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Escuela de Ingeniería de Bilbao

Departamento de Ingeniería Química y del Medio Ambiente

Integrated Hydrometallurgical process for Paval valorization

Dissertation submitted to fulfill the final requirements to obtain the degree of

Ph.D. in Engineering of Materials and Sustainable Processes

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A mis padres, por su apoyo absoluto y incondicional

A Maitane, somos un equipo

A Iker, que me metió en esto y luego me ayudó a salir

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Summary

This PhD thesis was carried out in the Sustainable Process Engineering (SuPrEn) research group of the Chemical and Environmental Engineering Department - Faculty of Engineering of Bilbao, University of the Basque Country, under the supervision of Prof. Dr. José Francisco Cambra Ibáñez and Prof. Dr. Pedro Luis Arias Ergueta.

Along these years, this work allowed to propose an integrated process for salt cake Paval valorization (through fluoride content reduction) *via* a hydrometallurgical process and the treatment of the generated effluent for its recycling, thus, reducing total waste production. This research is presented in eight chapters:

- Chapter 1 of this research provides a general overview of primary and secondary aluminum production, along with a brief description of the main wastes generated in these industries and their possible uses, including the production of Paval, the material of interest in this thesis.

- Chapter 2 of this PhD thesis consists on a description of the two main techniques for fluoride removal from solid matrixes: *(i)* Thermal treatments and *(ii)* hydrometallurgical treatments, such as chemical leaching.

- Chapter 3 of this PhD thesis sets the objectives and scope of this research, *i.e.* the design of a Paval valorization integrated process technically and economically viable to allow its industrial implementation.

- Chapter 4 summarizes the main experimental procedures used during the realization of this thesis to help the fluency of the following chapters dealing with the experimental results, discussion and conclusions.

- Chapter 5 studies the effect of the main operating parameters (acidic and basic leaching agents, temperature, pH, reaction time and solid/liquid ratio) on the selective fluoride leaching from industrial Paval samples. This was studied while minimizing aluminum removal *via* a Taguchi Design of experiments and an ANOVA analysis.

- Chapter 6 is a review of the industrially employed sulfate removal methods: *(i)* precipitation, *(ii)* membranes, *(iii)* ion exchange, *(iv)* adsorption, and *(v)* biological mechanisms.

- Chapter 7 studies the recyclability of the effluent produced in the hydrometallurgical process proposed in Chapter 5 to minimize the overall

waste production. In addition, some applications for the produced by-products are proposed.

- Chapter 8 summarizes the conclusions obtained after carrying out this PhD thesis, and proposes future research areas that could benefit from the present research.

Resumen

Esta tesis doctoral se llevó a cabo en el grupo de investigación SuPrEn (Ingeniería de Procesos Sostenibles/Sustainable Process Engineering) del departamento de Ingeniería Química y del Medio Ambiente de la Escuela de Ingeniería de Bilbao de la UPV-EHU, bajo la supervisión del Prof. Dr. José Francisco Cambra Ibáñez y del Prof. Dr. Pedro Luis Arias Ergueta.

Tras estos años de trabajo se ha conseguido proponer un proceso integrado de valorización de Paval de escoria salina mediante la reducción de su contenido en flúor mediante tratamiento hidrometalúrgico, así como el posterior tratamiento y reintroducción del efluente obtenido y tratado al proceso hidrometalúrgico. Esta investigación se ha estructurado en ocho capítulos:

- El capítulo 1 proporciona una visión general de la producción de aluminio, junto con una breve descripción de los principales residuos generados en esta industria y sus actuales salidas, incluyendo la producción de Paval, el material de interés en esta tesis doctoral.

- El capítulo 2 describe las principales técnicas de eliminación de flúor en sólidos: *(i)* tratamientos térmicos, y *(ii)* tratamientos hidrometalúrgicos, especialmente la lixiviación química, y concluye, tras un análisis comparativo de estas técnicas, que la hidrometalurgia es la vía más indicada para la extracción de flúor de Paval.

- El capítulo 3 establece como objetivo de esta investigación el desarrollo de un proceso integrado de valorización de Paval que sea técnica y económicamente viable para su posterior implantación industrial, desarrollando este objetivo general en otros más concretos.

- El capítulo 4 contiene la descripción de los principales procedimientos experimentales utilizados en la realización de esta tesis doctoral, de forma que se agilice la comprensión de los siguientes capítulos, que contienen resultados experimentales, su discusión y las conclusiones.

- El capítulo 5 estudia el efecto de los principales parámetros de operación (agentes lixiviantes ácidos y básicos, temperatura, pH, tiempo de reacción y ratio sólido/líquido) en la lixiviación selectiva de flúor y aluminio de muestras industriales de Paval, con ayuda del Método Taguchi de diseño de experimentos y el análisis de la varianza (ANOVA).

- El capítulo 6 analiza y compara los principales métodos industriales de eliminación de sulfatos en efluentes, *(i)* precipitación, *(ii)* membranas, *(iii)* intercambio iónico, *(iv)* adsorción, and *(v)* métodos biológicos, y selecciona la precipitación química como la vía más indicada para el efluente obtenido en el capítulo 5.

- El capítulo 7 estudia la reciclabilidad del efluente producido en el capítulo 5, para minimizar la producción global de residuos, además de proponer posibles aplicaciones para los productos obtenidos en el proceso integrado.

- El capítulo 8 resume las conclusiones obtenidas en el transcurso de esta tesis doctoral, y propone futuras líneas de investigación que podrían beneficiarse de la investigación actual.

Chapter 1

Introduction

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1.1   Introduction

This chapter provides a general overview of primary and secondary aluminum production, along with a brief description of the main residues generated in these industries and their possible uses, including the production of Paval, the material of interest in this PhD thesis.

1.2   Aluminum production

Aluminum is the most abundant metallic element in the Earth's crust and the third most abundant element by mass after oxygen and silicon. However, it is not found as pure metal in nature due to its strong tendency to form highly stable oxides. Consequently, its existence was not established until 1808. Bauxite, a clay-like ore, aluminum oxide rich material, was found in 1821 and became the primary source of aluminum. The industrial-scale production and use of aluminum are barely a century old, yet in that time, the industry has grown until it is second only to the iron and steel industry among metal producers. Primary aluminum is produced from virgin ore found in deposits in the Earth's crust and secondary aluminum refers to recycled aluminum, produced from scrap.[1–3]

1.2.1   Primary aluminum

In 1886 Charles Martin Hall in the United States and Paul Louis Héroult in France simultaneously and independently patented an identical process. In this process, known as Hall-Héroult process, aluminum ore is dissolved in a bath of molten cryolite (Na_3AlF_6) at 960 °C, and the aluminum is precipitated using electricity. It is still the most efficient method to produce aluminum in commercial quantities.[1,2,4]

The production of primary aluminum is accomplished in three stages:[1]

i. Mining the raw ore (fundamentally bauxite): The most important parameter used to determine bauxite suitability for primary aluminum production is its Total Available Alumina (TAA, g of extractable Al_2O_3 per g of material), often estimated *in situ* prior to mining, as it gives an idea of the aluminum that can

be extracted by the Bayer process.[5,6] Commercial bauxites typically present TAA 35–50%.[7]

ii.   Production of alumina (Al_2O_3): In this step, bauxite ore, containing 30 to 60 % Al_2O_3) is refined to obtain smelter grade alumina of 99.5 % Al_2O_3). Karl Bayer developed a process (Figure 1.1) in which alumina contained in bauxite was selectively dissolved by heating in a sodium hydroxide solution under pressure to form a sodium aluminate solution, from which aluminum in hydroxide form precipitates. This precipitate was then filtered, washed, and calcined to produce high-purity crystalline alumina, and a caustic alkaline liquor to be recycled.[1,3,8] Although the Bayer process is the principal industrial means of refining bauxite to produce alumina (Al_2O_3) pure enough for aluminum electrolysis, there are three other alternatives: The Sinter process, the combined/parallel Bayer–Sinter process and the Nepheline-based process. These alternative processes, through which 17% of the world´s alumina is produced, mainly aim at accommodating different raw materials and improving the recovery rate of alumina.
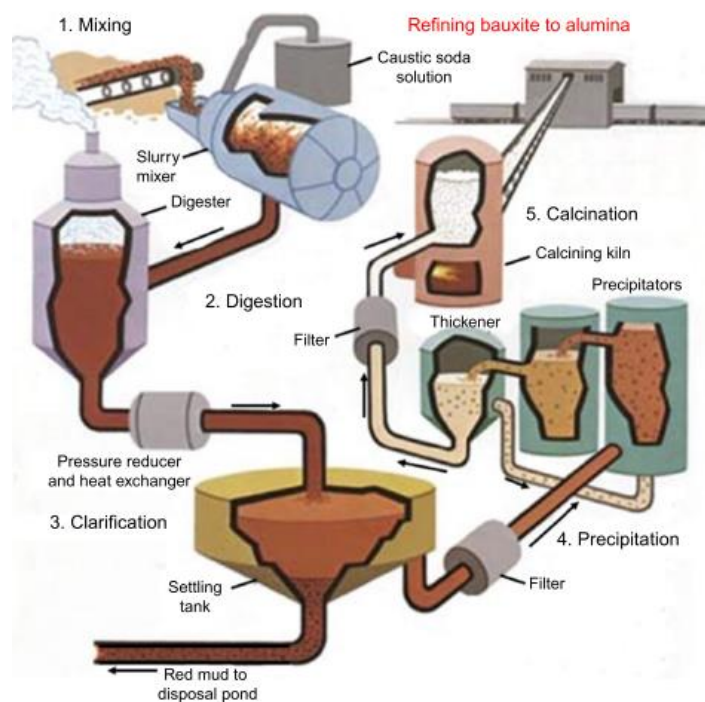
Figure 1.1.- Scheme of the Bayer process.[8]

iii. Conversion of alumina into metallic aluminum by Hall–Héroult process: The purified alumina is first dissolved in a bath of molten cryolite (Na_3AlF_6, 80-85 %), calcium fluoride (CaF_2, 5-7 %), aluminum fluoride (AlF_3, 5-7 %) and alumina (Al_2O_3, 2-8 %) at 960 °C and then reduced by electrolysis. Cryolite is used because it is the best fluxing agent for alumina, and AlF_3 and CaF_2 in order to lower the melting point of the electrolyte. The electrolytic reduction process requires high purity aluminum oxide, carbon, and electrical power. It takes place in carbon-lined (carbon lining serves as cathode of the cells) steel electrolytic Hall cells, or 'pots'.[1,2,4,8–13]

