Supporting Information for

Valorization of an industrial pollutant residue as a teaching tool: Extraction of Al^{3+} from aluminum saline slag

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I. GENERAL INFORMATION

A. Aluminum Production and waste generated

The scientific and technological development that has taken place from the First Industrial Revolution to the present day has led to an improvement in human living and working conditions, and in many cases to major industrial and economic development. However, it has also brought a series of problems and new challenges. Among these are those related to waste generation and environmental damage. According to Eurostat, a total of 2,153 million tons of waste related to economic activities and households were generated in the European Union (EU) during 2020, amounting to a total of 4,813 kg of waste per capita. The high contribution of construction (37.5%) together with mining (23.4%), followed by wastewater (10.8%) and manufacturing processes (10.7%) is noteworthy. Within the industrial sector, the metal industry is of vital importance for the economy, competitiveness and industrial development, both globally and in the EU. According to the World Economic Forum[3], industrial (non–ferrous) metals are widely used in the manufacture of steels, in construction, in the preparation of alloys, etc. Among these metals, the high production of one of them, aluminum, stands out, accounting for almost 40 % of the total world production of non–ferrous industrial metals in 2021; the world production of industrial metals is 181.6 million tons (Mt). The high production of aluminum is related to the high consumption of this metal due to its excellent properties that make it applicable in sectors such as aeronautical and marine engineering, construction or transport. These properties include its low density (2.70 g/cm^3), low melting point (660ºC) and high resistance to corrosion. This metal is produced on an industrial scale by two processes: the *Primary Aluminum Production* (PAP) and the *Secondary Aluminum Production* (SAP). PAP employs bauxite as mineral resource, and is based on the combination of the Bayer Process (purification of bauxite) and Hall–Héroult Process (electrolytic reduction of molten alumina, containing flux salts, mainly cryolite), while SAP is based on another of the most interesting properties of aluminum: its ability to be recycled an infinite number of times without losing properties compared to aluminum produced by PAP. Figure S1 shows the annual evolution of total aluminum production in the period from 1950 to 2020, showing an increase from about 40 Mt in 2000 to more than 70 Mt in 2020. Figure S1 also shows the annual evolution of PAP and SAP, showing a slight decrease since 1970 in PAP, while the amount of aluminum produced by SAP has been increasing since 1970. Since 2000, both the decrease in PAP and the increase in SAP have softened, although SAP continues to increase.

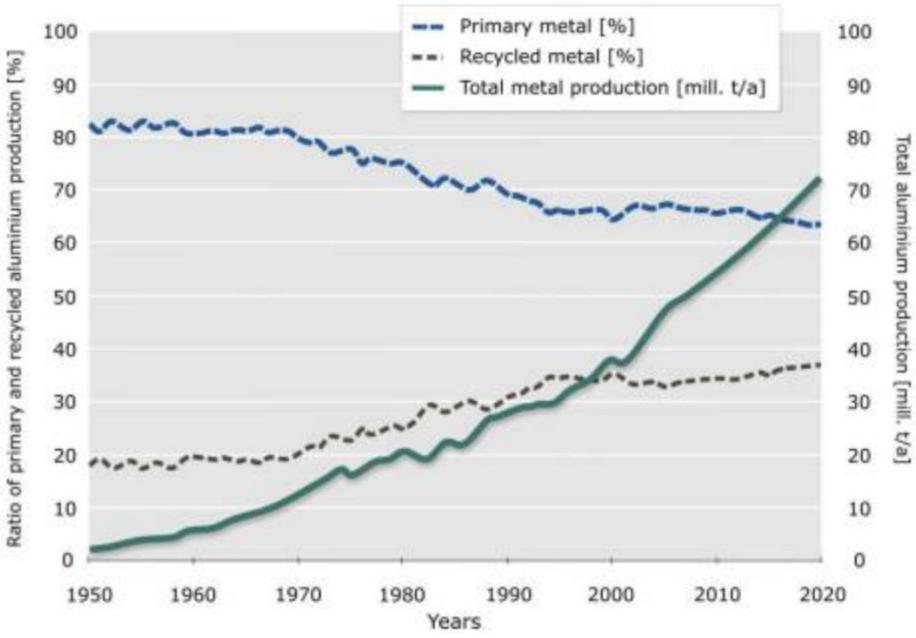


Figure S1. Total aluminum production and ratio of primary and secondary aluminum production.

