl and S) is lower.
- The chloride precipitation in this stage makes the final product not acceptable in order to use it as a direct feeding in the electrolytic zinc process. Therefore, the design of a finishing stage in order to remove the chlorides or the selection of DLWO as raw material of the designed methodology can be two interesting alternatives.

4.4.7. CONCLUSIONS OF THE DESIGN AND OPTIMIZATION OF WASHING STAGE

The conclusions after the in-depth study about the washing stage are:

- The quality of the final product after leaching with sodium carbonate liquor and a final washing with water increases very significantly. The obtained product is appropriated in order to be used as raw material in the zinc electrolytic obtaining process. Moreover, the quality of the final product increases with the concentration of sodium carbonate liquor in the first step of the washing.
- As a final conclusion it can be indicated that the studied hydrometallurgical processes allow to reaching the required quality from Waelz oxide in order to produce electrolytic zinc. Hence, the need for extracting minerals, the mineral beneficiation process and the roasting stage before the conventional hydrometallurgical process could be reduced significantly. The environmental benefit will be remarkable, due to this important contribution in the industry of zinc recycling.

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Operario en batería de coke – Altos Hornos de Vizcaya (by Miguel Ángel Martínez Vitores)

Planta Waelz – BEFESA ZINC ASER (by BEFESA)

CHAPTER 5

5. GENERAL CONCLUSIONS

After all the results previously presented and discussed it can be concluded that some significant and innovative contributions have been developed in the two areas selected when this thesis was started.

First of all an extensive and exhaustive revision of the state of the art concerning hydrometallurgy and its applications to the valorization of industrial wastes containing heavy metals was carried out. This revision included not only scientific publications but also technological information available as patents or similar documents. This revision had to be extended to the area of gas absorption in order to also cover the topic of reactants recovery.

In what concerns the development of a hydrometallurgical process able to regenerate Waelz oxide leaching liquors from a hydrometallurgical process that produce commercial zinc oxide from Waelz oxide, the following conclusions can be derived from the work developed in this thesis:

1. Further refinements of previously development work related to the hydrometallurgical route from Waelz oxide to commercial zinc oxide production using ammonia leaching liquors have been carried out with an especial emphasis on exhausted liquors regeneration.
2. Throughout experimental work the optimal operation variables values for the Waelz oxide leaching using aqueous liquors prepared from ammonia carbonate and ammonia have been determined. The role of the carbonate/bicarbonate system to buffer the solution and to allow

higher ammonia concentrations in the leaching liquor has been studied within the optimal pH range (9,5-12,5). The opposite effect of temperature on zinc recovery from Waelz oxide and on ammonia concentration in the liquor has also been studied to fix room temperature as the most adequate to balance both phenomena. At this low temperature and operating at acceptable solid to liquid ratios the leaching kinetics implied that times of around one hour are required to maximize zinc recovery from Waelz oxide (above 92 %).

3. Iron removal from ammonia leaching liquors through air oxidation has also been optimized. Temperatures around 80 ºC are recommended in order to avoid significant zinc losses by precipitation and to reach iron eliminations higher than 75 % using in the experimental facility used air flows around 2,25 L/min. Kinetic experiments allowed to determine that this level of elimination under the conditions previously indicated requires oxidation (bubbling) times of around 70 minutes.
4. Additional cationic impurities reduction from the leaching liquors using a cementation step has also been investigated using zinc dust as cementation agent. Temperatures higher than room temperature do not facilitate higher reductions and operating at this temperature adding 1,33 g of zinc dust/L of liquor allowed the production of liquors with around 5 ppm of cationic impurities.
5. Final precipitation from the liquor of zinc hydroxide/carbonate has also been studied. 40 minute of CO_2 bubbling (6 L/min for the experimental facility used) at room temperature allowed the recuperation in the precipitate of 90 % of the zinc solved in the liquor. The exhausted liquor ended containing a bit more than 7 g of zinc/L and around 43 g of ammonia/L.
6. The precipitate can be calcined and the optimal temperature for this process is 600 ºC. At this temperature in a conventional laboratory furnace 45 minutes of calcination time are required to end with a zinc oxide of higher purity than 99 %.