The end of life of the electrolytic cell is set as the voltage increases or iron starts to be detected in the aluminum metal. When this occurs, the potlining is removed and the shell is re-lined. The spent potlining (SPL) generated is listed by various environmental bodies as a hazardous material because of its leachable cyanide (up to 1 wt.%) and fluoride (up to 20 wt.%) contents. The production of 1 t of aluminum typically requires 420 kg of carbon, 1920 Kg of Al_2O_3, 16 kg of AlF_3, and approximately 13.200 kWh of electricity. On the other hand, as presented in Figure 1.2, 1 t of pure aluminum generates 1.42 Kg of gas (CO_2 + CO), 6.7–9.7 kWh of heat, and 22-50 Kg of SPL, depending on the smelter.[8–10,14–18] As SPL is related to this thesis target, it is further discussed in section 1.3.
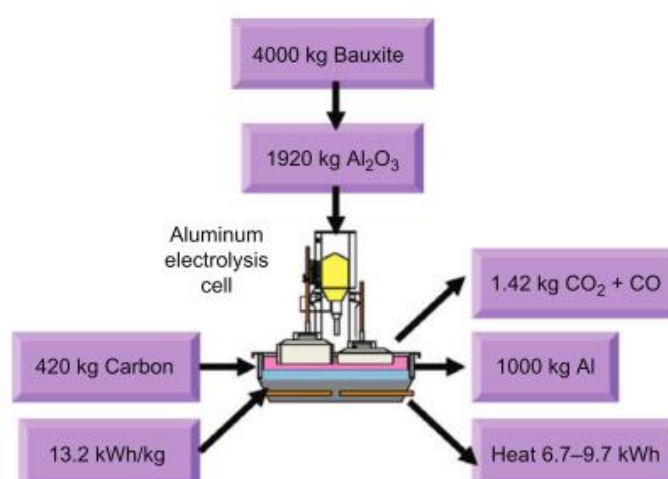
Figure 1.2.- Materials and energy consumption for the electrolytic production of 1 t aluminum.[8]

Due to the aluminum's attractive characteristics (high corrosion resistance, mechanical strength to mass ratio, excellent heat and electrical conductivity) aluminum alloys are used as a major structural material in aircrafts, buildings, machinery parts, beverage cans, and food wraps. Besides, the aluminum is the most recyclable of all materials, it is four times more valuable than any other recycled consumer materials. Moreover, aluminum's low melting temperature and Hall-Héroult process' high energy demand, makes its recycling 20 times more energy efficient and emits only 5% of the greenhouse gas as compared to its primary production.[1,2,8,19]

1.2.2   Secondary aluminum

In 1990, the secondary aluminum production was around 8 million metric tons (29 % of total aluminum production), in 2010 close to 18 million metric tons (32 % of total aluminum production), and it is estimated that by 2020 the secondary aluminum production will increase to 31 million metric tons (32 % of total aluminum production). Currently, more than half of the aluminum produced in Europe is obtained from recycled raw materials and that trend is clearly increasing.[20] Production of secondary aluminum is accomplished in two stages:

i.   Scrap gathering: Scrap is divided in two categories: new and old scrap, according to its origin. If it comes from end of life products is called old scrap, and if it comes from the production process, new scrap [1]. Typical sources of aluminum new scrap are process scrap, extrusions, turnings, and of old scrap are commercial scraps, used beverage cans (UBCs), foils, and old rolled or cast metal. Today, around 50 % of the scrap is old scrap.[20]

ii. Melting of the scrap: A complex combination of all types of aluminum scraps collected is loaded into the melting furnaces, which are most likely to be either reverberatory or rotary furnaces. Regardless the furnace type, a salt flux is used to reduce the melting temperature, protect the molten aluminum pool from oxidation losses, absorb oxides and contaminants from the scrap, and improve the metal recovery from the scrap. Usual fluxes consist of a mixture of chloride, and fluoride compounds, as fluoride additions greatly reduce the surface tension of the molten flux on molten aluminum. The most

used fluoride compounds are cryolite (Na_3AlF_6), sodium fluoride (NaF), potassium fluoride (KF), or fluorspar (CaF_2).[2,19] Once aluminum is melted, the final alloy components compositions are adjusted to achieve the desired quality. By these means, the removal of oxides and impurities from molten aluminum is enhanced

In the secondary aluminum manufacture, two wastes are generated along with molten aluminum, *i.e.* off-gas and dross. Aluminum dross (also known as skim) is a semisolid mixture of molten aluminum and different oxides and chlorides, depending on the melting practice and used fluxes. Drosses can be classified as non-salt dross (also known as black dross in Europe, and white or gray dross in the United States) if no flux is employed in the melting process, or salt dross, when saline fluxes are used. Salt dross usually contains less than 20 % of aluminum metal, 30 to 50 % of aluminum oxide and 30 to 50 % of fluxing salt.[1,2]

Although salt dross can be thermally processed, it is a common practice to recover much of its aluminum by crushing and concentration. The remaining solid, called salt cake or salt slag, contains 3–9 wt.% of Al, 15–30 wt.% of Al_2O_3, 30–55% of NaCl, 15–30% of KCl and, depending on the scrap type may contain, carbides (Al_4C_3), nitrides (AlN), sulfides (Al_2S_3, Na_2S), phosphides (Si_3P_4), sulfates (Na_2SO_4), and also carbon and cryolite in smaller proportions.[1,2,7,19,21,22] As the salt cake is part of this thesis target, is further discussed in section 1.4.

1.3   Spent Potlining (SPL)

As described in section 1.2, SPL is a hazardous waste generated at the end-of-life of the carbon cathodes in aluminum smelting electrolysis cells or pots, *ergo*, produced by the primary aluminum industry. The cell's cathode is replaced when operational failure or poor cell performance, caused by carbon cathode lining degradation, forces the cell shutdown. Cathodes are discarded after 3-10 years, typically 5-6 years, and then named SPL. The SPL composition highly varies due to the differences in the cell lining components, dismantling procedures, and how long the pot has operated. Nevertheless, it usually includes aluminum (5-20 %), refractory bricks (20-50 %), fluorides (20 %),

carbon (5-50 %), sodium (7-20 %), calcium (1-3 %), cyanides (0.1-0.7 %), and polycyclic aromatic hydrocarbons (PAHs).[4,10–13,15,17,23–26] Thus, SPL is classified as a hazardous waste according to the European Waste Catalogue and Hazardous Waste List, (European Waste Code (EWC) 10 03 07*) and to the Environmental Protection Agency of the United States (EPA waste code K088).[18,27] It is considered highly flammable (H3-A[1]), corrosive (H8[2]) and leachable (H13[3]) due to its fluoride content.

A schematic diagram of an Electrolytic/Halt-Héroult cell is shown in Figure 1.3. SPL (Items 12, 15, 16, 18, 20 and 21) is usually classified into 1st cut (portion above the collector bars) and 2nd cut (fraction below the collector bar). The 1st cut is the cathode, which conducts electricity and consists mainly on carbonaceous material blocks with graphitized carbon. The refractory layer that is located below the cathode carbon layer is one of the main constituents of the 2nd cut lining.[15,28]
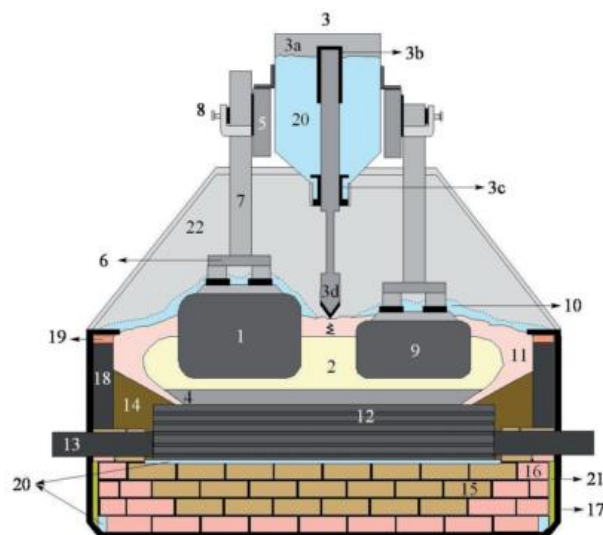
Figure 1.3.- Electrolytic/Halt-Héroult cell schematic diagram. (1) anode (prebaked); (2) electrolyte (bath); (3) Alumina point feeder, (3a) alumina hopper (3b) air cylinder, (3c) metering chamber, (3d) crust breaker; (4) aluminium pad; (5) anode beam (current supply); (6) anode yoke and stubs (iron); (7) anode rod (aluminium); (8) anode clamp; (9) spent anode (butt); (10) alumina crust/ cover; (11) crust (side ledge); (12) cathode carbon block; (13) current collector bar (steel); (14) ramming paste; (15) refractory; (16) insulation; (17) steel shell; (18) sidewall block; (19) cast able; (20) alumina; (21) rock wool and (22) gas collection hood (removable).[28]

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[1]H3-A: substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.
[2]H8: substances and preparations which may destroy living tissue on contacts.
[3]H13: substances and preparations capable by any means, after disposal, of yielding another substance, *e.g.* a leachate, which possesses any of the characteristics listed above.