Table S1 shows a comparison between PAP and SAP from the environmental point of view, showing that SAP is much more environmentally friendly, as it involves lower energy consumption, lower gas emissions and less solid waste generation. However, both industrial processes generate solid waste that is polluting and hazardous to the environment (Table S2), the most abundant being *red mud* in PAP and *slag* in SAP. Obtaining alumina from bauxite by the Bayer process generates the so–called *Red mud* as a waste, originating between 0.3 and 2.5 $t_{red\ mud}/t_{Al_2O_3}$. Due to its composition and high alkalinity, it is considered a hazardous waste, although it is valorized as a raw material for the preparation of some value–added materials. Another type of hazardous waste generated during the aluminum production cycle is the so–called slag, which is produced when the molten metal comes in contact with oxygen in the air, reacting with it to form a layer of oxides on the surface of the molten metal, which protects it from oxidation. The amount of slag produced depends on the type and quality of the starting materials and the operating conditions. It is estimated that for each ton of molten aluminum between 300 and 600 kg of dross are generated. The *European Waste Catalogue* classifies aluminum dross as potentially hazardous and polluting waste. The classification of the different types of slag is based on the composition and content of aluminum metal present in

the slag. Taking these criteria into account, three types of slags are generated during the smelting process: *White dross*, *Black dross* and *saline slags*.

- White dross: this type of dross is generated during the PAP and is valorized in the SAP and in the steel industry. The composition of the residue depends on the operating conditions of the plant in which it is generated, its typical composition being as follows: 15–80 % aluminum metal, 20–30 % oxides and less than 5% salts. This dross is processed at PAS and according to the European Waste Catalogue it is considered as hazardous waste (EWC 100304).

- Black dross: this slag is produced during the SAP. The starting raw material, as well as the metallurgical process applied in its processing, determines its chemical and mineralogical composition. The aluminum content in this residue varies between 5% and 50 %. In addition, it contains between 30–50 % salts and the rest is non–metallic fraction. Typical compounds present in black dross are: Al_2O_3, SiO_2, $MgAl_2O_4$, Fe_2O_3, $NaAl_{11}O_{17}$, AlN, Al_5O_6N, NaCl, KCl, and other minority constituents such as Al_4C_3, Al_2S_3 or AlP . Black dross can react with water generating toxic gases such as NH_3, CH_4, H_2, H_2S or PH_3. For this reason, it is classified by the *European Waste Catalogue* as hazardous waste (EWC 100309).

- Saline slags: the use of fluxing salts in primary and secondary aluminum smelting processes is necessary due to their multiple functions: a) they facilitate heat transfer to the metal; b) they prevent contact of the molten metal with the atmosphere, thus avoiding oxidation of the melt; c) they favour mechanical distribution in the furnace; d) some aluminum oxides can be dissolved by chemical reaction with the fluxing salts. When the aluminum scrap and/or slag used in the PAS is melted in a rotary furnace by using fluxing salts (RSF), a new residue called saline slag or salt cake is generated, whose composition depends on the starting materials used. Like black dross, salt cake can react with water, releasing gases that are harmful and toxic to the environment and health, such as NH_3, CH_4, H_2, H_2S or PH_3. In addition, due to its high salt content (mainly NaCl and KCl), a large amount of chloride could leach into the environment, which would generate an additional environmental pollution problem. Salt cake is classified as hazardous waste by the *European Waste Catalogue* (EWC 100308).

Table S1. Comparison between primary (PAP) and secondary (SAP) aluminum production processes.

