



A comparative study of acid and alkaline aluminum extraction valorization procedure for aluminum saline slags

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ABSTRACT

A management process for saline slags, one of the wastes from Secondary Aluminum Production, is proposed. The process begins with a grinding step, followed by washing with water, which removed the fluxing salts but provoking the hydrolysis of AlN, yielding Al(OH)₃ and ammonia. Sieving of the solid generated an intermediate and a fine fraction. The first one was rich in metallic aluminum, and can also be returned to the Secondary Aluminum Production. The fine fraction was submitted to an extraction process in acid (HCl or HNO₃) or alkaline (NaOH, KOH or CsOH) conditions, under reflux at 90 °C, obtaining an Al(III) solution that can be used in the synthesis of aluminum-based solids. HCl (1–8 mol/L) and NaOH (1–4 mol/L) were used as reference solutions, HNO₃, NaOH and KOH were used under specific conditions; the slag fraction:extraction solution solid:liquid ratio was also varied. The optimum extraction conditions were: extraction time 2 h, solid:liquid ratio 3:10, concentration 3 mol/L for the NaOH medium and 4 mol/L for the HCl medium. More than 30% of the aluminum present in the fraction smaller than 0.4 mm was recovered (the remaining aluminum was present as insoluble phases, corundum and spinel). Acid or basic media can be selected depending on the final use of Al(III) solutions, the basic medium leading to an Al(III) solution with a lower amount of impurities. The hazardousness of the solid obtained after the extraction process was greatly decreased, making possible the use of this solid residue in sectors such as construction.

1. Introduction

Aluminum has excellent properties for application in various sectors such as aerospace and marine engineering, construction or transportation [1–3]. Among these properties, low density (2.70 g/cm³), low melting point (660 °C) and corrosion resistance can be mentioned [4]. On an industrial scale, aluminum is produced through the *Primary Aluminum Production* (PAP) and the *Secondary Aluminum Production* (SAP) processes. PAP is carried out by combination of the Bayer and Hall–Héroult processes [5], while SAP is based on another interesting property of aluminum: this metal can be recycled an infinite number of times without losing its properties and quality compared to the aluminum produced by PAP [5]. Total production of refined aluminum (PAP and SAP aluminum) has increased in recent years [6]. According to the World Bureau of Metal Statistics, total production in 2019 was 63.7 million metric tons [6], with an increase of 51% in only nine years (42.3 million metric tons in 2010, see Fig. 1). In the same way, SAP production was 16.3 million metric tons in 2019, while 11.9 million metric tons in

2010, which implies an increase of 37% in nine years [6]. Although the percentage of aluminum produced by SAP has remained constant (close to 26 – 28%) and it has even decreased in recent years with respect to total aluminum production, more than a quarter of the world's aluminum is produced by SAP [6].

The comparison between PAP and SAP (Table 1) [3] indicates that SAP is more respectful with the environment due to lower energy consumption, lower gas emissions and lower generation of solid waste. Recycling 1 kg of aluminum saves 4 kg of bauxite, 2 kg of chemical reagents and 7.5 kWh of electricity [7]. However, both aluminum production processes generate solid wastes that are dangerous and harmful to the environment and human beings; Table 2 shows the most important solid wastes from various sectors of the aluminum production cycle. *Red mud* is generated during the Bayer process to obtain alumina in the PAP, in an amount of 0.3 – 2.5 tons of waste for each ton of alumina [5, 8]. Due to its composition and high alkalinity, it is considered a hazardous waste [3,5,9]; nevertheless, it can be used as a raw material to obtain added-value materials. Another type of hazardous waste is the

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so-called dross. *White dross*, *black dross* and *saline slag* are generated during the melting processes. The amount of dross produced depends on the type and quality of the raw materials and the operating conditions [3,5,7,8,10–12], but on average, for every ton of molten aluminum, between 300 and 600 kg of aluminum dross are generated [11]. When the molten aluminum surface becomes in contact with the atmosphere, dross is formed, consisting of a metallic fraction and a non-metallic fraction (salt and oxide) [5,10,11,13].

Pyrometallurgical and hydrometallurgical ways for managing aluminum dross have been reported [12]. The pyrometallurgical process for managing aluminum dross allows a high percentage of aluminum to be recovered from the dross, but the technology needed and the high temperatures required present a major drawback [12,17]. He et al. [1] have very recently reported an alkaline sintering process to produce high purity γ -Al₂O₃ from aluminum dross. On the other hand, hydrometallurgical processes involve lower energy consumption and simpler technology, are easier to apply and also allow high percentages of aluminum to be recovered from the dross [3,8,12]. The hydrometallurgical processes used for the extraction of aluminum from dross are based on the amphoteric character of this metal [18], allowing to use two routes: alkaline leaching and acid leaching [3,12]. For the alkaline leaching route, Davies et al. [19] proposed to treat saline slags by aqueous leaching and Bayer-type digestion. Tsakiridis et al. [20] used a high-pressure alkaline leach, using 260 g/L NaOH at 240 °C for 100 min, recovering 57.5% aluminum. In the acid leaching route, Das et al. [21] treated aluminum dross with H₂SO₄ and recovered around 84% aluminum. Other authors [18,22–26] have used hydrochloric acid (HCl) to treat aluminum dross to obtain added-value materials from the extraction solution. Pospiech and Warzecha [27] recovered 75.2% aluminum from the residue using oxalic acid.

However, very few studies have been carried out using saline slag (which chemical and mineralogical composition is different from that of black dross) as the starting reagent [3,12,23]. Bruckard and Woodcock [28,29] proposed to recover metallic aluminum from saline slag, underlying that further studies were needed on the recovery of aluminum from salt cake using the hydrometallurgical process, following both acid and basic routes. Extraction solutions, whether acid or basic, can serve as a source of aluminum for preparing value-added materials [8,30,31]. The solid waste produced after saline slag treatment in acid or basic media is non-hazardous and it could have applications in the

Table 1

Comparison of primary (PAP) and secondary (SAP) aluminum production processes [3].

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})	2100 – 3650	400

Table 2

Solid wastes generated from aluminum production [3,5,9,14–16].

Waste	Process of generation
Red mud	Alumina production from bauxite
White dross	Primary melting process
Black dross	Secondary melting process
Saline slag	Melting process in rotary furnace
Grinding filter powder	Aluminum dross
Furnace gas filter powder	Melting furnace
Skimming	Furnaces without brine

construction sector [12,13,17,23,32,33].

The aim of this work is to evaluate the extraction of aluminum from saline slags by systematic treatment of the waste in acid or basic media, and to analyze the effect in the process of the following parameters: nature of the acids or bases used, their concentration, extraction time, solid-liquid (S:L) ratio, and number of extractions. The proposed methodology does not only allows to recover part of the aluminum and other components present in the saline slag, but also eliminates the hazardousness of the final solid waste, leading to pure Al(III) solutions that can be used in the synthesis of catalysts and adsorbents with applications in processes of environmental interest. The strategy proposed in this work is in line with the *Circular Economy* paradigm, in which a waste to be discarded, being itself an environmental problem, receives an added value, changing from an end-of-life situation to an upcycling situation.