The 2nd cut is also separated according to the expected contamination degree, thus it is usual to find three different cuts:[26] *(i)* 1st Cut, the carbon liner, *(ii)* 2nd Cut,the part of the refractory material that was close to the carbon lining (Chamotte stone), and *(iii)* 3rd Cut, the part of the refractory expected to be least contaminated (Moler stone).
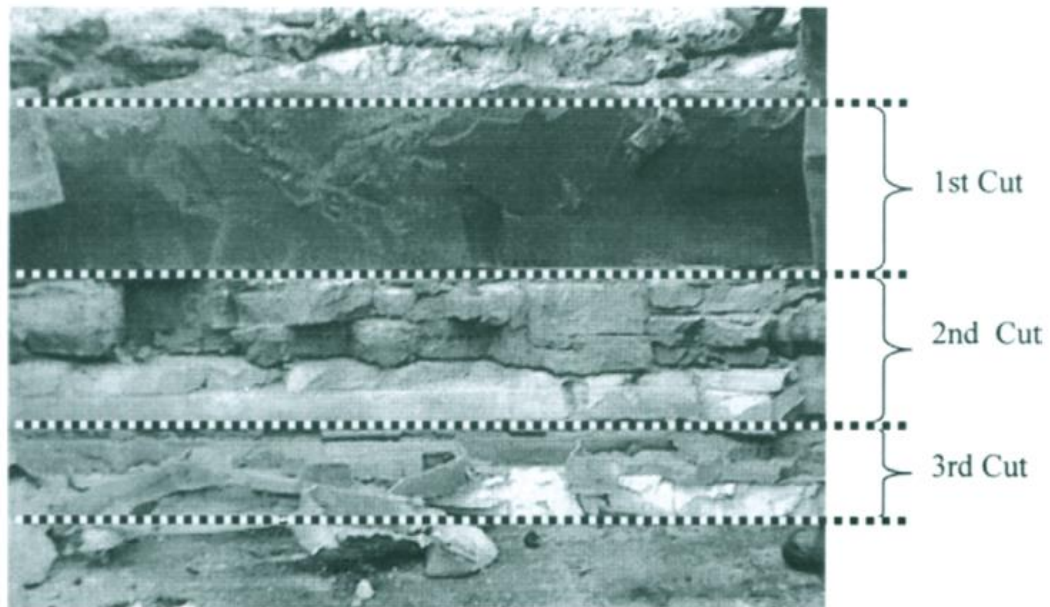
Figure 1.4.- SPL 3 cuts, carbon liner, Chamotte stone and Moler stone[26]

The fraction of interest in this PhD thesis is the second cut, as it is the fraction co-processed with salt slag by Befesa Aluminium and converted into Paval, which is the studied material.

1.3.1   2nd cut SPL chemical and mineralogical characteristics

The SPL composition highly varies due to the different technologies employed to build cell linings, and to the residual aluminum and flux remaining with the original cell lining components, which vary depending on the dismantling procedures. The composition also depends on how long the pot operated, as sodium and fluoride will have diffused deeper inside the lining for pots that have operated longer, increasing the sodium and fluoride content in SPL. This will also depend on the type of brick.[15] A typical composition of 2nd cut SPL is presented in Table 1.1.

Table 1.1.- 2nd cut SPL average elemental composition (wt%)[26]

Al (total)	F	Si	Na	Fe	Ca	C	CN
16-10	16-20	7-10	0.7-15	3	1-2	2	0.1-0.3

1.3.2   SPL management

As the SPL is subjected to high temperatures, some water reactive chemicals, such as cyanides, metals (Al, Li, and Na), reactive metal oxides (Na_2O), nitrides, and carbides, are generated and absorbed into the lining during the cell life. These compounds react with moisture and produce $NaOH$, H_2, C_2H_4, and NH_3.[12,15,17,18,24,26] It is well stablished that improper SPL disposal results in a substantial hazard to the environment due to migration, mobility and persistence of cyanides. Its management should, therefore, be carried out in compliance with current legislation.[16,24,26,27] In the past, the SPL water reactivity was used to break loose the lining by soaking the complete cell in water. However, because of health safety and environmental concerns, this practice is now abandoned, and today the lining is removed dry.[15] As the SPL is toxic, corrosive, and reactive with water, its processing is a tremendous challenge, along with its handling, transportation and storage.[15]

Although the SPL has been treated for many years just to minimize its fluoride leachability in water in order to enable its disposal in landfills[18,29–31], a number of SPL treatment technologies have been developed over the years mainly focused on recycling SPL. These can be classified into five categories: *(i)* recycling in other industries *e.g.* cement, mineral wool, iron and steel industries, *(ii)* physical separation methods, *(iii)* thermal treatment for the carbonaceous material *e.g.* fluidized bed combustion, pyrosulfolysis, and pyrohydrolysis, where the presence of H_2O and HF at extreme temperatures cause corrosion problems,[32] *(iv)* chemical leaching approaches for cryolite recovery and *(v)* co-processing of SPL in third-party industries, where either its fluoride or carbon fraction can be used.[12,13,15–18,23,26,33] Two of the above mentioned technologies have been considered for development at industrial level, a thermal approach by Ausmelt Alcoa to produce AlF_3 and Alcan's caustic leaching to produce NaF or CaF_2.[23] As SPL is a hazardous waste, its treatment goals should include *(i)* minimum number of steps, to minimize cost and allow ease of implementation, *(ii)* recovery of valuable materials from SPL: graphite and fluorides (as AlF_3 or CaF_2), *(iii)* destruction of cyanides, *(iv)* generation of no further environmental problems, *(v)* low energy demand and *(vi)* recycling of virtually all chemical reagents employed.[34]

The co-processing of SPL with Salt Cake is one of the most promising approaches reported. Indeed, Befesa Aluminum found a synergy by blending salt slag and 2nd cut SPL that reduces the energy input to operate their water leach process to produce Paval, a sub-product suitable for the cement or mineral wool industry, which is the material studied in this PhD thesis.[15]

1.4 Salt Cake

As described in section 1.2, aluminum salt cake is produced by the secondary aluminum industry, during scrap/dross melting. Depending on the kind of furnace used and the raw mix of scrap being melted, the amount of salt slag produced per metric ton of secondary aluminum ranges from 200 to 600 kg,[2,19,22,35,36] and it contains 15–30 % of aluminum oxide, 30–55 % of sodium chloride, 15–30 % of potassium chloride, 5–7 % of metallic aluminum and impurities (carbides, nitrides, sulfides, phosphides, sulfates and cryolite).[1,2,7,19,22]

According to the European Waste Catalogue and Hazardous Waste List, salt cake is classified as a hazardous waste (European Waste Code (EWC) 10 03 08*).[27] It is considered highly flammable (H3-A[4]), irritant (H4[5]), harmful (H5[6]) and leachable (H13[7]).[27,37] It reacts with water or moist air to release an array of explosive and toxic gases, *e.g.* CH_4, H_2, NH_3, PH_3 and H_2S, in addition to leaching of toxic ions to the ground.[2,38] Its management should, therefore, be carried out in compliance with current legislation, which forbids landfill direct disposal in most European countries.[1,2]

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[4] H3-A: substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities

[5] H4: non-corrosive substances or preparations which through immediate prolonged or repeated contact with the skin or mucus membrane can cause inflammation

[6] H5: substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, involve limited health risk

[7] H13: substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.

1.4.1 Salt Cake chemical and mineralogical characteristics

Salt cakes are complex mixtures of several compounds in different proportions depending on the production process variables and used raw materials.[38] This variability is highlighted by the different literature compositions showed in Table 1.2. Total aluminum concentration varies between 25 and 37%, from which aluminum metal is between 1 and 7%, as it has been previously removed from salt slag. Other typical major elements found in salt slag are chlorine, sodium, nitrogen, fluorine, potassium, magnesium, silica, iron and calcium.

Table 1.2.- Elemental composition (wt.%) of Salt slag samples from literature

	Al (total)	Al (metallic)	Cl	Na	N	F	K	Mg	Si	Fe	Ca
Sample 1[39]	25.5	3.04	0.59	0.66	0.54	3.87	0.49	6.69	3.40	1.58	1.23
Sample 2[40]	25	7.25	-	21.89	0.71	-	7.47	2.83	3.69	0.50	1.07
Samples 3	37.2	1.22	9.39	8.52	7.53	5.15	3.18	2.59	2.07	0.82	0.72
and 4[7,38,41]	36.8	2.79	6.79	5.20	1.96	5.50	3.74	0.70	1.03	5.85	-

1.4.2 Salt Cake management

As salt cake direct/untreated disposal in landfills is either banned or too expensive, its treatment goals should include:[1,19,38]

i. An as low as possible cost and complexity for the process.

ii. A minimal environmental impact of the process.
   - Minimizing or eliminating the residue to be discarded.
   - Generating a nonhazardous residue that can be discarded if necessary.

iii. Recovering the salt content (NaCl and KCl) in the feed.

iv. Recovering the metallic aluminum in the feed.

v. Recovering alumina-containing compounds.

vi. Recovering hydrogen.