Parameter	PAP	SAP
Consumption of energy (GJ/t_{Al})	174–186	10–20
Atmospheric emissions (kg/t_{Al})	204	12
Consumption of water (kg/t_{Al})	57	1.6
Solid waste (kg/t_{Al})	2,100–3,650	400

Table S2. Solid waste generated during the industrial production of aluminum.

Waste	Process in which it is generated
Red mud	Production of alumina from bauxite ore
White dross	PAP
Black dross	SAP
Saline slag	SAP in rotatory furnace
Grinding filter powder	From aluminum dross
Furnace gas filter	Melting furnace
Skimming	Melting furnace without fluxes (brine)

The management and handling of slag is a major problem, difficult to solve. *White dross* is recovered in SAP, but generally both *black dross* and *saline slags* are deposited in controlled landfills that occupy large areas of land and present a certain environmental risk. An alternative to controlled landfills is the chemical treatment of the waste, which decreases the hazardousness and valorizes the waste. Various methodologies have been described in the literature with the aim of valorizing aluminum slags, predominantly the recovery of metallic aluminum and the preparation of materials based on the Al^{3+} cation. In this sense, three routes can be differentiated: pyrometallurgical, hydrometallurgical and hydrothermal. The choice of a route is decided according to the content of metallic aluminum present in the slag. Each of them is described below.

- Pyrometallurgical: Pyrometallurgical routes are applied when the metallic aluminum content is high and are based on melting the metal. When melting, the metal is separated from the slag. These routes allow recovering a high percentage of metallic aluminum, but the technology and the high temperatures required are their major disadvantages. Within this type of route, there are in turn two types.
    a) Rotary furnaces using fluxing salts. This methodology uses up to 50 % of the scrap mass or aluminum dross with fluxing salts, mainly NaCl and KCl; when the salt content is increased, the amount of recovered metallic aluminum increases, but so does the amount of dross generated, in this case the so–called salt cake.
    b) Salt–free technology. In this methodology, no fluxing salts are used, which represents an advantage with respect to the rotary furnace method, but the energy consumption is considerably higher. There are different techniques within this methodology such as the Alcan plasma torch, the DROSCAR graphite arc process of Hydro–Quebec or the ALUREC, ECOCENT or ALUR processes.

- Hydrometallurgical: These routes are applied when the aluminum metal content in the slag is low and are based on the amphoteric character of this metal, allowing the use of two routes, acid and basic, which depend on various factors, such as acid or base concentration, time or temperature. A pretreatment consisting of grinding, washing and sieving of the slag is common. Each of these is described below:
    a) Acid route. The solution obtained from the acid treatment of aluminum slags can be used as a source of aluminum in the preparation of Al^{3+} based materials. Several authors have reported the use of an acid medium to recover part of the aluminum present in the slags.
    b) Alkaline route. By treating the slag in a basic medium it is also possible to obtain a source of aluminum to synthesize different value–added materials based on Al^{3+}.

- Hydrothermal: These routes are based on the treatment of aluminum slags in aqueous media, but under high pressure conditions in a hydrothermal reactor. By this route it is possible to synthesize Al^{3+} based materials, such as zeolites or other molecular sieves and Layered Double Hydroxides (LDHs).

This work proposes a procedure for the management, handling and valorization of saline slags generated during SAP based on a hydrometallurgical process with acid and basic routes. This procedure can be considered as a laboratory practice for students in the 3rd and/or 4th year of Chemistry, Environmental Engineering, Chemical Engineering, Materials Engineering, or related University Degrees. By carrying out this laboratory practice, the students consolidate the contents explained during the theory lectures related to general concepts of Metallurgy, but also to several other concepts of Analytical, Inorganic and Physical Chemistry, as chemical behavior of *p*– and *d*–block metallic elements, solubility, pH, acid–base properties, redox reactions, speciation diagrams of the elements. Besides, this laboratory practice not only allows the students to consolidate these concepts, but also to be introduced to the Chemistry of Materials and to contact with a characterization technique such as Powder X–ray Diffraction (PXRD), as well as to begin to familiarize with research tasks. Likewise, it also allows the students to work on and reinforce important concepts such as the *Circular Economy* and the *Sustainable Development Goals* set by the 2030 Agenda, which aims to decrease the pressure on the environment derived from industrial and social development.

