

# Extraction of antimony from a hydrochloric acid side stream of copper electro-refining by hydrolysis

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## ABSTRACT

This work explores the feasibility of recovering antimony, present in a side stream of hydrochloric acid resulting from a copper electro-refining process, by hydrolysis with water. A range of variables that can affect the process have been studied. According to the results, under optimal conditions (pH = 0.645  $T = 34$  °C), antimony extraction yield is 94.4%. The reaction product is amorphous, with antimony content close to 70% and Cl and O contents similar to the stoichiometric ratios of complex oxychloride compounds. Moreover, significant amounts of arsenic and bismuth have been revealed. The presence of bismuth affects the extraction performance, while arsenic impairs its potential commercialisation.

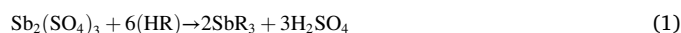
## 1. Introduction

In recent years, antimony production has grown steadily, mainly linked to its use in flame-retardant compounds. Over 50% of antimony production is devoted to this application, and has only a few potential substitutes. It is also employed in lead-acid batteries and as a catalyst and stabiliser in the manufacture of plastics, glass, and ceramics (Anderson, 2012; Klochko, 2021). Furthermore, the electronic, optical, and optoelectronic properties of antimony compounds are attracting growing attention due to their potential use in batteries (Xie et al., 2017) and in photovoltaic cells (Jin et al., 2020). The specific use of compounds in these types of applications, such as antimony oxide and antimony oxychloride, has been related to the presence of nanostructures (Lv et al., 2015), which can also improve performance in conventional applications, such as flame retardants (Chen et al., 2008).

Antimony is classified as a critical metal in the European Union (EU Commission, 2017). There are several reasons for this decision: (i) China's dominance in production, its mining of >52% of the global primary antimony, and its ownership of most of the declared resources; (ii) the lack of political and social stability of other producing countries; (iii) economic importance; (iv) abundance; (v) the existence of possible substitutes; and (vi) the low recycling rate and high environmental risks, among other factors. In this context, the search for secondary antimony extraction methods is of major interest.

Potential candidate secondary sources of antimony include the by-

products of pyrometallurgical copper extraction and refining. The final stage of the copper process involves electrolytic refining from 99.7%-pure copper anodes. These anodes contain impurities from ore concentrates, which are incorporated in the electrolyte along with copper. Elements of concern include As, Sb, and Bi since their presence can negatively affect the final quality of the copper cathode (Arbizu et al., 2010; Artzer et al., 2018; Verbruggen et al., 2022a; Verbruggen et al., 2022b). Consequently, control of such impurities in the electrolyte is of major importance. One of the most widely used method is reducing Sb and Bi content by means of amino-phosphoric acid chelating resin (HR) treatment. The electrolyte is fed through a column reactor containing the resin. Ion exchange occurs as follows (Eq. 1) (Dreisinger et al., 1995):



The resin is subsequently regenerated by eliminating the retained cations. This is carried out by elution with HCl in accordance with Eq. (2):



The product or effluent at this stage, commonly referred to as an eluate, consists of an acid stream with chloride concentrations of approximately 170 g/l and a variable content of Sb, Bi, and other impurities. The typical composition of eluate is shown in Table 1. The eluate temperature is 35 °C (Arroyo-Torralvo et al., 2017).

According to González De Las et al. (2020), antimony is found in the

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**Table 1**  
Typical composition of ion-exchange facility eluate.

Elements	As	Bi	Sb	Cl <sup>-</sup>	Others
Composition (g/L)	2–5	8–10	9–10	170	<1

**Table 2**  
Composition of the main components of eluate used in this study<sup>1</sup>.

Element	As	Bi	Sb	Cl <sup>-</sup>
Content (g/L)	2.3	9.5	8.9	170

<sup>1</sup> The measured pH is – 0.68 at 20 °C.

electrolyte in Sb(III) and Sb(V) oxidation states in an approximate distribution of 50%, while arsenic is mostly in As(V) state and bismuth is fully Bi(III). According to Riveros (2010), this kind of resin has the capacity to retain 100% of Sb(III) and Bi(III). However, the resin does not retain Sb(V). The retention and elution capacity of Sb(V) is lower and is generally associated with a decrease in resin durability. Consequently, it is estimated that, in the eluate, antimony is distributed 75%–25% Sb(III)-Sb(V) while Bi is 100% in Bi(III) form. The presence of other metals mainly depends on the ore concentrate feed to the process. The most common elements are usually identified as being Cu, Pb, Ni, and Fe.