Some of the industrial plants that recycle salt slag are Engitec Technologies S.p.A., Berzelius Umwelt-Service AG (B.U.S.), Alustockach, Kali & Salz AG, RVA, Alumitech (Aleris), Alreco's (MHM Metals), Alcoa, ALNAK, Alsa, Alumaxm Reynolds, and Befesa Aluminium, which has plants in Spain, Germany and UK.[2,19,42]

Although there can be some variations, typical treatment includes the five steps described below and shown in Figure 1.5:[1,2,19]

i. Grinding and screening. This step is required to recover most of the aluminum metal. During the grinding process, while the salt slag compounds exhibit brittle behavior, the metallic aluminum exhibits plastic/malleable behavior, depending on the alloy, and is, thus, not reduced in size. Screening allows the coarse aluminum metal particles to be concentrated from the fine fractions, with a diameter of less than 3 mm, which tend to contain mainly metal oxides, other metal compounds, and flux salts. Although this is a usual step in salt slag recycling, a method which skips this step and still recovers 80% of the metallic aluminum has been reported.[1,2,19,38]

ii. Water leaching. It is also known as the reaction step. The water-soluble salts contained in the slag are dissolved and the reactive species decomposed. This step can be carried out at ambient temperature (taking into account that salt's dissolution heat rises temperature up to 60 °C) or at higher temperature and pressure (known as High-Temperature/High-Pressure Process), depending on the reactive compounds. As water will have to be removed later, a brine with 22-25% salt concentration is typically generated. As previously described, this process releases flammable gasses. Therefore, it is necessary to either maintain their concentration below the ignition point by air dilution or to prevent the entry of air.[1,2,7,19]

iii. Gas Treatment. According to Berzelius Umwelt-Service AG (B.U.S.), about 10 Nm^3 of H_2, NH_3, PH_3, H_2S, and CH_4 are produced per metric ton of feed material. NH_3 is scrubbed from the off-gas with a sulfuric acid solution and activated carbon filters are used to adsorb the toxic PH_3 and the H_2S from the remaining off-gas. Kali & Salz AG purify the off-gases by transformation into ammonium sulfate, sodium phosphate and sodium sulfate. The cleaned gas consists mainly of CH_4 and H_2 and is used for heating in drying operations and for steam production (instead of natural gas).[2,19]

iv. Solid–Liquid Separation. The brine is then separated from the solid phase – non-metallic product (NMP) by filtering. A reduction in the amount of chlorides in the NMP is essential for its possible commercialization if the aluminum oxide containing material will be used in the production of cement, mineral fibers, and ceramic materials. In this regard, it is imperative to obtain chloride contents lower than 2 wt.% as the only possible outcome for materials with higher contents is landfill disposal. NMPs are marketed under various names, including Oxiton, Noval, Valoxy, Paval, and Serox. The samples of Paval and Serox used in this PhD thesis were provided by Befesa Aluminio.

v. Water removal. Usually water removal is achieved by an evaporator-crystallizer. Some alternative processes such as Freeze-Crystallization, Solvent/Antisolvent, Common Ion, and Electrodialysis have also been proposed. The result of crystallization is wet salt crystals that are subsequently air-dried and reused as flux. As KCl is preferentially vaporized during melting from the melting flux, the recovered salt from the brine has a higher NaCl/KCl ratio than the original flux, and fresh KCl must be added to bring the ratio to the desired values.
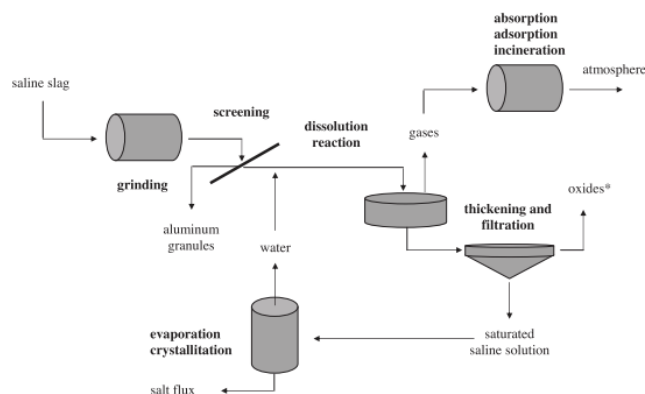
Figure 1.5.- Typical salt slag treatment flowchart.[19]

The Befesa's salt slag recycling process is almost identical to that described above: The first step is the mechanical crushing, in order to separate aluminum from the salt cake, and to reduce particle size to enhance reaction of the hazardous components in the next step. The second step is a water treatment in which salts are dissolved and hazardous components are eliminated. In order to control the gases emission during

leaching, the slurry is fed to reactors until the reaction is completed. Then, the brine is separated from the leach residue, by vacuum filtration. Finally, the NaCl and KCl contained in the brine are crystallized.

This process yields metal concentrates (Al) ready for melting, secondary oxide products (NMP), and flux salts to be recycled to the melting step. The NMP is called Paval by Befesa Aluminium and so will be in this thesis. This material mainly consist of alumina and other oxides, aluminum nitride and carbide[21] and is usually disposed in landfills as a nonhazardous material, sold to cement producers or used in calcium aluminate production.[1] As Paval is the material studied in this thesis, it will be further discussed in the next section.

1.5   Paval

Paval is the material studied in this PhD thesis. This denomination comprises a variety of materials resulting from primary and secondary aluminum industry residues (SPL and salt cake) valorization by Befesa in its four Salt Slags Recycling plants (Valladolid, Salzchlacke, Lunen and Whitchurch). In these plants 630.000 t/year of salt slag and SPL are valorized to produce 270.000 t/year of salt (a mixture of NaCl and KCl) and 360.000 t/year of Paval (also known as BFA, Serox, and BPL, depending on the country).
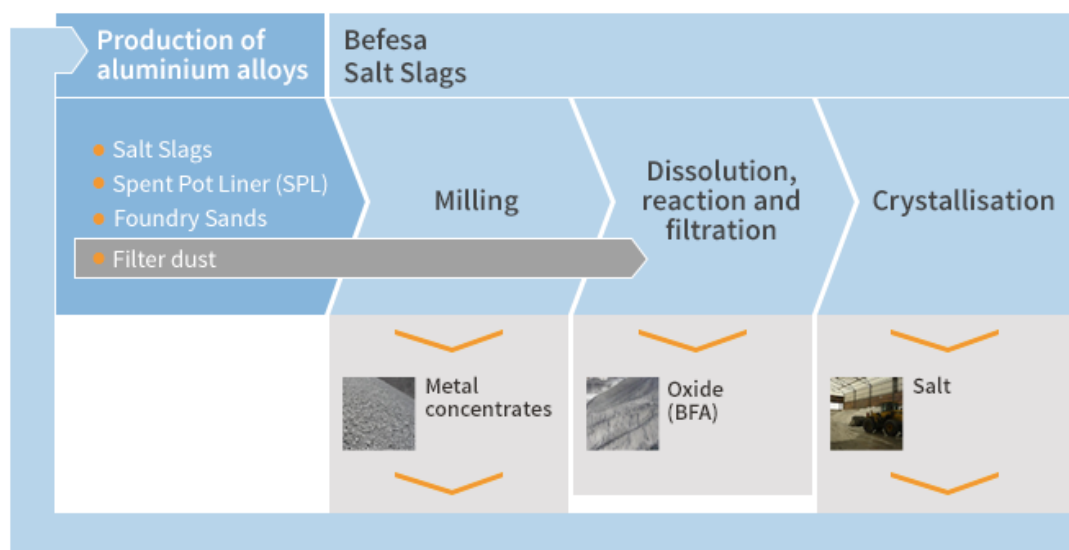

Figure 1.6.- Befesa's salt slag and SPL recycling services.[43]

The most usual direct applications for Paval-like materials are inert filling for construction, road paving, and mortar components. Some examples are listed below:[19]

i. Berzelius Umwelt-Service AG (B.U.S.), specify that their NMP containing primarily alumina and other alloying elements can be used, *after washing (or calcination)* in various industries (cement, ceramic, building industries).[2]

ii. Alsa Technologies, subsidiary of Germany's AGOR Group propose their NMP as a raw material in cement clinker, mineral wool, synthetic calcium aluminates, ceramics, refractory materials, abrasives, glass and as a filler.[2]

iii. Alustockach offer their NMP as a substitute for bauxite, and as a raw material for the cement, refractory, steel, and ceramics industries.[2]

iv. Kali & Salz AG in Germany affirms that their NMP (mainly aluminum oxide) is used to cover and foster tailings piles.[2]

v. RVA sells their NMP as raw material for cement or ceramic industries.[2]

vi. Alumitech (Aleris) further processes NMP for separate sale. NMP is divided in *i)* aluminum containing oxides, which are sold to the steel industry for use in exothermic compounds, de-oxidations materials and slag conditioner; and *ii)* aluminum free oxides, which are further processed to produce ceramic fibbers used as insulation in industrial applications, where temperatures can reach above 1100 °C.[2]

Befesa's current proposal for Paval potential industrial applications are similar to other companies:

i. Inorganic charge in plastic and rubber formulations.
ii. Flame retardant in rubber formulations.
iii. Alternative to Bauxite in refractory materials manufacturing.
iv. Raw material for ceramic materials, primary aluminum production, cement manufacturing, ceramics industry, chemical industry, metallurgical industry and agriculture.

One of the highest value-added applications for Paval is as raw material for calcined bauxite based refractory bricks production. However, in recent years, refractory manufacturers have limited the fluoride and sodium contents in the raw materials to avoid the formations of undesired compounds in the process.[14] The fluoride content has been limited to 1.0 wt% because, at the high temperatures involved in refractory manufacturing, fluoride containing gases would be produced and these emissions are limited by law. Some examples of refractory manufacturers that request this reduction in F content are Insertec, Refralia, Cerámica del Nalón, and Arciresa in Spain, and Imerys or Saint Gobain in Europe.