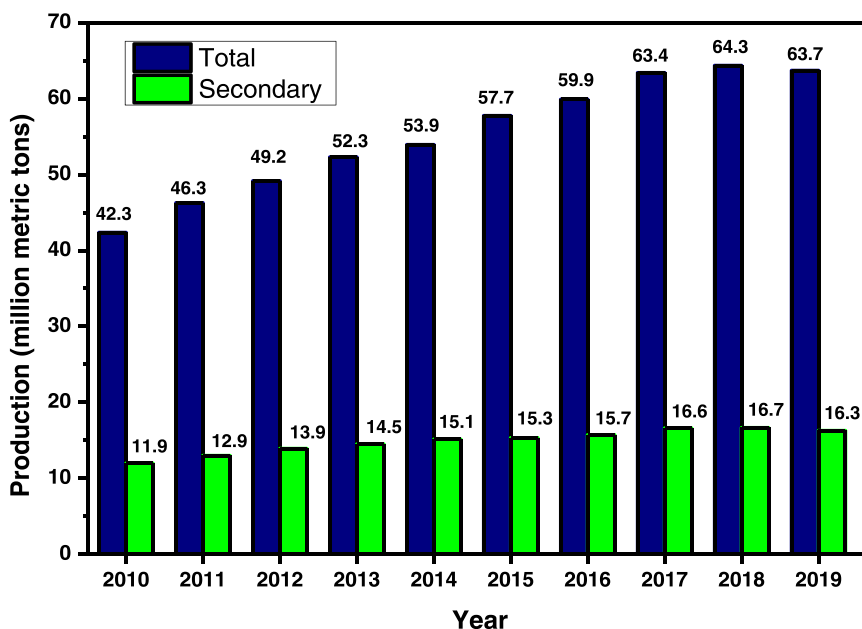


Fig. 1. Production of refined aluminum since 2010 [6].

2. Experimental

2.1. Raw materials

Saline slags were kindly supplied by IDALSA (*Ibérica de Aleaciones Ligeras S.L.*, Spain). Raw waste was made up of aggregates of several sizes, containing various aluminum species (various Al_2O_3 phases, $\text{Al}(\text{OH})_3$, metallic Al, AlN , etc.). Saline slags were ground in a ball mill, using an alumina jar and alumina balls, and then it was sieved with a 1 mm light screen. The fraction smaller than 1 mm (*saline slags-1 mm*) was washed with distilled water several times maintaining a S:L= 1:20 until chloride test was negative, and then it was air dried in an oven at 70 °C overnight [30,31]. The amount of ammonia (NH_3), product of the hydrolysis of AlN , generated during the washing process at several temperatures and times, was evaluated by collecting it over 50 mL of a 0.2 mol/L standardized HCl solution and then 5 mL aliquots were titrated with 0.1 mol/L standardized NaOH. These experiments were carried out by treating 6.5 g of the fraction smaller than 1 mm in 130 mL of distilled water (S:L=1:20). The experiments were performed in triplicate and a scheme of the system used is shown in Fig. 2. After the washing treatment, the chloride-free saline slags were sieved with a 0.4 mm light screen. The fraction larger than 0.4 mm was denoted as *intermediate fraction*, while the fraction smaller than 0.4 mm was named as *fine fraction*. Both fractions were analyzed by powder X-ray diffraction and X-ray micro-fluorescence. To study the recovery of aluminum from the fine fraction by acid or basic leaching, the factors taken into account were time (t), acid or base concentration ([HA] or [MOH]), S:L ratio and the use of various monoprotic acids and alkaline hydroxides, always carrying out the experiments under reflux conditions, at 90 °C and under magnetic stirring (500 rpm). The values of the different parameters tested were chosen based on our previous studies [30,31] and from bibliographic literature reports [23,24,28,29]. To determine the optimum acid and base leach conditions, a one-factor-at-a-time (OFAT) was carried out adapting previous studies [23,25]. The extraction liquors and final solid waste were named as follows: Liquor or solid-name of the reagent (monoprotic acid or alkaline hydroxide)-concentration of the reagent (M)-time of extraction (h)-S:L. For instance, for sample S-HCl-3 M-2 h-3:10, the solid waste was treated with HCl with concentration 3 mol/L for 2 h and with a S:L ratio of 3:10. Finally, the acid and basic leach residues were analyzed by powder

X-ray diffraction and X-ray micro-fluorescence.

The reagents used in this work were HCl (Pharma grade, 37%), HNO_3 (Pharma grade, 65%), LiOH (technical grade), NaOH (technical grade), KOH (technical grade, 85%), all from Panreac (Spain); and $\text{CsOH}\cdot n\text{H}_2\text{O}$ (99.5%) from Sigma Aldrich, all being used as received, without any further purification.

2.2. Extraction test

The extraction experiments in both acid and basic media were carried out in the system described in the former section, although without collecting up the evolved gases (Fig. 2). A 100 mL round bottom flask containing 25 mL of the acid or basic solution of a given concentration was heated to 90 °C and then the appropriate amount of the fine fraction was added according to the S:L chosen for each experiment. After treatment at reflux for the time and under the conditions selected for each experiment, the solid residue was separated from the solution by vacuum filtration. The extraction solutions were brought to a final volume of 50 mL and the content of aluminum and other elements were determined by ICP-OES. The reproducibility of the experiments was tested by carrying out in triplicate some experiments, the difference in the values obtained always being between 0.1% and 0.2%. A second extraction in the resulting solid was tested, but the aluminum extracted was one twelfth than that in the first process.

The percentage of aluminum extracted was calculated from the concentration of the aluminum present in the extraction liquor and the total amount of aluminum present in the fine fraction, using the following equation:

$$\% \text{Al}_{\text{extracted}} = \frac{m_{\text{Al extracted}}}{m_{\text{total Al fine fraction}}} \bullet 100 \quad (1)$$

which is converted to:

$$\% \text{Al}_{\text{extracted}} = \frac{V_f(\text{mL}) \bullet [\text{Al(III)}] \left(\frac{\text{mg}}{\text{L}}\right) \bullet 10^{-6}}{0.406 \bullet m_{\text{fine fraction}}(\text{g})} \bullet 100 \quad (2)$$

where V_f is the final volume of the liquor, $[\text{Al(III)}]$ is the concentration of this element in this liquor, and $m_{\text{fine fraction}}$ is the mass of the fine fraction used for the extraction test. The factor 0.406 reflects the mass ratio between aluminum and aluminum oxide, and the factor 10^{-6} is needed for homogenization of the units.