B. Characterization and measurement techniques

Powder X–ray diffraction (PXRD)

Powder X–Ray diffraction (PXRD) is a non–destructive characterization technique that allows the identification of crystalline phases in a wide range of materials, being the most widely used for the identification and characterization of minerals and crystalline solids in general. The PXRD pattern is the fingerprint of a material, as it is characteristic of each one of them. To understand the basis of this technique it is necessary to consider the interaction of X–rays with matter, since X–rays are scattered by the entities (atoms, molecules, ions, etc.) that form crystals. When the wavelength of the incident radiation is of the order of the interatomic distances within a crystal structure, interference of the scattered X–rays with the periodic structure of the crystal occurs. These interferences can be destructive or constructive, depending on the difference in optical paths traversed. Constructive interference occurs when the difference in the optical path followed by the beams is an integer multiple of the wavelength, known as the diffraction condition or Bragg condition (Figure S2 and Eq. S1).

$$n \lambda = 2 \, d \, \mathrm{sen}\theta \qquad \text{Eq. (S1)}$$

where n is the diffraction order, λ is the X–ray wavelength, d is the interplanar distance and θ is the Bragg angle formed by the incident beam and the sample. From the equation of Bragg's law, it is possible to determine the interplanar spacing (d in Figure S2) of a family of parallel planes (hkl). The PXRD diffractograms were performed in a Siemens D–5000 diffractometer (Figure S3), using the Kα radiation of copper (λ = 0.1548 nm) and a nickel filter. The conditions used were a current of 30 mA, a voltage of 40 kV, a scanning speed of 2º/min with steps of 0.05º and a time per step of 1.5 seconds on powder samples.

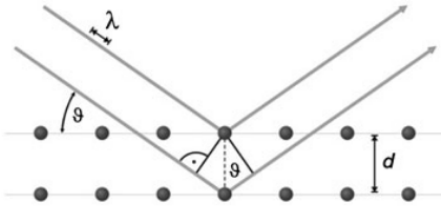


Figure S2. Graphical representation of Bragg's law.



Figure S3. Siemens D–5000 Diffractometer.

The PXRD technique was used to determine the crystallographic composition of the different fractions of the salt slag. The diffractograms obtained were analyzed using the *PANalytical X'Pert HighScore Plus* software, and compared with the Joint Committee on Powder Diffraction Standards–International Centre for Diffraction Data (JCPDS–ICDD®) file patterns.

X–ray microfluorescence (XRF)

X–ray microfluorescence is a characterization technique that allows qualitative and quantitative analysis of elements with atomic numbers between 11 (Na) and 92 (U) in solid samples, without the need for preparation or pretreatment procedures. In addition, it allows the analysis of areas of different sizes, and it is a non–destructive technique.

The basis of the XRF technique is based on X–ray–matter interaction. There are different types of X–ray interaction with matter that can be used in the characterization of materials, such as absorption, fluorescence emission, scattering, diffraction, refraction or emission. When X–rays are absorbed by matter they can generate phonons or excite atoms by emitting a photoelectron. X–rays are ionizing radiation that can strip an electron from the inner shells of atoms, causing their excitation. If the generated hole is occupied by a more external electron, the atom returns to the ground state and can emit energy in the form of electromagnetic radiation. This radiation has energy in the X–ray range and the process is called X–ray fluorescence, each atom showing a characteristic radiation, which can be used to determine the elemental composition of a sample.

XRF analyses were performed by the X–ray Diffraction Service of the Nucleus Research Support Platform of the University of Salamanca on a Bruker model M4 microfluorescence spectrometer (Figure S4). The technique was used to determine the elemental composition of the salt cake and the solid residues generated after the extraction process.



Figure S4. Bruker microfluorescence spectrometer model M4 of the Nucleus Platform X–Ray Diffraction Service at University of Salamanca.

Elemental chemical analysis: Inductively Coupled Plasma Mass Spectrometry (ICP–MS).