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Chapter 2

State of the art

Table of contents

2.1   Introduction

As presented in Chapter 1, Paval has a high fluoride concentration that hinders its use as raw material for high value-added applications like the Bayer process and refractory manufacturing. Having the objective of reducing fluorine content in Paval-like materials, two main techniques were reported: *(i)* Thermal treatments (pyrohydrolysis, pyrosulfolysis, and fluidized bed combustion) and *(ii)* hydrometallurgical treatments such as chemical leaching. There is significantly more research performed on SPL recycling, including a significant number of US patents filed in the 80's and 90's proposing both thermal and hydrometallurgical processes to reduce SPL toxicity. It is probable that this results from SPL being considered a hazardous waste in the United States since 1988 (code K088). On the contrary, salt cake is still not considered hazardous and its disposal in landfills is permitted,[1] thus, not much research effort has been devoted to its recycling in the US.

2.2   Fluoride selective removal alternatives

The thermal treatments reported to reduce the fluoride and cyanide contents in SPL are combustion at temperatures higher than 1000 °C,[2–6] pyrohydrolysis, and pyrosulfolysis. Pyrohydrolysis involves contacting the SPL with H_2O or steam at high temperatures to produce HF. A patented pyrohydrolysis process for SPL consisted in subjecting crushed SPL to 1150-1250 °C temperatures in the presence of water. NaF and HF vapor were recovered from the off-gases, and the solid residue immersed in a dilute caustic solution at 200 °C to leach out the alumina. This process requires very large and expensive reactors and their high capital and operating costs makes it uneconomical to operate. Moreover, although AlF_3 pyrohydrolysis is known to be relatively easy, the reaction of CaF_2 and NaF is challenging.[7–10]

Sulfolysis was also proposed and patented as a method to recover HF and AlF_3/cryolite from SPL. The process includes a first combustion step prior to the sulfolysis reaction for the carbonaceous material. Then, the oxidized material is attacked with a

sulfur source (as H_2SO_4 or SO_2) to produce HF.[11] Other patent consists on reacting SPL with O_2, H_2O and SO_2 at 600 to 1200 °C to produce an HF enriched gas.[12]

Thermal approaches shared the setback of dealing with H_2O and HF at extreme temperatures, which causes severe corrosion problems.[13] Hydrometallurgical processes, on top of not having these limitations, had a lower energy demand and therefore an smaller environmental impact. They were also susceptible to recycle the chemical reagents employed. Taking into account all of the mentioned above, this research was focused on removing fluoride from Paval by chemical leaching.

2.3   Fluoride selective leaching

As stated in the previous chapter, Paval is a material obtained from spent pot lining, salt slag or a mixture of them. Therefore, the literature concerning fluoride selective lixiviation can be divided into three mayor streams according to the matrix from which the fluoride is leached: *(i)* Spent pot lining (SPL), *(ii)* salt cake (also known as salt slag or saline slag), and *(iii)* other solid matrixes.

The elemental and phase composition of the materials is a critical variable in the leaching processes and therefore, the literature concerning fluoride leaching from salt cakes and SPL is presented in first place, and then the literature concerning fluoride leaching from other various matrixes.

2.3.1   Fluoride selective leaching from salt cake

The research concerning salt cake recycling is mainly focused on recovering metallic aluminum, sodium and potassium chlorides by wet treatments as well as removing other main compounds such as Al_4C_3, AlN, and Al_5O_6N. This processes usually release noxious gases such as H_2, NH_3, CH_4, PH_3, and H_2S.[14–16,18,19] The remaining residue, Paval, is employed in low-value applications or disposed in landfills,[15–17] therefore, there is little research about recycling it by hydrometallurgical processes.

To the best of our knowledge, the only hydrometallurgical process proposed in the literature to further recycle salt cake consists on a first aqueous leaching -which would

be the equivalent of Paval production from salt cake- and an alkaline leach at 60 °C. The proposed process consists of two steps: first, a water leach for 1 h at 25 °C, by which 90 % of the Cl, 55 % of the Na, and 45 % of the K can be leached. The same researchers proposed a modification to enhance the performance of the process consisting on further grinding in the water leach step, screening and filtering. Grinding enhanced fluoride extraction from 60 to 71 % and screening and filtering enhanced Al metal extraction. In the second step the material from the first step was put into contact with a 150 g/L NaOH aqueous solution for 15 min at 60 °C, and a S/L of 100 g/L.[18,19]

2.3.2   Fluoride selective leaching from SPL

The hydrometallurgical processes proposed in the literature can be divided in two main classes: Processes that include an initial aqueous treatment and processes that do not. This is an important distinction in this thesis because the material in this research is more similar to an aqueous washed SPL than to a SPL itself, as soluble fluoride compounds such as NaF are removed from the material in the water treatment.[20] The most common process in the literature to produce 'SPL Paval' consists on contacting <1.18 mm particle size SPL with milliQ grade water for 4 h at 25 °C, and S/L ratio of 240 g/L.[20–23]

Aluminum is widely used in fluoride leaching as they are known to form soluble and highly stable fluoro-aluminum complexes[24] which enhance fluoride leaching yields from fluoride-bearing materials, including CaF_2.[14,20,25–27] As a result, the three proposed leaching steps that follow the water treatment described above rely on aluminum affinity with fluoride. One of the methods leaches <1.18 mm particle size 'SPL Paval' with a 135 g/L of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) aqueous solution for 24 h at 25 °C, and a S/L ratio of 150 g/L (the ratio is actually higher because the leaching losses in the water step are not taken into account).[21] A more aggressive alternative was proposed by adding 0.5 M HNO_3 to the $Al(NO_3)$ solution, raising the temperature to 60 °C, and reducing S/L ratio to 120 g/L. This allows the reaction time to be lowered to 4 h. The two proposed treatments aim to solubilize the cryolite (Na_3AlF_6) and fluorspar (CaF_2) present in SPL. While almost total cryolite leaching was achieved, solubilization of CaF_2 was only partial. Nonetheless, 96.3 wt% of the fluoride remaining after the water

wash step was extracted with this process.[20] Another process from literature used a mixture of H_2SO_4 0.7 M and Al^{3+} 0.20 M. The solution was put into contact with the SPL Paval for 4 h at 60 °C and using a S/L ratio 120 g/L (minus water leach losses) resulting in a fluoride removal of 83.2 wt%.[22,23]

A water leach at 20 to 70 °C and a S/L ratio between 250 and 333 g/L for 10 to 20 minutes was patented to dissolve all water-soluble fluorides in an SPL sample ground below 300 µm as previous step to an alkaline leaching process. The second step of this process used an aqueous solution of 30 to 40 g/L NaOH with a S/L ratio of 167 g/L for 40 to 80 minutes at 60 to 95 °C.[28]
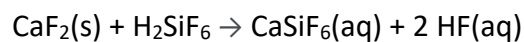
Alternatively, a method to leach cryolite from SPL comprising H_2SO_4 and $Al_2(SO_4)_3$ was also patented. 93 %F extraction was achieved at 95 °C by maintaining the $Al_2(SO_4)_3$/H_2SO_4 ratio between 0.84 and 0.90, and the aluminum concentration below 0.1 M to avoid fluoride precipitation according to the authors.[29] Later, these researchers proposed an alkaline pretreatment to improve the results. The SPL was wet-ground to <100 µm in a 25 % slurry, and washed in counter current with a 14 g/L NaOH solution. 55 % of the fluoride present in the SPL was leached and the solution could be fed to a Bayer process. The solid was then filtered and fed to the $Al_2(SO_4)_3$-H_2SO_4 process described previously.[30]

Calcination is sometimes used prior to the hydrometallurgical treatments to destroy cyanides. In a reported work, after calcination, 30 g of SPL ashes were mixed with 12 g of concentrated H_2SO_4. Once homogenized, 3.7 g of H_2O were added and the mixture was maintained at room temperature for 2 h. Then, a 74.5 g/L $Al_2(SO_4)_3 \cdot 18 \cdot H_2O$ aqueous solution was added, and the temperature risen to 93 °C for 1 h. The result was a fluoride extraction of 97 %.[31] Cyanides are also reported to be decomposed by heating the treated SPL to 160-220 °C.[32] In this case, the reported leaching solution was alkaline, and contained between 10 and 60 g/L of NaOH, which was put into contact with <600 µm SPL for 0.5 to 3 h at 60 to 90 °C and a S/L ratio from 100 to 120 g/L. In this process the cyanides were destroyed by heating the treated SPL at 160-220 °C.