7. The ammonia recovery from exhausted liquors and its further absorption to prepare fresh leaching liquors has also been experimentally studied. This recovery stage has been developed starting by a careful estimation of all possible ammonia losses from the different stages of the hydrometallurgical process. For some liquid mixtures ammonia recovery implies the use of stripping operations that have also been considered. Then both experimentally and using mathematical simulation the absorption of ammonia containing gaseous mixtures into aqueous solutions has also been investigated taking into account the influence of carbon dioxide simultaneous absorption/desorption.
8. The ammonia absorption mathematical model developed and experimentally tested can also be applied to other processes where gaseous ammonia must be recovered as aqueous solutions.

In what concerns the development of a hydrometallurgical process able to convert Waelz oxide into a mixture fulfilling all the specifications required to be used as a feed to the electrochemical production of metallic zinc, the following conclusions can be derived from the work developed in this thesis:

9. Fluorine content is the most limiting characteristic of Waelz oxide if its use as a feed for electrochemical liquors preparation is desired. In order to selectively separate fluorine using leaching procedures different liquors have been studied. The most promising alternative is the use of aqueous solutions of aluminum salts at acid pH (2 - 4) through the formation of soluble complex ions of fluoride and aluminum ions. Increasing the pH a selective precipitation of the aluminum fluorides is possible and in order to avoid zinc losses pH must remain below 5. Throughout experimental work it has been found that the optimum precipitation pH is 4,6 at room temperature. Under these conditions around 88 % of the fluorine content can be removed with zinc losses

below 2 %. As the remaining fluoride in the solution is as AlF^{-x} complexes its impact on the electrodes of the metallic zinc production can be minimized.

10. All the information gathered in the experimental work previously cited has been crucial for the development of a leaching process using aluminum salts and sulfuric acid. After this leaching most of the fluoride content can be separated through selective precipitation and then zinc can also be precipitated generating a solid concentrate with low fluoride content. The characteristics of this solid concentrate can be improved using an additional double washing stage to also eliminate most of its chlorine content. This washing stage has been carried out using aqueous solutions of sodium carbonate. As a result a solid product with less than 0.005 % of fluorine and less than 0,01 % of chlorine can be produced. Substantial reductions of the Cd, Pb, Sn, Cu and Mn are also obtained and the iron content of this product is around 0,34 % making easier and cheaper any possible farther oxidation and cementation stages.
11. Through conventional leaching electrochemical liquors were prepared and all the specifications of the ones used for metallic zinc electrochemical production were fulfilled with the exception of the iron content, but this content can be easily reduced through an oxidation stage.

Batería de coke – Altos Hornos de Vizcaya (by Miguel Ángel Martínez Vitores)

Interior del horno Waelz – Befesa Zinc Aser (by BEFESA)

APPENDIX

A. ANALYTICAL METHODS

In this chapter, the used analytical methods used during the experimental work of this thesis have been described.

A.1 Metallic composition

The composition of the liquors and the solids has been analyzed by ICP-OES (2000-DV, Perkin Elmer). Obviously, the solids must be disaggregated before the instrumental analysis. The used disaggregation methodology was the following one:

PROCEDURE:

- Weight 0,05 g of the solid sample into the Teflon vessel. Dosage a 13 mL of hydrochloric acid and 7 mL of nitric acid.
- Disaggregate into a microwave digester during 20 minutes at 200 ºC.
- Transfer the obtained liquid to a 100 mL volumetric flask with distilled water.

MEASUREMENTS:

- The samples must be in liquid solution (without solids) and acidified.
- The samples and the calibration solutions must have the similar composition and conditions in order to minimize the matrix effect.
- Calibrate the instrument and measure the sample concentration according to the instruction manual of the ICP-OES.