Chemical compositions of the solids were determined by Inductively Coupled Plasma Mass Spectrometry (ICP–MS) in an Agilent 7800 apparatus (Figure S5, Nucleus Research Platform, University of Salamanca). A very good linear calibration plot (0–100 ppm) was applied to quantify the metal content, and internal standards were used for MS measurements. Digestion was carried out in acid medium, in a closed Teflon vessel, using concentrated HNO_3 as a reagent. For the digestion a Milestone Microwave equipment model UltraWAVE with temperature and pressure control was used.



Figure S5. Agilent 7800 equipment for ICP–MS of the Chemical Analysis, Chromatography and Mass Analysis Service of the Nucleus Platform at University of Salamanca.

C. HAZARDS AND SAFETY PRECAUTIONS

All students must wear gowns, gloves and safety glasses while performing the laboratory work. The reagents used are saline slag and fractions of various particle sizes, hydrochloric acid (HCl), sodium hydroxide (NaOH) and silver nitrate ($AgNO_3$). For all reagents used, students should avoid direct contact with skin and eyes and oral and respiratory inhalation. NaOH and HCl are strong base and acid respectively, and are highly corrosive, in case of contact with skin or eyes wash with plenty of water. Silver nitrate can cause skin irritation and severe skin and eye burns. Regarding the slag, according to its chemical and mineralogical composition, it can release toxic gases when reacting with water and cause skin irritation. In addition, it is suspected to cause cancer by inhalation.

On the other hand, as commented in the manuscript, various gases may be emitted during the hydrolysis of the saline slag, mainly H_2 and NH_3, reason by which the hydrolysis must thus be done in a fume hood, and also having a proper ventilation in all the laboratory.

Hydrogen is highly flammable, so ignition sources should be avoided. Ammonia can cause respiratory issues (coughing, shortness of breath, and chest pain) and skin and eye irritation. Teachers must ensure that the fume hoods are working perfectly and that they are properly closed, and the use of masks is recommended.

If this methodology is applied for the extraction with other acids or bases, as HNO_3, KOH or CsOH, specific safety precautions may be adopted. Nitric acid is extremely corrosive and can cause severe chemical burns very rapidly. It produces toxic, corrosive, and flammable vapors. If inhaled, it produces corrosion of mucous membranes and delayed pulmonary edema. Contact with eyes can cause permanent damage. It must be handled inside a chemical fume hood and in proximity to eyewash and safety shower stations. Contact with skin, eyes and clothing must be avoided, wearing compatible gloves, safety goggles, and a lab coat. Potassium and cesium hydroxides are highly corrosive and their contact can irritate the skin and eyes, and also the nose and throat. Inhalation can irritate the lungs. In any case, it must be considered that no commercial nitric oxide (> 15 M) should be used for these experiments; the solutions required (1–4 M) are much less dangerous. The same applies for potassium and cesium hydroxides solutions.