Although the use of Al^{3+} to dissolve fluorides in SPL is reported to be the key, it is not always necessary to add it externally, as it can be leached from the material.[13,27,33,34]

A process using the aluminum present in SPL was patented where < 7 mm SPL particles were leached with 0.5 M H_2SO_4 for 1 h at 90 °C and a S/L ratio of 100 g/L. Under these conditions, at the end of the reaction the Al^{3+} concentration in the solution was 0.21 M, the F:Al atomic ratio 1.99, and the pH 2.2. The result was 93.3 % fluoride and 89.5 % aluminum leaching.[13] Another aluminum free treatment was a combination of acid and basic leaching steps. First, a NaOH 2.5 M solution was put into contact for 180 minutes at 100 °C, and a S/L ratio 220 g/L to dissolve Na_3AlF_6, NaF, and Al_2O_3 into the solution. Second, the filtered solid was mixed with HCl 9.7 M for 180 minutes at 90 °C and a S/L ratio 250 g/L to further dissolve the CaF_2 and $NaAl_{11}O_{17}$.[33]

Fluoride leaching was also studied using synthetic mixtures of the main fluoride species in SPL, *i.e.* NaF, Na_3AlF_6 and CaF_2. Na_3AlF_6 was found to be fully dissolved after 16 h reaction time with a 120 g/L $Al(NO_3)_3 \cdot 9H_2O$ solution at 25°C and a S/L ratio of 33 g/L. CaF_2, however, required a more concentrated leaching solution (150 g/L), two times higher leaching solution to liquid ratio (15 g/L) and longer reaction times (24 h). This results highlight the stability of the CaF_2 and, hence, its resistance to leaching.[35] Na_3AlF_6 solubility was further studied in an 107.7 g/L $Al_2(SO_4)_3$ aqueous solution at 95-98 °C. It was found that, due to Na_2SO_4 formation, fluoride solubility was lowered from 25 to 21 g/L.[36] A different approach to dissolve cryolite and fluorspar was reported, where fluoride compounds were used as leaching agents. It was based on the following reactions:

$$2 \ Na_3AlF_6(s) + 3 \ H_2SiF_6(aq) \rightarrow 2 \ AlF_3 \ (aq) + 3 \ Na_2SiF_6(s) + 6 \ HF(aq)$$

$$CaF_2(s) + H_2SiF_6 \rightarrow CaSiF_6(aq) + 2 \ HF(aq)$$

Hexafluorosilicic acid (H_2SiF_6) digests cryolite and fluorspar forming hydrofluoric acid and soluble fluoride compounds.[24]

As fluoride leaching by hydrometallurgical processes is not a common research line, there is not a large amount of information available. Therefore, it was also considered interesting to research methods to leach fluoride from other solid matrixes.

2.3.3   Fluoride selective leaching from other solid matrixes

There is a need to reduce fluoride levels in other materials such as lead, zinc and copper sulfides prior to smelting because at levels above 100 ppm fluoride may interfere with the smelting process. A method for extracting fluoride from minerals or mineral species by lixiviation was patented in order to solve it. The patent was again based on the high stability of fluoride-aluminum complexes, several orders of magnitude above the bond strength of fluoride in minerals. If $Al_2(SO_4)_3$ and H_2SO_4 were employed, the pH was proposed to be between 3.0 and 4.3 because aluminum is soluble as aluminum sulfate and fluoride can exist in the free ionic F^- state according to the inventors. On the other hand, if $AlCl_3$ and HCl were used, the pH was set between 1.0 and 2.0 due to the fluoride equilibrium between hydrogen fluoride and chloride. Cl^- will compete with F^- in the combination reaction with aluminum, and thus, reduce the efficiency of the fluoride removal reaction. The F:Al atomic ratio was set between 1:1 and 5:1, and preferably between 2:1 and 5:1 in order to minimize the formation of insoluble fluoride and aluminum species.[37]

In good agreement with this patent, the mixture of sulfuric acid and aluminum sulfate was reported to be efficient for the selective fluoride leaching from zinc concentrates: CaF_2 was successfully leached from a zinc concentrate (produced from zinc sulfide ore) following the patented method described above: H_2SO_4 and $Al_2(SO_4)_3$ maintaining a 3.3 pH and a F:Al ratio above 0.5.[19] Similarly, 92% fluoride removal from Double Leach Waelz Oxide (DLWO), a zinc concentrate produced by Befesa Zinc Aser S.A., was reported using a 70 g/L $Al_2(SO_4)_3$ solution maintaining the pH at 2 with a S/L ratio 240 g/L.[39]

The alternative mixture proposed in the previous patent, $AlCl_3$-HCl was useful to leach 99 % of the fluoride contained in a mixed rare earth concentrate. This concentrate was leached with a 4 M HCl and 1.5 M $AlCl_3$ mixture with a 50 g/L S/L ratio for 90 minutes at 85 °C.[40] When fluoride and the matrix containing it are not strongly bonded, the presence of aluminum may not be necessary. For example, HCl was used to leach fluoride from coal fly ash.[41] Fluoride in wastes produced by the pesticide industry is

typically found as NaF which can be leached with a 99 % yield by washing the waste with a NaOH solution with a S/L ratio of 25 g/L, for 4 h at 75 °C.[42]

Table 3.1.- Fluoride leaching conditions from literature

Material	Leaching agent	Concentration (g/L)	t (h)	T (°C)	S/L (g/L)	[Al^{+3}] (M)	Particle size (mm)	F:Al	pH	wt. % F leached	wt. % Al leached	Ref
Salt Cake Paval[a]	NaOH	150	0.25	60	100	na	<2, <0.150	na	na	60-71	20	[18,19]
SPL Paval[b]	Al(NO$_3$)$_3$·9H$_2$O	135	24	25	150	0.36	<1.18	na	na	na	na	[21]
SPL Paval[b]	Al(NO$_3$)$_3$·9H$_2$O + HNO$_3$	135 Al(NO$_3$)$_3$·9H$_2$O 31.5 (HNO$_3$)	4	60	120	0.36	<1.18	na	na	96.3	na	[20]
SPL Paval[b]	H$_2$SO$_4$ + Al^{3+}	68.6	4	60	120	0.20	<1.18	na	na	83.2	na	[22,23]
SPL[c]	NaOH	20-50	0.7-1.3	60-95	50	na	<0.300	na	7-10	na	na	[28]
SPL	H$_2$SO$_4$ + Al^{3+}	na	na	95	na	<0.1	na	na	na	93	na	[29]
SPL	NaOH	14	na	na	na	na	<0.100	na	na	na	na	[30]
SPL[d]	Al$_2$(SO$_4$)$_3$·18 H$_2$O	74.5	1	93	62	6.0	<0.600	na	na	na	na	[31]
SPL	NaOH	10-60	0.5 – 3	60-90	100 – 120	na	<0.600	na	na	na	na	[32]
SPL	H$_2$SO$_4$	49	1	90	100	0.21	<7	1.99	0-3	93.30	89.50	[13]
SPL	NaOH	100	3	100	220	na	na	na	na	na	na	[33]
	HCl	354	3	90	250	na	na	na	na	na	na	
CaF$_2$, Na$_3$AlF$_6$	H$_2$SiF$_6$	100-200	na	na	na	na	na	na	na	na	na	[24]
Na$_3$AlF$_6$	Al$_2$(SO$_4$)$_3$	107.7	na	95-98	na	na	na	na	na	na	na	[36]
CaF$_2$, Na$_3$AlF$_6$	Al(NO$_3$)$_3$·9H$_2$O	120 (Na$_3$AlF$_6$) 150 (CaF$_2$)	16 (Na$_3$AlF$_6$) 24 (CaF$_2$)	25	33 (Na$_3$AlF$_6$) 15 (CaF$_2$)	na	na	na	na	na	na	[35]
Minerals and other matrixes	Al$_2$(SO$_4$)$_3$ + H$_2$SO$_4$	na	na	na	na	na	na	2-5	3.0-4.3	na	na	[37]
	Al$_2$(SO$_4$)$_3$ + H$_2$SO$_4$	na	na	na	na	na	na	>0.50	3.3	na	na	[38]
	Al$_2$(SO$_4$)$_3$	70	na	na	240	5.7	na	8	2	92	na	[39]
	HCl-AlCl$_3$	146 (HCl), 20 (AlCl$_3$)	1.5	85	50	1.5	na	na	na	98.74	na	[40]
	NaOH	na	4	75	25	na	na	na	12	99	na	[42]
	HCl	na	na	na	na	na	na	na	2.5	na	na	[41]

a) Previously washed with milliQ, for 1 h at 25 °C, b) Previously washed with 240 g/L milliQ, for 4h, at 25 °C, c) Previously washed with 250-333 g/L milliQ, for 10-20 minutes, at 20-70 °C d)Previously calcined to destroy cyanides + acid treatment S/L= 30/15,7 g/g (1406 gH$_2$SO$_4$/L), 2h

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Chapter 3

Objectives and scope of the thesis

In the first chapters of this Ph.D. thesis a general description of the aluminum production process was presented in order to contextualize the nature of the produced residues and its scale of production. Several applications of the Non-Metallic Product (Paval henceforth) were listed and the purification requirements for high-end applications such as refractory manufacturing (<1.0 wt% F) described. In chapter 2, a critical review of fluoride leaching processes was provided, showing the necessity of further research on fluoride selective leaching from this type of materials.

Against this background, the primary objective of this thesis is the design of a valorization process which selectively leaches fluoride from Paval and results in a treated material with a fluoride content below 1.0 wt%, while leaching the minimum aluminum possible. This process needs to be technically and economically viable to allow industrial implementation, hence, the following characteristics need to be part of the design: *(i)* simple process layout, *(ii)* low energy demand, *(iii)* minimum environmental impact, *(iv)* inexpensive chemical reagents, *(v)* mild reaction conditions in order to avoid expensive installations *(vi)* chemical reagents recycling, and/or *(vii)* value-added compounds recovery.

In order to achieve the primary objective of the thesis, a series of milestones need to be fulfilled.

- Selection of the most suitable leaching agent for selective fluoride removal. The literature review showed that many different leaching agents (acids and bases) have been used for fluoride selective leaching from different wastes; hence, the first objective should be the selection of the best one for our material.
- Optimization of the leaching conditions. The complexity of the raw Paval and the numerous parameters that play a role in fluoride and aluminum leaching result in a complex system whose study will be favored by the use of a Design of Experiments approach and an ANOVA analysis.
- Recyclability study of the generated by-product streams to reduce the inlet material requirements and material disposal costs.

The focus of this PhD thesis is a compromise between a rigorous academic approach and an industry-oriented research, which will contribute to the circular economy development through wastes transformation and their introduction as raw materials into other industrial manufacturing processes.