2.3. Characterization techniques

The powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-5000 instrument using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) with fixed divergence, from 5° to 80° (2 θ) at a scanning rate of 2°(2 θ)/min with steps of 0.05° and time per step of 1.5 s. The JCPDS-International Centre for Diffraction Data (ICDD®) database was used to identify the crystalline phases.

The X-ray micro-fluorescence spectroscopy (XRF) analyses were carried out using a Bruker M4 model micro-fluorescence spectrometer model (Nucleus Research Platform, University of Salamanca, Spain).

The scanning electron microscopy (SEM) analyses were carried out in a Zeiss EVO HD 25 Scanning Electron Microscope equipped with an Energy-Dispersive X-ray spectroscopy (EDS) microanalysis accessory, at the Nucleus Research Platform, University of Salamanca, Spain.

Element chemical analyses for several elements were carried out by ICP-OES in a Yobin Ivon Ultima II apparatus (Nucleus Research Platform, University of Salamanca, Spain).

3. Results and discussion

3.1. Waste characterization

The chemical compositions of all three fractions are given in Table 3.

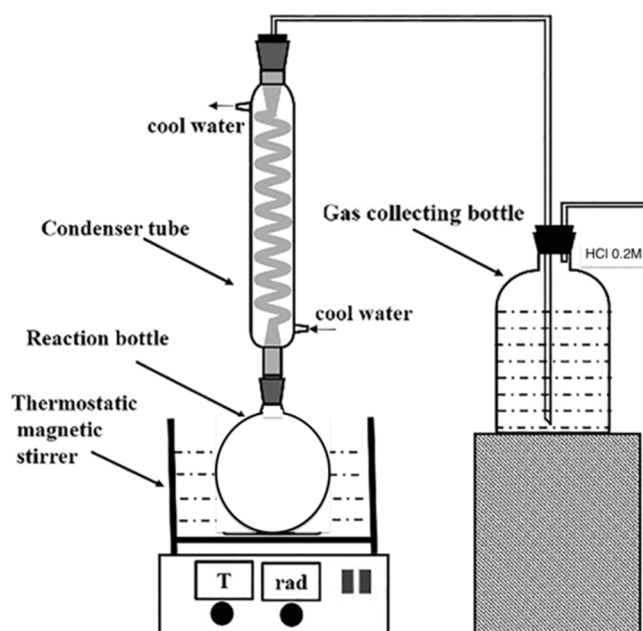


Fig. 2. Scheme of the leaching system.

Table 3

Chemical composition (wt%) of saline slags-1 mm, intermediate fraction and fine fraction.

Component	Saline slags-1 mm	Intermediate fraction	Fine fraction
Al ₂ O ₃	21.3	70.0	76.8
Na ₂ O	18.9	Not detected	Not detected
MgO	1.30	4.50	10.3
SiO ₂	2.20	15.0	5.30
SO ₃	0.240	0.290	0.500
Cl	33.9	0.900	0.210
K ₂ O	19.8	1.10	0.450
CaO	0.720	4.10	2.12
TiO ₂	0.190	0.700	0.760
Fe ₂ O ₃	0.700	1.40	2.00
CuO	0.340	1.10	0.780
ZnO	0.150	0.600	0.280

The oxide content of other elements – V, Cr, Mn, Ni, Pb – was ≤ 0.1%.

The chemical analysis (expressed as oxides, except for chlorine) shows a complex chemical composition. In addition to the elements shown in Table 3, the content of other elements such as V, Cr, Mn, Ni or Pb was ≤ 0.1%.

3.1.1. Saline slags-1 mm

Its chemical composition was consistent with previous data published in the literature for the same saline slags [10,31]. The total aluminum content present in the salt slag, expressed as Al₂O₃, is 21.6%; however, this value did not give information on the recoverability of aluminum. The highest percentage corresponded to chlorine, with high percentages of Na and K (expressed as oxides but actually existing as chlorides in the waste). Consequently, the content of salts, mainly NaCl and KCl, was higher than 30 wt% for each one. The hazardousness of the saline slags is in part due to its high chloride content which is easily released into the aqueous environment, so in terms of decreasing the hazardousness and encouraging product recycling, the recovery of the fluxing salts become mandatory. To recover part of the aluminum from saline slags by obtaining an Al(III) solution that can be used as a source of aluminum in the preparation of catalysts and adsorbents based on Al³⁺ [8,30,31,34,35], the elimination of the fluxing salts is also necessary, as their presence can have a negative effect on the aluminum extraction process [3,18,22–24,30,31,36]. The mineralogical phases

detected by PXRD in salt cake-1 mm (Fig. 3) were corundum (α -Al₂O₃, ICDD 43–1484), spinel (MgAl₂O₄, ICDD 21–1152), halite (NaCl, ICDD 5–628), sylvite (KCl, ICDD 41–1476) and AlN (ICDD 25–1133). The hydrolysis of AlN will be discussed in Section 3.2.

Fig. S1 shows two SEM micrographs of saline slags-1 mm (S1A and S1B). Aggregates of particles of different sizes, all smaller than 500 μ m and of non-systematic shapes, are observed in SEM micrograph S1A, while small aggregates of crystallites corresponding to aluminum oxides and spinel are found in micrograph S1B. In addition, AlN particles in the form of fibrous crystals are observed. Al(OH)₃ is present in the form of needle-shaped and prismatic crystals 10 μ m in size. [2,17,20,32].

3.1.2. Intermediate fraction

Its chemical composition is shown in Table 3. Sodium was not detected and the amounts of chlorine and potassium were drastically decreased, confirming that the washing process was effective in removing the fluxing salts. According to Gil and co-workers [11,37], a slag is considered to be salt-free when its salt content is less than 2 wt%, so the intermediate fraction matches this requirement. As mentioned above, the presence of chlorides can lead to a decrease in the efficiency of the extraction process and can also contaminate the Al(III) solution used as a source of aluminum in the preparation of advanced materials, contaminating the latter as well [3,12,18,22,36]. On the other hand, removal of the soluble component causes the non-soluble components to show a large increase in their relative content. The aluminum content expressed as Al₂O₃ amounted 70 wt% of the sample mass. Mineralogical analysis by PXRD showed that the most intense peaks corresponded to metallic aluminum (Al, ICDD 4–787) [31]. Furthermore, no diffraction peaks corresponding to AlN, NaCl and KCl phases were observed, which also confirmed that the washing process was effective in reducing the hazardousness of the residue. This fraction, having a high content of aluminum in the metallic phase, could be incorporated into the aluminum recycling process. Similarly, fluxing salts can be recovered from the wash water by evaporation [10] and can also be reused in the recycling process.