A.2 Fluorine concentration

The fluorine concentration of the liquors and the solids has been analyzed by fluorine ion selective electrode (ISE Fluoruros, Crison Instruments). Obviously, the solids must be treated before the instrumental analysis. Therefore the separation methodology (for minerals with 0 – 0,2 % of fluorine content) was the following one:

PROCEDURE:

- Weight 0,25 g of the solid sample and mix with 0,25 g of silica into a small capsule.
- Introduce into a tubular oven during 40 minutes at 1100 ºC.
- Collect the obtained hydrofluorosilicic acid into a 25 mL of distilled water.

MEASUREMENTS:

- The samples must be in liquid solution (without solids) and an at pH of approximately 5,00 – 8,00.
- The samples and the calibration solutions must have the similar composition and conditions in order to minimize the matrix effect.
- Transfer 25 mL of the liquid sample into a beaker with 25 mL of TISAB solution (type of TISAB solution depends on the Al or Fe concentration).
- Calibrate the instrument and measure the sample concentration according to the instruction manual of the fluorine ion selective electrode.

A.3 Chloride concentration

The chloride concentration of the liquors and the solids was analyzed by argentometry using Ag ion selective electrode (SALT-Matic 23, Crison Instruments). Obviously, the solids must be treated before the instrumental analysis. Therefore the used separation methodology has been the following one:

PROCEDURE:

- Weight 0,500 g of the solid sample into the 100 mL beaker. Dosage a 10 mL of nitric acid.
- Disaggregate into a ultrasonic bath during 10 minutes at 40 ºC.
- Transfer the obtained liquid to a 100 mL volumetric flask with distilled water.

MEASUREMENTS:

- The samples must be in liquid solution (without solids) and acidified.
- 20 mL of liquid sample have been titrated with analytical $AgNO_3$ solution (0,01 or 0,1 N depend on the chloride concentration in the sample).
- Calibrate the instrument and measure the sample concentration according to the instruction manual of the Ag ion selective electrode.

A.4 TOTAL SULPHUR CONTENT

The total sulphur content of the solid samples was analyzed by elemental microanalysis (CHNS-932, LECO). This technique is totally automated, it consists in the controlled combustion of the sample at 950 ºC – 1.100 ºC with pure oxygen.

MEASUREMENTS:

- Weight 0,02 g of the solid sample into a small capsule.
- Introduce the capsule into the oven of the equipment.

- Calibrate the instrument and measure the sample concentration according to the instruction manual of the CHNS analyzer.

A.5 SOLVED AMMONIA CONCENTRATION

The solved ammonia concentration of liquors was analyzed by NH_3 selective electrode method (Thermo Scientific ORION High Performance NH_3 ISE). The sample is made alkaline with sodium hydroxide to convert ammonium ion to ammonia. The ammonia thus formed diffuses through a gas-permeable membrane of a selective ion electrode and alters the pH of the internal solution which in term is sensed by a pH electrode. The potential is measured by means of the pH-meter or ionanalyzer.

MEASUREMENTS:

- Transfer 100 mL of the sample into a 150 mL beaker.
- Add the stirring bar and mix on the magnetic stirred.
- Immerse the electrode into the sample.
- Add 2 mL of 10 M NaOH solution. The NaOH solution should be added just prior to measurement.
- Calibrate the instrument and measure the sample concentration according to the instruction manual of the NH_3 selective electrode.

A.6 SOLVED TOTAL CO2 SPECIES CONCENTRATION

The solved carbonates concentration of liquors as CO_2 combined was analyzed by CO_2 selective electrode method (Thermo Scientific ORION High Performance CO_2 ISE). The sample is made acid with sulphuric acid to convert carbonate and bicarbonate ion to carbon dioxide. The carbon dioxide thus formed diffuses through a gas-permeable membrane of a selective ion electrode and alters the pH of the internal solution which is sensed by a pH electrode. The potential is measured by means of the pH-meter or ionanalyzer.