Hydrolysis appears to be the most appropriate technique for antimony extraction, although other procedures may be of valid application to the case study. The main reasons for their application include the fact that the process is simpler and with less energy consumption than other reported techniques. A review of the literature related to hydrolysis processes under the Sb-Cl-H<sub>2</sub>O system has been carried out. The main results are presented in the Supplementary Information Section. As a conclusion of interest in the present study, it seems reasonable that, by evaluating a pH range between 0.25 and 1, it is possible to obtain the hydrolysis of antimony, thereby obviating the precipitation of bismuth hydrolysis products.

The results reported in the literature are subject to certain limitations. First, the majority thereof were obtained under controlled laboratory conditions using synthetically prepared solutions. Very few contributions (Tian et al., 2016a; Ye et al., 2019) consider the effect of impurities that might be present in industrial processes. Furthermore, when impurities are indeed present, they are removed before the hydrolysis or prior to the analysis of the solid generated, and in no case is their effect reported. The second limitation refers to the temperature effect since most of the experiments are carried out at room temperature. Although Ye et al. (2019) do evaluate the effect of temperature, the hydrolysis is carried out using NH<sub>4</sub>OH instead of water. To conclude, although there may be general coincidences in terms of the behaviour trends between reports in the literature and the present case, it is necessary to ascertain the optimum hydrolysis conditions of pH and temperature and the effect of other metals present in this specific case. This work reports on the results of the tests carried out to extract antimony in the eluate by direct water hydrolysis. Furthermore, the characterisation of the resulting products is also given in order to verify the validity of the procedure and the effects of the pH, temperature, and other metals present in the eluate. The objective involves maximising the extraction yield of antimony.

## 2. Materials and methods

### 2.1. Materials

Eluate samples have been drawn directly from the Atlantic Copper industrial process (Atlantic Copper, 2023). The eluate composition can therefore be expected to have a certain dispersion related to the ore mix feeding the copper-production plant. Thanks to the historical

compositional data provided by Atlantic Copper, a range of values has been established for the research test conditions. The composition, typical of that range, of the eluate sample employed in the tests reported in this paper are shown in Table 2.

### 2.2. Methods

The hydrolysis tests were carried out in glass flasks with 50 ml of solution. The flasks were placed in a thermostatic bath to maintain the reaction temperature within  $\pm 1$  °C, using continuous stirring. Distilled water with conductivity lower than 5  $\mu$ S/cm was utilised to modify the pH changes. The reaction time was for 1 h from the moment the selected pH was reached. The pH and temperature were continually monitored using a pH-meter (Labprocess violab PH60, Barcelona Spain) with a pH accuracy of 0.01.

The precipitated solid was vacuum-filtered with 0.65- $\mu$ m pore membrane filters and was dried at 60 °C for 1 h. X-ray diffraction (XRD) patterns of solid dry hydrolysed products were obtained in  $\theta/2\theta$  geometry using an X'Pert Pro instrument (Malvern Panalytical, Malvern, UK), with Cu-K $\alpha$  radiation source (40 kV, 40 mA). A secondary K $\beta$  filter and a secondary diffracted beam monochromator were employed to reduce the fluorescence. The XRD patterns were collected by scanning between 0° and 80° in the step-scan mode with 0.03° steps and 5 s dwell time.

Scanning electron microscopy (SEM) images were acquired on a FEI Teneo microscope (FEI, Eindhoven, The Netherlands) operating at 15 kV. This microscope is equipped with an energy-dispersive X-ray spectroscopy system (EDS-SEM) for composition analyses.