The SEM micrographs in Fig. S1 shows aggregates of particles of various sizes, the size difference between particles being smaller than in the case of the salt cake (S1A), while micrographs S1C and S1D shows aggregates of crystallites corresponding to aluminum oxides and spinel. Needle-shaped crystals of 10 μ m size corresponding to Al(OH)₃ were

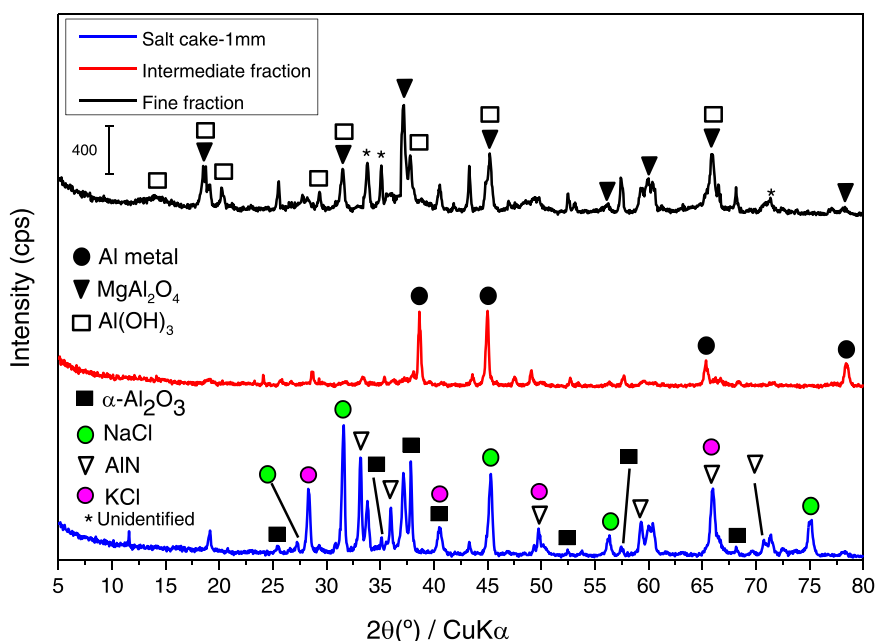


Fig. 3. Powder X-ray patterns of saline slags-1 mm, intermediate and fine fractions.

also observed. No fibrous crystallites corresponding to AlN were observed. EDS analysis results are shown in Fig. S2.

3.1.3. Fine fraction

The chemical composition of this fraction is also included in Table 3. In this case, the aluminum content was high, 76.8 wt%, expressed as Al₂O₃; however, it is necessary to identify the aluminum phases present in order to study the recovery of this element. The mineralogical phases identified by PXRD were corundum, spinel, gibbsite, bayerite (Al(OH)₃, ICDD 22–11) and boehmite (AlOOH, ICDD 21–307). Both the chemical and mineralogical composition were in agreement to those reported in the literature [3,12,13,19–21,28,29,31]. The main difference with respect to *saline slags–1 mm* was the absence of the soluble or hydrolysable components AlN, NaCl and KCl phases and the presence of Al(OH)₃ as a product of the hydrolysis of AlN and other hydrolysable compounds during the washing process (see Fig. 3). The absence of the aforementioned phases (AlN, NaCl and KCl) implied a reduction of the hazardousness of the original residue, that is, one of the objectives of the present work has already been achieved. Taking into account that the intermediate fraction can be incorporated into the aluminum recycling process, the fine fraction was selected as a raw material to study the recovery of aluminum as a function of various factors (time, acid or base concentration, S:L, and monoprotic acids or alkaline hydroxides) and to obtain acidic or basic aluminum solutions that can serve as a source in the synthesis of Al³⁺-based materials [3,8,12,30,31,38]. The aluminum phases identified by PXRD in the fine fraction can be dissolved under the proposed experimental conditions, due to the amphoteric character of aluminum [18]. In the SEM S1E micrograph, rounded particles of similar size between 300 and 400 μm were observed; these particles had a rough appearance. In the higher magnification micrograph (Fig. S1F), aggregates of crystals corresponding to Al₂O₃ and MgAl₂O₄ can be seen. In addition, needle-shaped crystallites of size 5–10 μm corresponding to Al(OH)₃ were observed. EDS analysis are shown in Fig. S3.

Comparing the different fractions, it may be considered that metallic aluminum is commonly found as very small particles occluded within “large” particles of non-metallic phases. Thus, it would be highly dispersed and in very low concentration. Moreover, due to the high number of poor-crystalline phases, aluminum diffraction peaks are not identified or are overlapped with other phases. During the milling process, the non-metallic fraction was broken down, liberating those small Al particles (due to their plastic behavior they do not break on grinding under the conditions used) leaving the non-metallic fraction as a very fine powder. When sieved through a 0.4 mm sieve, the fine powder passed through the sieve, generating the so-called fine fraction, while these spherical metallic particles were retained.

3.2. Evaluation of the amount of NH₃ generated during the washing process

One of the mineralogical phases present in the *saline slags–1 mm* fraction is AlN (Fig. 2), which hydrolysis produces NH₃ and Al(OH)₃ [3, 5,10,12], this being other reason for considering the saline slags as a hazardous waste. In this sense, the washing process would also remove (by decomposition) AlN and other hydrolysable compounds that also generate harmful gases, decreasing the toxicity of the waste. However, it is not only important to decrease the toxicity of the solid waste, but also to avoid emission of polluting gases into the atmosphere [1]. For this reason, and also for the value of the NH₃ generated, the amount of this compound produced during saline slags washing process was studied as a function of washing time and temperature. The amount of NH₃ produced during the washing at several temperatures and times of *saline slags–1 mm* is presented in Fig. 4. An increase in the washing time while keeping the temperature constant produced an increase in the amount of NH₃ generated. Similarly, an increase in the temperature of the washing process implied a higher hydrolysis of AlN [39]. The maximum amount of NH₃ generated (1.25 mmol NH₃/g saline slags–1 mm) was produced

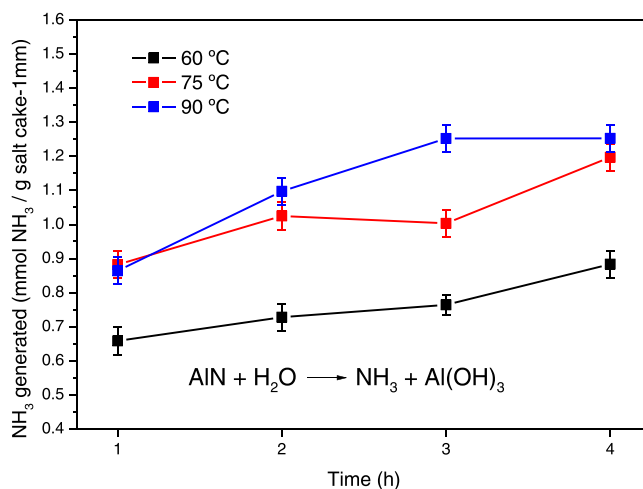


Fig. 4. Hydrolysis of AlN as a function of temperature and time reaction. Sample used: saline slag–1 mm.

when treating for 3 h at 90 °C. Assuming that under these conditions (time 3 h, temperature 90 °C and S:L 1:20) all AlN was hydrolyzed (see Fig. 4), the percentage of AlN in *saline slags–1 mm* was 6.25%. At 60 and 75 °C some ammonia may remain dissolved in the washing solution (located at reaction bottle in Fig. 2) [40]. In order to improve the efficiency of the acid leaching and to reduce the toxicity and hazardousness of its residue, a washing step was necessary to remove fluxes, and therefore possible interferences in the extraction process. In addition, the efficiency of the extraction process was improved, as the soluble aluminum content increased due to the hydrolysis of AlN, which in an acid medium would not be hydrolyzed (According to Krnel et al. [41, 42], hydrolysis of AlN does not take place at pH below 1) and would therefore remain as such in the final solid waste. Finally, generated NH₃ can be collected and used as a reagent in the preparation of compounds of interest [43,44].