D. OTHER USEFUL INFORMATION

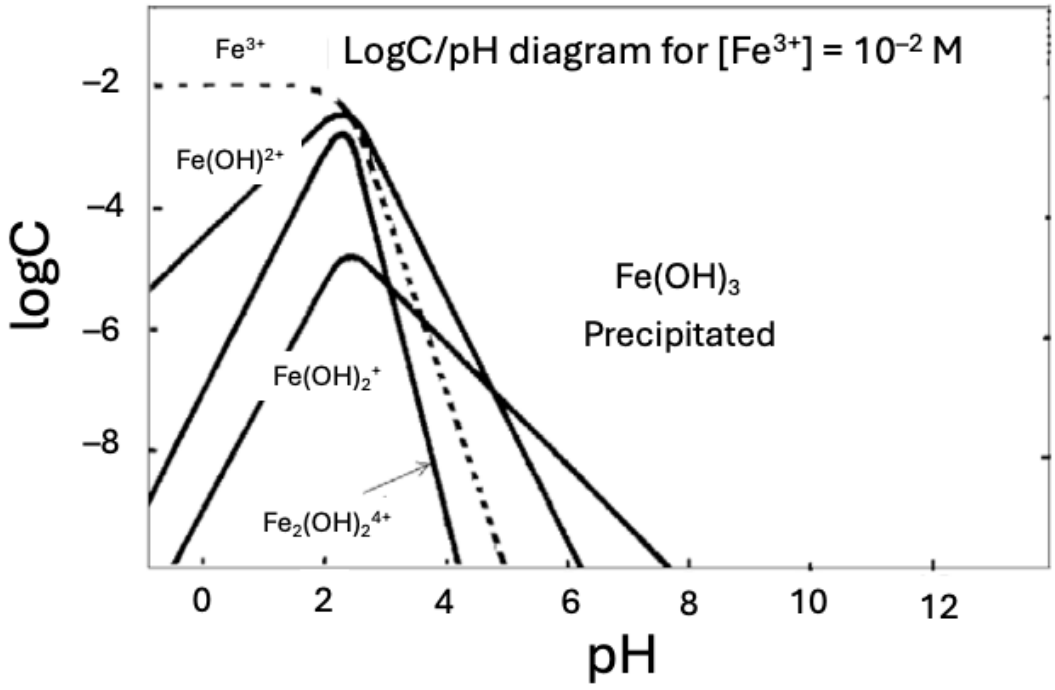


Figure S6. Iron speciation diagram for total concentration 10^{-2} M (elaborated by the authors).

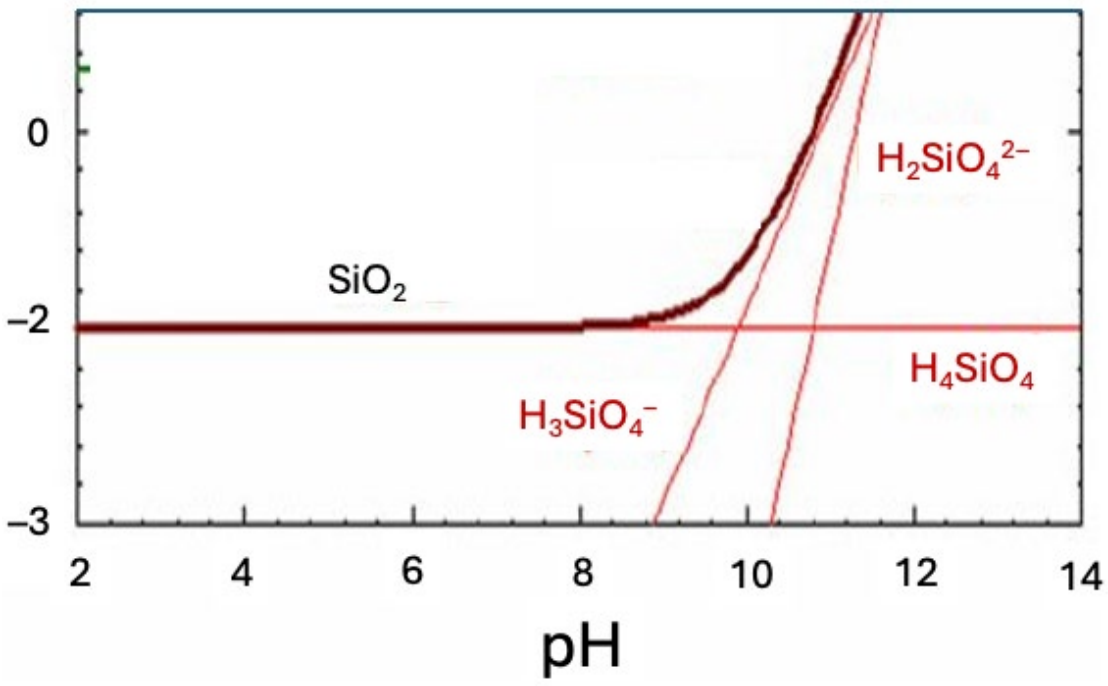


Figure S7. Silicon speciation diagram for total concentration 10^{-2} M (elaborated by the authors).