MEASUREMENTS:

- Transfer 50 mL of the sample into a 150 mL beaker.
- Add the stirring bar and mix on the magnetic stirred.
- Immerse the electrode into the sample.
- Add 50 mL of distilled water and 10 mL of 70 % of H_2SO_4 solution. The sulphuric acid solution should be added just prior to measurement.
- Calibrate the instrument and measure the sample concentration according to the instruction manual of the CO_2 selective electrode.

B. USED CORRELETIONS IN ORDER TO STADY OF THE LIQUOR REGENERATION SYSTEM

B.1 Equilibrium constants

- $CO_2\ (g) + H_2O\ (l) \Leftrightarrow CO_2\ (aq)$

$pK_{CO2} = -2622.38/T - 0.0178471T + 15.5873$ *(Harned and David, 1943)*

- $CO_2 + OH^- \Leftrightarrow HCO_3^-$

$K_1 = (\exp(-12092.1/T - 36.789\ LnT + 235.482))\rho_{L,H20}/K_w$ *(Versteeg et al, 2005)*

- $HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$

$LogK_2 = (1568.924/T - 2.5865 - 6.737.10^{-3}T)$ *(Hikita et al, 1976)*

- $NH_3\ (g) + H_2O\ (l) \Leftrightarrow NH_3\ (aq)$

$K_{NH3} = [(\log H_{NH3} = -1.69 + 1477.7/T) / RT]$ *(Hales and Drewes, 1979)*

- $NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

$LnK_3 = 97.97152 - 5914.082/T - 15.064LnT - 1.101.10^{-2}T$ *(Kawasuishi and Prausnitz, 1987)*

- $NH_3 + HCO_3^- \Leftrightarrow NH_2COO^- + H_2O$

$LnK_4 = 20.15214 + 604.1164/T - 4.017263LnT + 0.5031.10^{-2}T$ *(Kawasuishi and Prausnitz, 1987)*

- $H_2O \Leftrightarrow H^+ + OH^-$

$LnK_W = 148.98 - 13847.26/T - 23.654LnT$ *(Dickson and Riley, 1979)*

B.2 Kinetic constants

- $CO_2\ (aq) + OH^- \leftrightarrow HCO_3^-$

$Logk_1 = 13.635 - 2895/T\ (dm^3/mol.s)$ *(Pinsent et al, 1956)*

- $2\ NH_3 + CO_2 \rightarrow NH_2COO^- + NH_4^+$

$k_{NH3}^T = 3,996\ .10^8 \exp(-\ 4455,0/T)\ (m^6/Kmol.s)$

- $NH_3 + CO_2 + H_2O \rightarrow NH_2COO^- + H^+$

$k_{H2O}^T = 47,314 \exp(-\ 306,48/T)\ (m^6/Kmol.s)$

B.3 Diffusion coefficients

The diffusion coefficient of CO_2 in aqueous NH_3 solution was estimated from the solution`s viscosity using a modified Stoke-Einstein equation:

$\mathbf{D_{CO2,L} = D_{CO2,H2O}(\mu_{H2O}/\mu_L)^{0.8}}$ (m^2/s) *(Versteeg and Van Sawaaij, 1988)*

With the viscosity given by:

$\mu_{H2O} = 1.18.10^{-6} \exp(16400/RT)\ (Pa/s)$

$\mu_{NH3} = (0.67 + 0.78x).10^{-6} \exp(17900/RT)\ (Pa/s)$

$D_{CO2} = 2,35.10\text{-}6 \exp(-2119/T)\ .\ [(1,18.10^{-6} \exp(16400/RT))/(0,067 + 0,78x).10^{-6} \exp(17900/RT)]^{0,8}\ (m^2/s)$