3.3. Extraction tests

3.3.1. Acid extraction route

In the acid extraction route, various acids have been proposed in the literature to treat aluminum dross, among them HCl, H₂SO₄ or oxalic acid [7,18,22,24,25,27]. HCl and H₂SO₄ provide strongly acidic media, able to dissolve aluminum easily, while oxalic acid, although a weak acid, forms a highly stable (K_f = 10^{13.3}) coordination compound with Al³⁺ (namely [Al(ox)₃]³⁻).

In this work, HCl and HNO₃ were used. While HCl has been widely reported for extraction of aluminum in acidic media [24,25], there is hardly any report in the literature on the use of HNO₃. The use of the extraction solution as a source of aluminum for the synthesis of Al³⁺-based value-added materials would require that the counteranion has no detrimental effect in the synthesis of such compounds, which encouraged us to explore the use of HNO₃. For instance, if extracted Al³⁺ is used to prepare Layered Double Hydroxides (LDH) with a certain anion in the interlayer space, it is necessary to avoid anions whose affinity to occupy this space is higher than that of the desired anion (for instance, multivalent anions, such as sulfate). The first factor studied was the effect of the extraction time under reflux conditions at 90 °C. For this purpose, the remaining parameters were fixed. In the literature collected so far, the maximum extraction time was 120 min. In this work, long extraction times have been used in order to study whether the percentage of aluminum extracted increased when using times longer than 2 h. Fig. 5A shows how for a given HCl concentration and a S:L= 3:10, an increase in time led to a slight decrease in the percentage of aluminum extracted for a concentration of 2 mol/L HCl. The

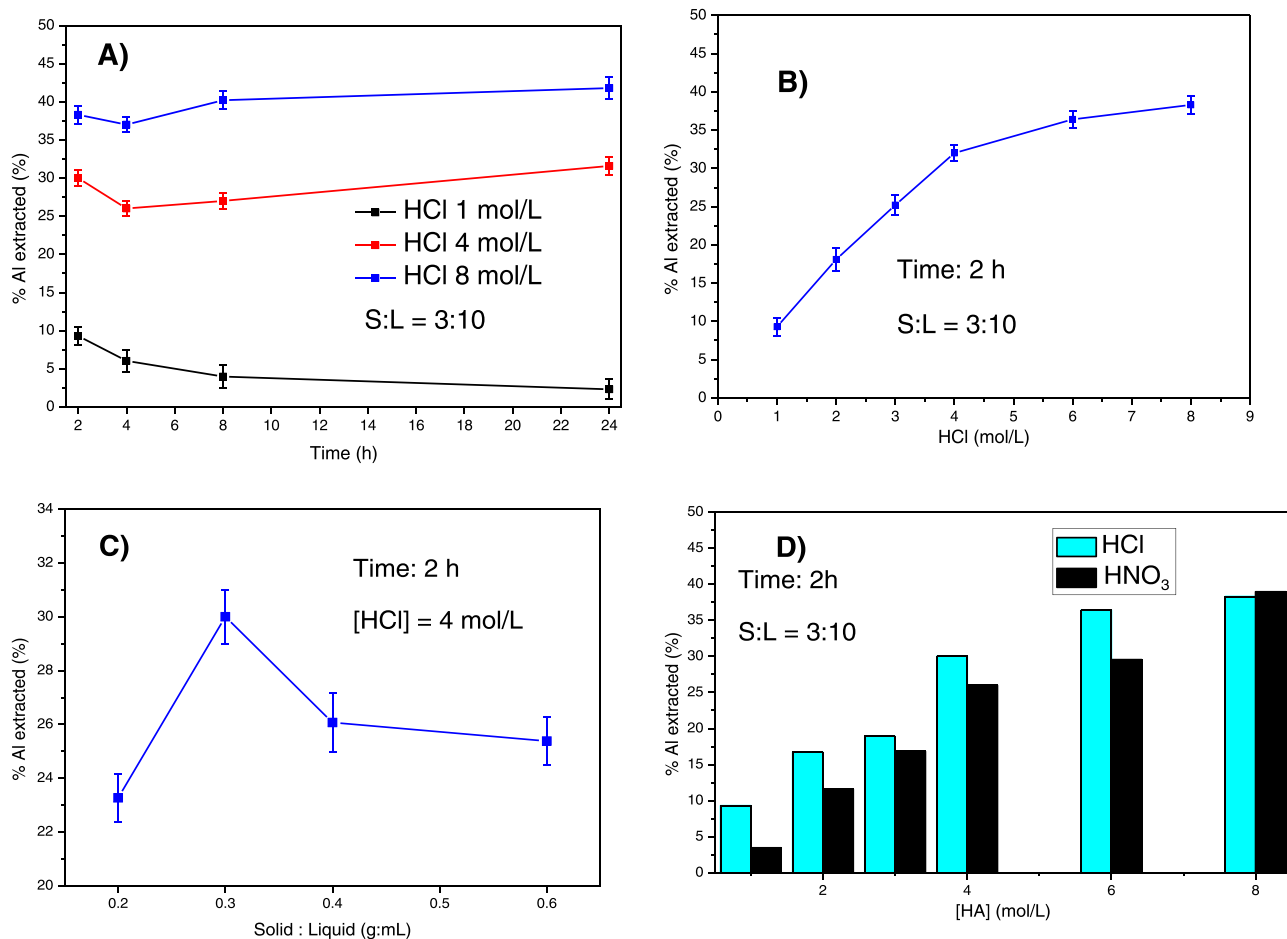


Fig. 5. Parameters studied in acid medium. Effect of time of treatment (A), of HCl concentration (B) and of S:L (C) in the amount of aluminum extracted. Comparative study of the use of HCl and HNO₃ for extraction of aluminum (D). Sample used: fine fraction.

percentage of extracted aluminum halved with increasing time from 2 to 24 h. When a HCl concentration of 4 mol/L was used, the percentage of aluminum extracted also decreased after 4 h reaction, but it was recovered and continued steadily increasing even up to 24 h, although after this time the amount extracted was almost identical to that after 2 h extraction. When HCl concentration was 8 mol/L, the behavior was similar than when using a 4 mol/L HCl concentration. Moreover, after 2 h of reaction, no linear increase of the amount extracted was observed with increasing HCl concentration: 10%, 30% and 36%, respectively for 2, 4 and 8 mol/L HCl. The decrease in the amount of aluminum extracted after 2 h reaction (and its recovery for HCl concentrations of 4 or 8 mol/L), can be tentatively related to formation of some insoluble Al (III) compound, which was redissolved as the reaction time was increased, such a recovering being faster as the HCl concentration increased. Unfortunately the nature of such a compound remained unknown. As no relevant increase in the amount of aluminum extracted was observed at HCl concentrations of 4 or 8 mol/L as the reaction time was increased, its optimum value was taken as 2 h.