Chapter 4

Experimental

Table of contents

4.1. Introduction

This chapter will summarize the main experimental procedures used during the realization of this PhD thesis. This way, the technique used for the design of the experiments along with all the characterization and analytical details will be easy to find and it will help the fluency of the following chapters dealing with the experimental results, discussion and conclusions.

4.2. The Taguchi method for design of experiments and variance analysis

The traditional design of experiments (DOE), known as factorial design, is the technique of defining and investigating all possible conditions in an experiment involving multiple variables (called factors in DOE and henceforth). Taguchi DOE method uses the same principles as factorial design, in a simplified and standardized version. The most important differences between the traditional method and the Taguchi's one are the number of experiments and the approach to quality. A full factorial design needs L^m experiments (where L is the number of levels for each factor, and m the number of factors), whereas Taguchi only needs a fraction of that number to obtain almost the same amount of information by using Orthogonal Arrays (OA). The main setback of DOE by OAs is that performance estimation at the optimum conditions can be inaccurate when there are strong nonlinear interactions between factors.

Moreover, traditional DOE is focused on how different design factors affect the average result level, whereas Taguchi's DOE studies how different parameters affect the mean and variance of a factor variation to achieve a robust design. As it can be observed in Figure 4.1, the traditional model for quality losses does not consider losses within the specification limits, and Taguchi's quality loss is zero only if the parameter is on target.
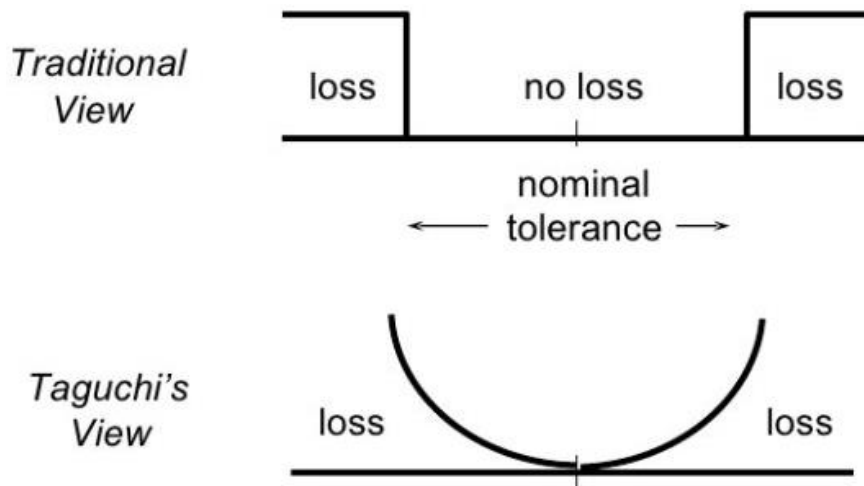
Figure 4.1.- Quality loss in Traditional and Taguchi´s view (Adapted from [1])

Taguchi's DOE is, therefore, an experimental method to achieve product and/or process quality through designing a system immune to uncontrolled variables (noise factors) based on statistical principles. It is an especially useful method when the number of variables is between 3 and 50, there are few interactions between variables, and only a small number of variables contribute significantly. The method is applied in four steps:

1. **Brainstorm the quality characteristics and design parameters important to the product/process.** Taguchi found brainstorming to be a necessary step for determining the full range of factors to be studied. In this PhD research, a number of preliminary experiments were carried out, based on the literature consulted for chapters number one and two (Introduction and State of the Art). Thus, the factors and levels to include in the Taguchi OA were determined, and the presence of interaction between factors evaluated.

2. **Design and conduct experiments**. In order to get an efficient design of the set of experiments, it is important to understand the *degrees of freedom* (DOF) concept, which is a measure of the amount of information (number of effects) that can be determined from a given set of data. For example, it is possible to estimate n effects with n data points. Each interaction consumes DOF equal to the number of levels minus one (L-1). Therefore, an interaction in a two-level factor design will consume

one DOF and, in a three-level factor, two DOF. In Figure 4.2 the most common OAs are presented. As it can be seen, the smallest OA for 2 levels is L_4, which can handle up to 3 factors with 2 levels. For 3 levels, the smallest OA is L_9, which can handle up to 4 factors with 3 levels.

Array	Number of factors	Number of levels
$L_4(2^3)$	3	2
$L_8(2^7)$	7	2
$L_{12}(2^{11})$	11	2
$L_{16}(2^{15})$	15	2
$L_{32}(2^{31})$	31	2
$L_9(3^4)$	4	3
*$L_{18}(2^1,3^7)$	1 and 7	2 and 3
$L_{27}(3^{13})$	13	3
$L_{16}(4^5)$	5	4
*$L_{32}(2^1,4^9)$	1 and 9	2 and 4
$L_{64}(4^{21})$	21	4

*Mixed level arrays

Figure 4.2.- Common Orthogonal Arrays[1]

When possible, the tests should be run in random order to avoid the influence of the experimental setup. Besides, multiple runs of each test are recommended to increase the confidence of the results.

3. **Analyze the results to determine**:

   a. **The optimum conditions:** In order to select the optimum level for each factor, the average performance of each level and factor is calculated. For example, the average performance of factor A at level 1 is obtained by adding all the results for trials including factor A_1, and dividing by the number of trials. To better compare average performances (also called main effects), they are usually plotted in a 2D graphic, where the factors and levels are in the X-axis and the response in the Y-axis. Then, following the corresponding criteria (the smaller the better, target is best, or the bigger the better) a probable optimum set of conditions is selected. When there are interactions

between factors, combined average effects are calculated and plotted to correct the previously selected levels if necessary.

b. **Which factors contribute to the results and how much**: The relative contributions of the factors, expressed in percentage, are determined by an analysis of variance (ANOVA). Variance measures the data distribution about the mean value of the data. In the Taguchi method, the deviation from the target is considered more significant than from the mean and thus, in Taguchi method the mean is replaced by the target value.

Table 4.1.- ANOVA definitions

V	Mean squares (variance)	e	Error (experimental)	N	Number of trials
S	Sum of squares	F	Variance ratio*	CF	Correction factor
S'	Pure sum of squares	P	Percent contribution	n	Total DOF
f	Degrees of Freedom	T	Total (of results)	r	Number of repetitions

*Variance ratio is commonly known as the *F* statistic

Table 4.2.a is an example of the ANOVA table for a DOE with two three-level factors (A and B) and one interaction (AxB), and Table 4.2.b contains all the ANOVA formulae for the example:

Table 4.2.a.- ANOVA table for factors A and B and interaction AxB

Factors	f	S	V	F	S'	P
A	f_A	S_A	V_A	F_A	S'_A	P_A
B	f_B	S_B	V_B	F_B	S'_B	P_B
AxB	f_{AxB}	S_{AxB}	V_{AxB}	F_{AxB}	S'_{AxB}	P_{AxB}
error	f_e	S_e	V_e	F_e	S'_e	P_e
Totals	f_T	S_T				100

Table 4.2.b.- ANOVA definitions table for factors A and B and interaction AxB

Factors	f	S	V	F	S'	P
A	$3-1$	$\sum_{i=1}^{3}(A_i^2/N_{A_i})-CF$	S_A/f_A	V_A/V_e	$S_A-f_A*V_e$	S'_A/S'_T*100
B	$3-1$	$\sum_{i=1}^{3}(B_i^2/N_{B_i})-CF$	S_B/f_B	V_B/V_e	$S_B-f_B*V_e$	S'_B/S'_T*100
AxB	f_A*f_B	$S_{AB}-S_A-S_B$	S_{AxB}/f_{AxB}	V_{AxB}/V_e	$S_{AxB}-f_{AxB}*V_e$	S'_{AxB}/S'_T*100
error	$f_T-f_A-f_B-f_{AxB}$	S_e	S_e/f_e	1	$S_e+(f_A+f_B+f_{AxB})*V_e$	S'_e/S'_T*100
Totals	N-1	$S_e+S_A+S_B+S_{AxB}$			S'_T	100

Where:

- CF = T^2/N
    - $T = \sum_{i=1}^{N}(Y_i - Y_0)$
        - Y_i = result of test i
        - Y_0 = target value

- $S_{AB} = (\sum_{i=1}^{3}\sum_{j=1}^{3}(A_iB_j)/r_{ij}) - CF$
    - r_{ij} = number of test repetitions

When the contribution (P) of a factor is small, the factor is absorbed by the error, and therefore its f and S are added to f_e and S_e. This process is known as Pooling, and is recommended when a factor is determined to be insignificant. Taguchi recommends pooling factors until the error DOF is approximately half the total DOF of the experiment. Increasing the DOF for the error term, as a result of pooling, increases the confidence level of the significant factors.[2]

   c. **What will be the expected result at the optimum conditions:** Performance at the optimum condition is estimated only from the significant factors. It is the sum of the mean of all gathered responses, plus the difference between the average response of the optimum level for each significant factor and the media of all gathered responses. Following the example from Table 6.4, if only factors A and B are significant, and the optimum levels are A_1 and B_2, the expected result (ER) at the optimum condition will be:

$$ER = \bar{T} + (\overline{A_1} - \bar{T}) + (\overline{B_2} - \bar{T})$$

4. **Run a corroborative test(s) using the optimum conditions**. As Taguchi design includes only a small set of the full factorial experiments, the optimum set of conditions is usually not one of the trial runs. Thus, when the optimum set of conditions has not been tested, confirmation testing is a necessary and important step as direct proof of the methodology.[1]

4.3. Experimental set-ups

4.3.1. Sample preparation

Paval samples were dried for 24 h in an oven at 100 °C, crushed in a ceramic mortar, sieved below 1 mm, and stored in a desiccator with silica gel, which was regenerated once a day.