$D_{OH-} = (-0,1925 + 1,2291\sqrt{T}).10^{-3}\ RT/F^2\ (m^2/s)$

$D_{HCO3-} = 4,5.10^{-3}RT/F^2\ (m^2/s)$

$D_{CO3-2} = (3,11.10^{-5} + 2,63.10^{-10}(T)^3)RT/2F^2\ (m^2/s)$

$D_{NH3} = (1,65 + 2,47x).10^{-6} \exp(-2000/RT)$ (m^2/s) *(Frank et al, 1996)*

$D_{NH4+} = 8,931.10^{-10}T(l^o_{+}. l^o_{-}/\Lambda^0)(Z_{+} + Z_{-}/ Z_{+} . Z_{-}) = 9,6129.10^{-8}T$ (cm^2/s) (Perry and Chilton, 1973)

$D_{NH2COO-} = [(1,65+2,47x).10^{-6}\exp(-2000/RT)]/2$ (m^2/s)

$D_{H+} = (0,1724 – 40,803/T)RT/F^2$ (m^2/s)

$\mathbf{D_{CO2,G} = 7.84.10^{-5}(T)^{1.75}/P}$ (m^2/s) *(Hoff, 2003)*

$\mathbf{D_{NH3,G} = 1.7.10^{-5}(1.03)^{(T-293)}}$ (m^2/s) (Bruckler et al, 1989)

B.4 Physicochemical parameters

Ammonia:

Vapour: Density:

$\rho_{NH3,G} = P / 488,2(T+273)$ (Kg/m^3)

When: T(ºC) and P(Pa) (ASHRAE, 1989)

Viscosity:

$\mu_{NH3,G} = (0,353+0,03533T) 10^{-6}$ (Pa.s)

When: T(ºC) (ASHRAE, 1989)

Aqueous solution: Density:

$\rho_{NH3,L} = 1002,4 – 0,46449T + (1 – 277,94\exp(0,002815T)).x + (1 – 80,248\exp(0,0040810T).x^2$ (Kg/m^3)

When: $0 < x < 1$; -10ºC < T < 120 ºC (ASHRAE, 1989)

Viscosity:

$\mu_{NH3,L} = 10^{-6}(1 + 2x) \rho_{NH3,L}$ (Pa.s)

When: X< 0,26 (Weast and Atle, 1982)

$$\mu_{NH3,L} = (1{,}425x).10^{-6}\ \rho_{NH3,L}\quad \text{(Pa.s)}$$

When: X> 0,26 (Weast and Atle, 1982)

<u>CO$_2$:</u>

Vapour: Density:

$$\rho_{NH3,G} = P\ /\ 536{,}58(T+273)\quad (Kg/m^3)$$

When: T(ºC) and P(Pa)

Aqueous solution: Density:

$$P_{CO2,L} = \rho_W\,(1 + 0{,}275.x)\quad (Kg/m^3)$$

When: ρ_W = water density (Song et al, 2003)

C. PROCESS DIAGRAMS

In this appendix the simplified block diagram of the development hydrometallurgical processes are shown:

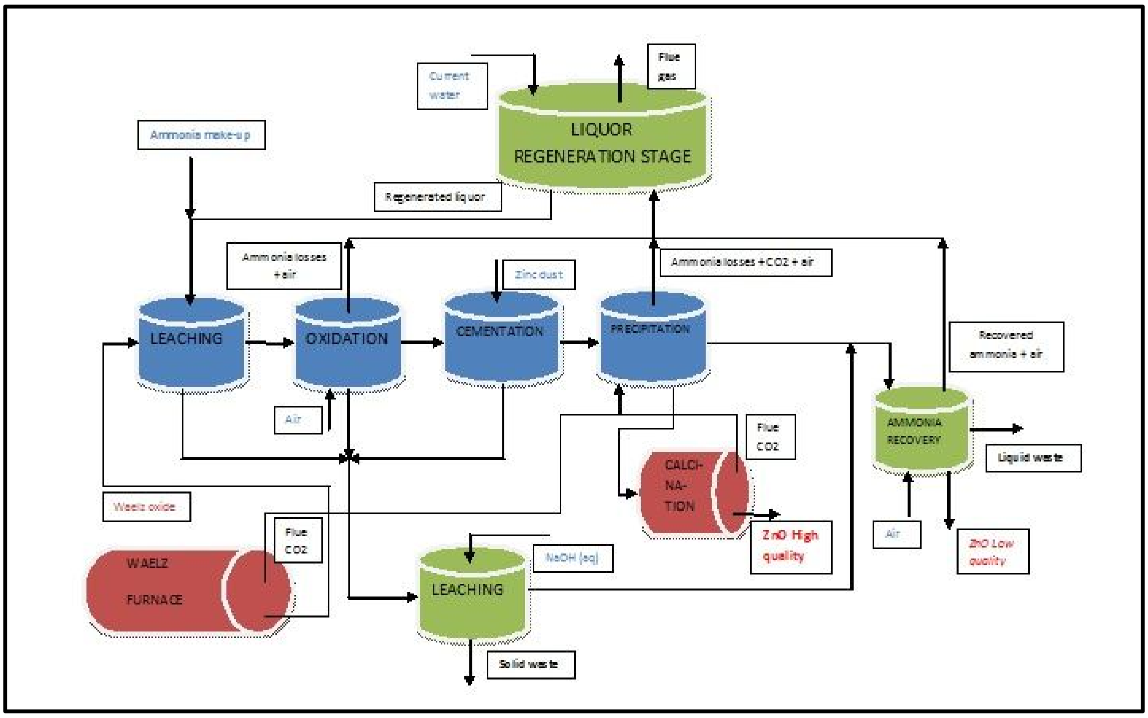

Figure C.1: Simplified block-diagram of the high purity zinc oxide production process

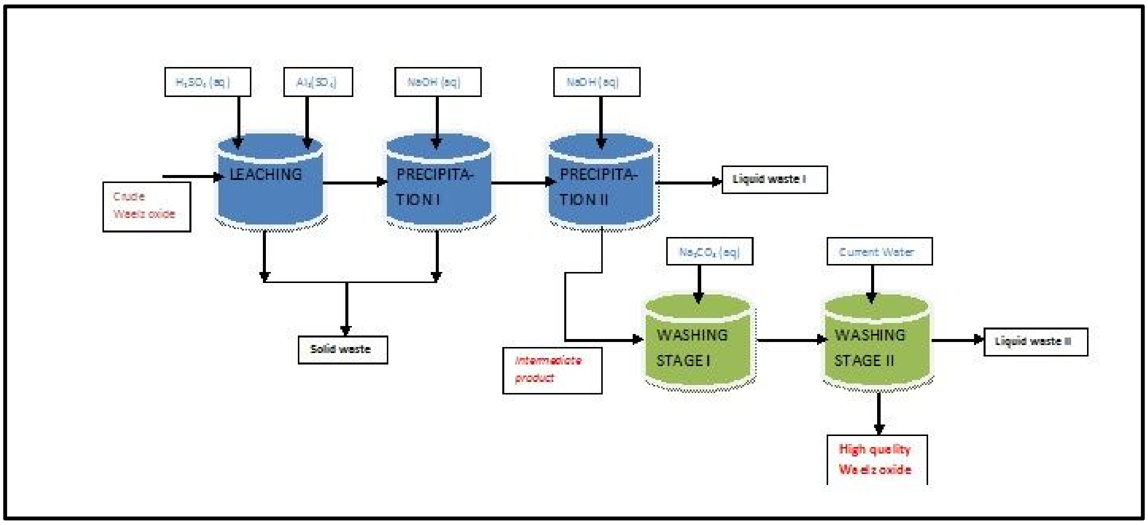

Figure C.2: Simplified block-diagram of the Waelz oxide purification process in order to use as main source in the electrolytic zinc production process.