Fig. 5B shows the effect of HCl concentration on the percentage of aluminum extracted when the time was set to 2 h and S:L to 3:10. An increase in the acid concentration produced an increase in the percentage of aluminum recovered. Going from a concentration of 1 mol/L to 2 mol/L and from 2 mol/L to 3 mol/L resulted in a slight increase in the percentage of aluminum extracted, but the largest increase occurred when using the 4 mol/L solution. Increasing the HCl concentration to 6 mol/L or 8 mol/L also implied a slight increase in the percentage of aluminum extracted, but this increase was rather small. Therefore, 4 mol/L HCl concentration can be set as the optimal concentration.

Another important factor involved in the extraction process is the S:L ratio used [22–24,28,29]. Fig. 5C shows the effect of the S:L ratio on the percentage of aluminum extracted. For this study, the HCl concentration was set at 4 mol/L and the reaction time at 2 h, varying the S:L ratio from 2:10–6:10. The highest percentage of extracted aluminum was achieved with S:L= 3:10. When a lower ratio was used, namely 2:10, the amount of aluminum extracted was 10% lower, while the use of higher ratios led to a decrease of about 5% with respect to this maximum value. When the S:L ratio was small, there was a large amount of acid available to attack the soluble aluminum compounds present in the fine fraction, but the amount of water in the solution is also small, which can make difficult the maintenance of aluminum in solution, causing its reprecipitation, and decreasing the percentage of aluminum extracted [22]. Conversely, when S:L was high, the amount of acid was not enough to attack all the soluble aluminum compounds, and consequently the percentage of aluminum extracted also lowered.

To conclude the analysis of the acid route of extraction, a comparative study was carried out about the effect of using HCl or HNO₃. The aim of this section is to check whether the use of one or the other acid, under specific extraction conditions, has a relevant effect on the percentage of aluminum extracted. As mentioned previously, one of the main objectives of this work is to obtain a pure Al(III) solution that can be used in the synthesis of Al³⁺-based materials. For example, the synthesis of LDHs with nitrate (NO₃⁻) as the interlayer anion would not be possible if aluminum is extracted with HCl, since chloride would occupy the interlayer space instead of nitrate [45]. For this reason, it is important to determine whether the nature of the acid changes appreciably the percentage of aluminum extracted. Fig. 5D shows a

comparative study between the use of HCl and HNO₃ as acid reagents in the extraction process under reflux conditions at 90 °C, setting the extraction time at 2 h and S:L= 3:10; several acid concentrations, 1, 2, 3, 4, 6 and 8 mol/L, were used (see also Fig. S4). The percentages of aluminum extracted were slightly higher when using HCl, except for the 8 mol/L concentration where the percentage of aluminum extracted was higher for HNO₃. Therefore, it can be concluded that HNO₃ also allowed

obtaining an extraction Al(III) liquor, but a high concentration was required to overcome the extraction performance of HCl. As indicated, the use of HNO₃ may be justified only for specific cases, for example, if nitrate–hydrotalcites should be prepared from the extracted solutions, as if the extraction is done with HCl, chloride may not be then exchanged by nitrate in the hydrotalcites.