Effluent samples were stored in polypropylene sample containers at room temperature. Before use, they were homogenized and filtered if necessary.

4.3.2. Hydrometallurgical tests

In Figure 4.3 a scheme of the leaching set-up for fixed temperatures from 25 °C and up to 100 °C is shown. The leaching tests were carried out in a flat-bottom borate glass flask, placed in a silicon bath, heated by a hot plate. A magnetic PTFE stirrer was placed in the glass flask and controlled by the magnetic stirring plate to achieve a vigorous stirring. In order to control the temperature, a glass thermometer was placed in one of the flask necks. In the other opening, a glass reflux condenser connected to tap water was place, in order to avoid vapor leaks.
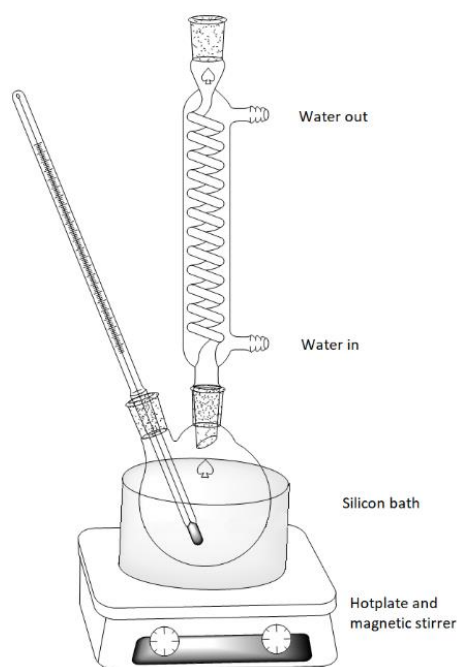
Figure 4.3.- Hydrometallurgical tests set-up

The Paval was weighed and fed to the flask, then, the liquid and the magnetic stirrer were introduced. The flask was placed in the preheated silicon bath, stirring adjusted, and the reaction time started once the slurry had achieved the target temperature. Once the reaction time ended, the flask was externally cooled with water and ice to stop the leaching reactions, and the slurry filtered immediately.

4.3.3. Set-up for precipitation tests

Precipitation tests were carried out at room temperature (25 °C) in an Erlenmeyer flask, on a magnetic stirrer. The precipitating agents were slowly added to the stirred solution with the aid of a funnel and a beaker. The reaction time started when all the reactants were in the Erlenmeyer. Once the reaction time ended, the slurry was filtered immediately.
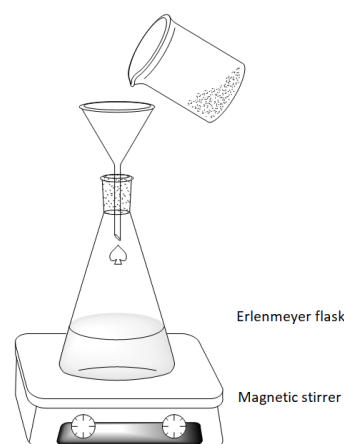

Figure 4.4.- Precipitation tests set-up

4.3.4. Solid/liquid filtration

Solid and liquid phases were filtered in a Millipore Sigma™ 142 mm Hazardous Waste Pressure Filter System lined with a PTFE coating which prevents heavy metal contamination and equipment deterioration. The filters used for all the solid/liquid separations were 0.45 μm pore size membrane filters from Merck (HAWP14250) together with glass fiber prefilters (AP2012450). The filtrations were carried out under 5 bar g of compressed air.

4.4. Analytical and instrumental techniques

4.4.1. pH and conductivity electrodes

The pH was measured with a Crison pHmeter 50 14 T, equipped with a temperature sensor Pt 100 which allows pH measuring at temperatures up to 100 ˚C . Calibration was carried out daily before use, with Crysolit pH buffers 4.01, 7.00 and 9.21.

Conductivity was determined with a Crison conductivimeter EC-Metro GLP 31. Calibration was carried out daily before use, with Crysolit standards 147 μS/cm, 1413 μS/cm y 12.88 mS/cm.

4.4.2.   Ion-Selective Electrodes

Fluoride and chloride contents in liquid samples were measured with a pH & Ion-Meter GLP 22+ equipped with a Ag/AgCl reference electrode, a 96 55 fluoride selective electrode, and a 96 52 chloride selective electrode.

Fluoride selective electrode was used together with a Total Ionic Strength Adjustment Buffer (TISAB) specific for fluoride determination in samples with a high Al^{3+} content, known as TISAB D.[3] It is composed by 230 g disodium tartrate dihydrate, 242 g tris, and 84 mL 37 % HCl per liter of solution. By adding 10 mL of TISAB D to 40 mL of sample, it measures 100 % of the fluoride ions when both Al^{3+} and Ca^{2+} concentration are below 100 mg/L, and above 98 % when Mg^{2+} concentration is below 50 mg/L. The electrode was calibrated daily before its use with freshly prepared NaF standards.

Chloride selective electrode was used together with 5 M $NaNO_3$ as TISAB, and calibrated daily before its use with freshly prepared NaCl standards.

4.4.3.   Ion Chromatography

The sulfate concentrations were analyzed using a liquid chromatograph Dionex IC 3000 equipped with a conductivity detector operating at 35 °C, a guard column Ion Pac AG19 (4x50 mm) and a column Ion Pac AS19 (4x250 mm), which separates F^-, Cl^-, NO_2^-, NO_3^-, $SO_4^=$, and PO_4^{3-}. As eluent, 14 mM NaOH was used in isocratic conditions, and the suppressor, Thermo Scientific Dionex DRS 600, was set at 35 mA to neutralize its conductivity.

4.4.4.   Alkalinity titration

Carbonate content in aqueous solution was determined by alkalinity analysis from pH 10.8 to 4.3 by titration with 0.01 N HCl and a pHmeter was used to accurately identify the endpoints. In Figure 4.5 the species involved in an aqueous solution as a function of the pH are presented.

As observed, OH⁻ is the responsible for the solution alkalinity (caustic alkalinity) above pH 10.8 and therefore the protons needed to decrease the pH from the starting point to 10.8 are used to neutralize OH^-. From 10.3 to 8.3, alkalinity is due to $CO_3^=$, and from 8.3 to 4.3 due to HCO_3^-. Although alkalinity is usually expressed in meq/L of OH^-, HCO_3^- or $CO_3^=$, in this PhD thesis total carbonate concentration was needed, and the result was given as mol $CO_3^=$/L.
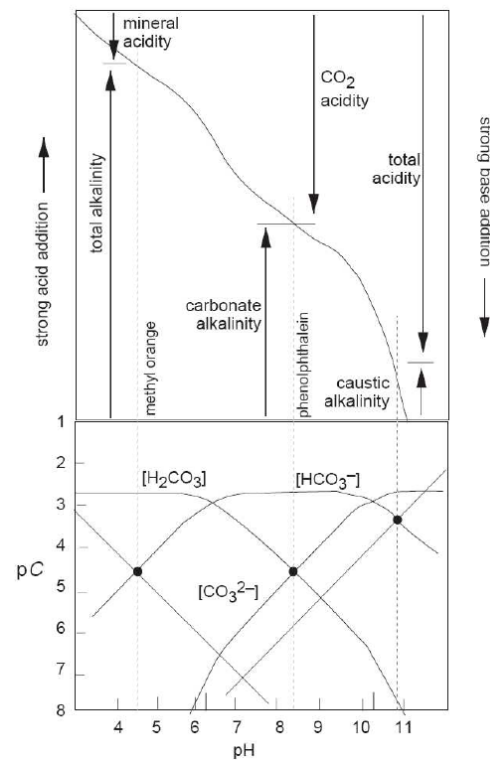

Figure 4.5.- Species affecting alkalinity and titration curves

4.4.5. Inductively Coupled Plasma Optical Emision Spectrometry

Elemental analysis was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 2000 OV device. The measured elements were calibrated daily before use.

4.4.6. X-Ray Fluorescence

The powdered Paval samples were mixed with Spectromelt A12 flux from Merck in a proportion of 20:1 and melted in an induction micro-oven to prepare a boron glass pearl for the analysis. The pearl chemical analysis was performed under vacuum with an AXIOS wavelength dispersion X Ray fluorescence sequential spectrometer from PANalytical, equipped with a Rh tube and three detectors: gas flow, scintillation, and sealed Xe. The calibration was made with international rock and mineral standards. The loss of ignition (LOI) was measured by calcining a portion of each sample in a muffle

oven at 1050 °C for an hour. The elements typically found in rocks were analyzed at a quantitative level, and Cl, F, and S at a semiquantitative level.

4.4.7. X-Ray Diffraction analysis

The powdered samples phase analysis was carried out by X-Ray Diffraction (XRD) with a PANalytical Xpert PRO diffractometer equipped with a copper tube ($\lambda Cu_{K\alpha mean}$=1,5418 Å, $\lambda Cu_{K\alpha 1}$=1,54060 Å and $\lambda Cu_{K\alpha 2}$=1,54439 Å), a vertical Bragg-Brentano goniometer, a programmable divergence slit, an autosampler, a graphite secondary monochromator, and a PixCel detector. The PANalytical X´pert HighScore software combined with the database PDF2 from ICDD were used for data treatment and phase identification.

4.5.   References

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Chapter 5

Hydrometallurgical process

Capítulo sujeto a confidencialidad por la autora

Chapter 6

Sulfate removal methodologies: A review

Capítulo sujeto a confidencialidad por la autora

Chapter 7

Effluent purification

Capítulo sujeto a confidencialidad por la autora

Chapter 8

Global conclusions and future work

Capítulo sujeto a confidencialidad por la autora