As shown in Table 3, the SiO₂ content in the fine fraction was 5.30 wt

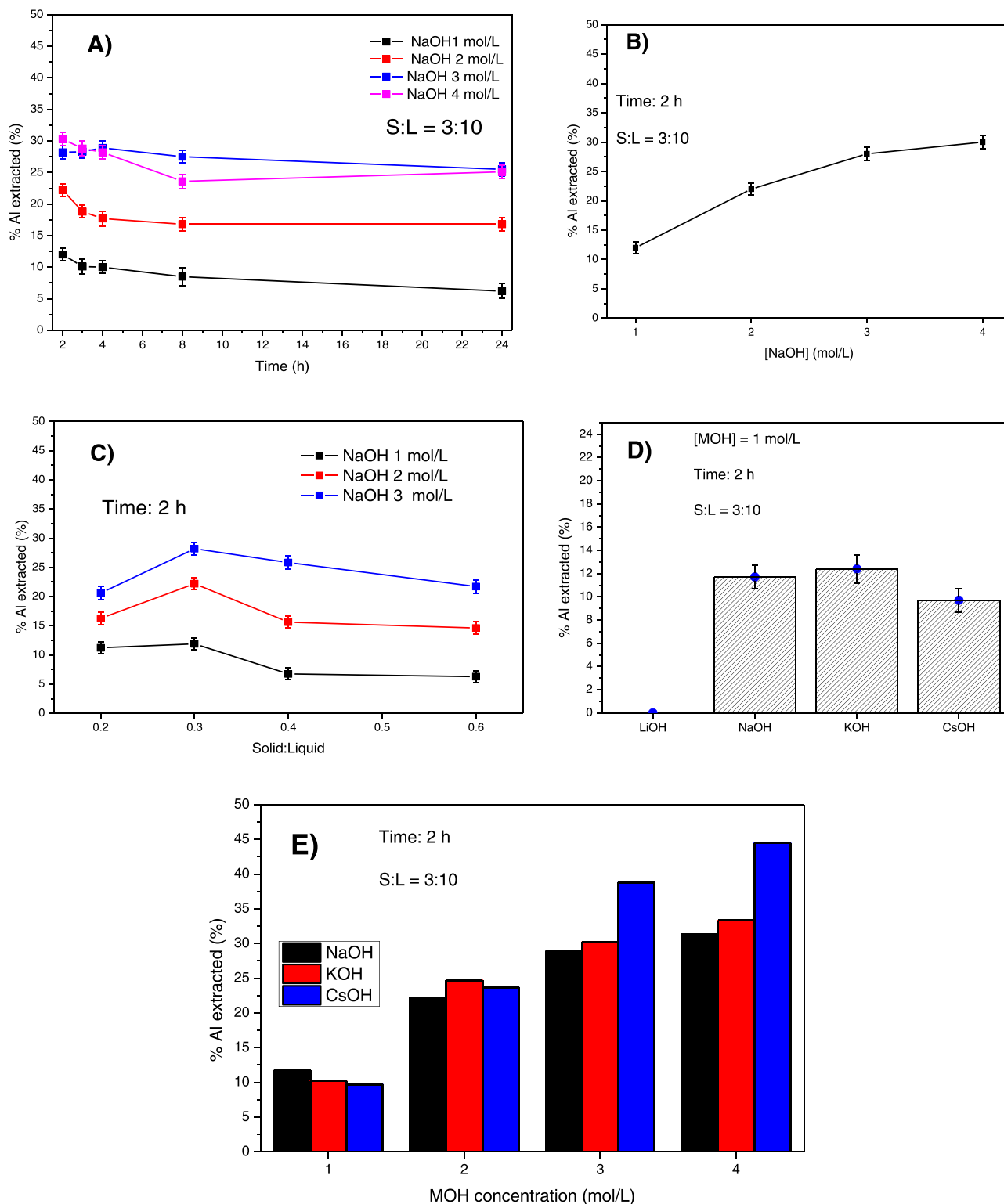


Fig. 6. Parameters studied in alkaline medium. Effect of time treatment (A), of NaOH concentration (B), of S:L (C) and on the nature of the hydroxide (D) on the amount of aluminum extracted. Comparative study of the use of the different hydroxides for extraction of aluminum (E). Sample used: fine fraction.

%). The acid treatment of this fraction could lead to the formation of silica gel [46–48], which could disturb the filtration of the extracted solution, making difficult the obtention of the Al(III) solution; however, the formation of silica gel was not observed in the present work. Nevertheless, this is an important point to be taken into account during the aluminum extraction in acid medium from slags with high SiO₂ contents.

3.3.2. Alkaline extraction route

NaOH is the most commonly used reagent in the alkaline aluminum extraction route, aluminum being extracted as sodium aluminate at atmospheric pressure or using high pressure and high temperature methods [1,3,20,28,29,32,36]. The effect of the same factors tested for the extraction in an acid medium (time, concentration, S:L ratio and various alkaline hydroxides) on the percentage of aluminum extracted when the fine fraction was treated under reflux conditions at 90 °C has been studied under alkaline conditions.

The first factor studied was the extraction time; for this study S:L was set at 3:10 and the NaOH concentration at 1, 2, 3 and 4 mol/L. Fig. 6A shows that, for a given concentration, there was a slight decrease in the percentage of aluminum extracted when the extraction time was increased up to 24 h. The effect of long extraction times (more than 2 or 3 h) has not been studied in the literature so far ([1,3,20,28,29,32,36]). It can be concluded that the highest percentage of aluminum extracted when the S:L is set at 3:10 and the NaOH concentration at 1, 2, 3 or 4 mol/L is achieved for a time of 2 h.

After determination of the optimal extraction time, the NaOH concentration to obtain the highest percentage of extracted aluminum was determined. Fig. 6B shows how the NaOH concentration affects the percentage of aluminum recovered when the reaction time was set to 2 h and the S:L ratio at 3:10. As for the extraction in an acidic medium, Fig. 5, the percentage of aluminum extracted increased with the concentration of the reagent. When the NaOH concentration was increased from 1 mol/L to 3 mol/L, there was a significant increase in the percentage of aluminum extracted from 12.5% to 28%. Using a concentration of 4 mol/L, around 30% of the aluminum present in the fine fraction was extracted, just a 2% increase. By this reason, the 3 mol/L solution was selected as the optimal concentration for further experiments.

The S:L ratio is a factor that has an important effect on the extraction process [22–24,28,29]. When the extraction time was set to 2 h and the NaOH concentration to 1, 2 or 3 mol/L, the highest percentage of aluminum extracted was obtained when S:L= 3:10.

In order to obtain a pure Al(III) solution free of interferences to be used in the synthesis of Al³⁺-based materials, the effect of the use of various alkaline hydroxides on the extraction percentage was evaluated (Figs. 6D and 6E). Jiménez et al. [31] recently reported that NaOH cannot be used as an alkaline extraction reagent in the preparation of pollucite (CsAlSi₂O₆·nH₂O), because sodium can occupy the positions which should be occupied by Cs, obtaining an analcime–pollucite solid solution instead of pure pollucite. Fig. 6D shows the percentage of aluminum extracted when using various alkaline hydroxides at 1 mol/L concentration, the time was 2 h and S:L ratio 3:10. There were only small differences in the percentage of aluminum recovered when NaOH, KOH or CsOH were used. However, no aluminum was extracted when LiOH was used as the extraction reagent. This was due to the fact that Al³⁺ and Li⁺ reacted with each other in strongly basic media to form the corresponding LDH [49–51]. So, aluminum initially dissolved but immediately reacted with Li⁺ forming LiAl–LDH. LiAl–LDH precipitated on the fine fraction residue making hard the separation of the two solids, thus remaining together with the extraction waste, mainly composed by corundum (see Fig. S5). Finally, Fig. 6E shows a comparative study between the performance of alkaline hydroxides NaOH, KOH and CsOH, using concentrations 1, 2, 3 and 4 mol/L, extraction time 2 h and S:L 3:10. The three hydroxides can be used as extraction alkaline reagents without significant variations in the percentage of aluminum extracted

(see Fig. S6). This percentage was similar for KOH and NaOH at all concentrations and slightly higher for CsOH when 3 or 4 mol/L concentrations were used.

The percentages of aluminum extracted were slightly higher in the acid extraction procedure. The optimum extraction time and the optimum S:L ratio were 2 h and 3:10, respectively, for both the basic and acid media. However, the optimum acid concentration was higher than the optimum base concentration. In the case of acid extraction, the percentage of aluminum extracted showed a slight decrease for a reaction time of 4 h, reaching again similar values to those at 2 h after 24 h reaction. In the case of the basic extraction (except for the concentration of NaOH 3 mol/L) a progressive decrease was observed, obtaining the lowest percentage of aluminum extracted after 24 h.

3.4. Characterization of solid extraction wastes and composition of the acid and basic extraction liquors

The solid residue generated remaining after the aluminum extraction process in basic or acid media was characterized by PXRD and XRF to identify the existing phases and components, in order to evaluate its hazardousness and its possible further application [3,8,12,33,52,53]. Table 4 shows the composition of the solid residue after treatment in basic (S–NaOH–3 M–2 h–3:10) and acid (S–HCl–4 M–2 h–3:10) media. In both cases the content of aluminum (expressed in the form of its oxide) was higher than 65%. This percentage showed that the residue after both treatments still contained a high amount of insoluble aluminum; however, it was necessary to identify the existing aluminum phases in order to evaluate its hazardousness and applicability. Fig. 7 shows the diffraction patterns of both residues. The aluminum-containing crystalline phases identified in both residues were corundum and spinel. These phases have a high thermodynamic stability, being very unreactive and practically insoluble, so they do not represent a risk to the environment or to human health [33]. When using S–NaOH–3 M–2 h–3:10, the additional Al(OH)₃ bayerite phase was identified. This phase also does not show any risk to the environment due to the low solubility of Al(OH)₃ under pH conditions close to that of natural waters (pH 5–8). Sodium was detected in the S–NaOH–3 M–2 h–3:10 residue, its content being 6.42 wt% (expressed in the form of its oxide) and it may exist in some form that was not detected by PXRD, while in S–HCl–4 M–2 h–3:10 it was not detected. The amount of potassium expressed in the form of its oxide was 0.24 wt % for the basic treatment residue and 0.40% for the acidic residue. Chlorine was not detected in the case of S–NaOH–3 M–2 h–3:10 but was detected (5.87 wt%) in the case of S–HCl–4 M–2 h–3:10. The diffractogram shown in Fig. 7 did not indicate the presence of fluxing salts (NaCl and KCl), however the XRF results showed the presence of chlorine, which suggested the existence of a small amount of fluxing salts or of some insoluble phase containing chlorine, in any case no additional phase was found by PXRD. On the other hand, the diffractograms shown in Fig. 7 did not identify any phases whose reaction with water could form toxic or harmful gases. For all these reasons, it can be concluded

Table 4
Chemical composition (wt%) of solid extraction wastes.

Component	S–NaOH–3 M–2 h–3:10	S–HCl–4 M–2 h–3:10
Al ₂ O ₃	66.3	69.1
Na ₂ O	6.42	Not detected
MgO	6.29	8.73
SiO ₂	8.63	10.6
SO ₃	0.140	0.340
Cl	Not detected	5.87
K ₂ O	0.240	0.400
CaO	3.59	0.750
TiO ₂	0.800	1.65
Fe ₂ O ₃	5.25	1.22

Elements with oxide content ≤ 0.1% are not included.

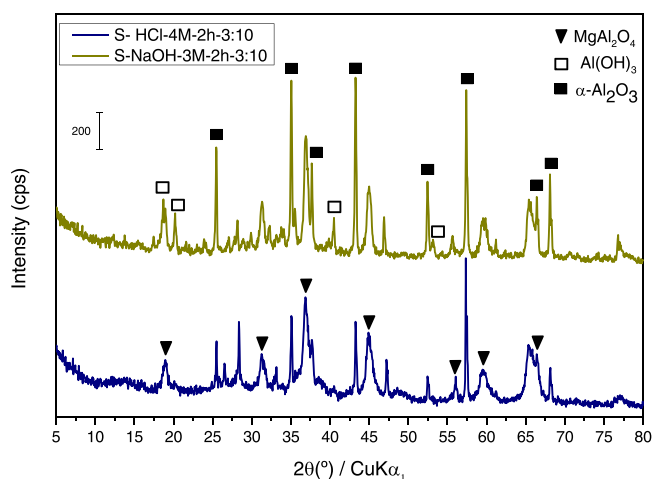


Fig. 7. Powder X-ray patterns of solid extraction wastes.

that the treatment proposed in this work reduced the toxicity of wastes from SAP, and these can be used in other fields or industrial sectors, taking into account the regulations concerning their use as adsorbent, building ceiling materials, cements, refractory materials and insulating filler material [3,8,12,33,52–54].

Fig. S7 to S9 show SEM micrographs and EDS analysis of the acidic and basic residues. Micrograph S7B shows aggregates of crystallites corresponding to Al_2O_3 and MgAl_2O_4 . In micrograph S7D, in addition to the crystallite aggregates mentioned above, some needle-shaped crystals corresponding to $\text{Al}(\text{OH})_3$ were observed [2,17,20,32]. These results are in agreement to the PXRD results.

Table 5 shows the composition of the extraction liquors in acidic (L-HCl-4 M-2 h-3:10) and basic (L-NaOH-3 M-2 h-3:10) media. The aluminum content in solution was slightly higher in the case of the acid medium, however both values were similar. Although the acid medium allowed obtaining a slightly higher aluminum content in solution, the Al (III) solution presented a lower purity due to the existence of several metals (Fe, Mg, Cu or Zn). These metals are soluble in acid medium, but they precipitate in the form of their hydroxides in basic medium. The opposite occurs with Si, the only additional metal present in the alkaline liquor, which dissolves as a silicate in a NaOH medium but is insoluble in acid medium. Therefore, the use of one or another medium will depend on the influence of the impurities in the synthesis of the final solid. Aluminum has an amphoteric character, i.e., it is soluble in acidic and basic media with its minimum solubility at neutral pH, so it would be possible to carry out the extraction in an acidic medium and then to increase the pH up to 12 in order to eliminate the impurities of metals such as Fe, Mg, Cu or Zn. Similarly, the extraction could be carried out in a basic medium and Si could be eliminated by using calcium salts [30] or lowering the pH to 1 to precipitate silica.

4. Conclusions

Management of saline slags, a waste from Secondary Aluminum Production, has been explored. Grinding and washing of this residue successfully removed toxic and environmentally hazardous components, NaCl and KCl were dissolved and the NH_3 produced by hydrolysis of AlN was collected over and acid solution, finally producing a solid residue from which up to 30 wt% of aluminum can be extracted by acid or basic treatment. The optimum extraction conditions for the acid medium were: time 2 h, HA concentration 4 mol/L and a S:L ratio of 3:10, while the optimum conditions for the basic medium were: time 2 h, MOH concentration 3 mol/L and S:L= 3:10. CsOH showed an excellent performance for the extraction of aluminum, better than other hydroxides; however, its cost is much higher than for other reagents, and its use may be justified only for the preparation of very specific compounds. The

Table 5
Chemical compositions of the extraction liquors.

Component (mg/L)	L-NaOH-3 M-2 h-3:10	L-HCl-4 M-2 h-3:10
Al	15914	18271
Si	165	a
Fe	a	1141
Mg	a	1648
Cu	a	7.36
Zn	a	40.9

^a Not detected

extraction solutions can be used as a source of aluminum in the synthesis of Al^{3+} -based catalysts and adsorbents, while the final solid residue obtained, composed by insoluble and inert phases isolated in previous steps, did not show a toxic or harmful risk to the environment, which opens new possibilities for their use, as construction binder or cement and mortar components.

CRedit authorship contribution statement

Alejandro Jiménez: Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Vicente Rives:** Conceptualization, Data curation, Formal analysis, Methodology, Supervision, Validation, Writing – review & editing. **Miguel A. Vicente:** Conceptualization, Data curation, Formal analysis, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing. **Antonio Gil:** Conceptualization, Data curation, Formal analysis, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2022.107546](https://doi.org/10.1016/j.jece.2022.107546).

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