The chemical composition of hydrolysis dry products was analysed by means of X-ray fluorescence (XRF) after the samples had been homogenised and pressed on a boric acid tablet. These XRF measurements were made in a Zetium Malvern Panalytical wavelength dispersion fluorescence spectrometer (Malvern Panalytical, Malvern, UK) using a semi-quantitative measurement method.

The content of Sb, Bi, and As in the liquid phase was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) in an Agilent 5800 spectrometer (Agilent Santa Clara, CA, US).

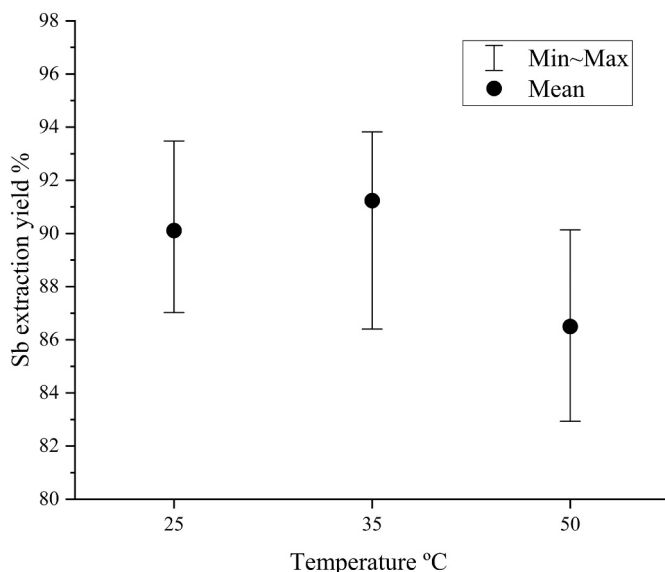
The ion chloride concentration of eluate samples was determined by titration with silver nitrate in an automatic titrator Metrohm 855 (Metrohm, Herisau, Switzerland).

### 2.3. Design of experiments (DOE)

Antimony hydrolysis depends essentially on chloride concentration, metal concentration, and pH. The first two factors are highly restricted by the industrial conditions of eluate production. Consequently, this research focuses on the pH effect. The temperature effect was also studied. Likewise, the effects of other major metals present in the eluate were evaluated by characterisation of the solids generated during the tests.

Several methods can be employed to design experiments, based on the test variables and objectives (Rutherford, 2002). The need to analyse non-independent variables, with either complex behaviour or with a lack of information, renders the use of the Response Surface Methodology appropriate. This statistical technique for the design of experiments enables a reduction in the number of tests needed to determine the behaviour and the relationship between variables, the prediction of responses at points within the range at which no experiences have been carried out, and the identification of the optimal experimental conditions (Montgomery, 2001). In this research, a face-centred central composite design (CCD) was employed in which all axial points fall on the surface of the faces of the design. This type of model enables the inclusion of both the maximum and minimum of the variables under analysis in the experiments. In every case, a minimum of 3 tests have been carried out under all conditions.

From the studies consulted (see the Supplementary Information Section S2), it can be concluded that, under conditions similar to those of



**Fig. 1.** Effect of temperature on the Sb extraction yield obtained in a hydrolysis experimental test ( $n = 10$ ) (pH 0.25 to 0.7). The bars represent the maximum and minimum values.

the eluate, the appearance of solid oxychlorides by hydrolysis, mainly forming  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , occurs at pH values up to 0 and is identified as the stable species at pH values above 4. Likewise, the study of the  $\text{Sb}-\text{Cl}-\text{H}_2\text{O}$  system and the  $\text{Bi}-\text{Cl}-\text{H}_2\text{O}$  system through predominance diagrams in the conditions of the eluate show that the appearance of oxychlorides begins at pH values close to 0.25 and the process of bismuth hydrolysis begins at pH values close to 2 (see the Supplementary Information Section S3). From the studies consulted in the literature, it can be concluded that under conditions like those of the eluate, the appearance of solid oxychlorides  $\text{SbOCl}$  and  $\text{Sb}_4\text{O}_5\text{Cl}_2$  by hydrolysis occurs at pH values above 0 and is identified as the stable species at pH values above 4. Likewise, the study of the  $\text{Sb}-\text{Cl}-\text{H}_2\text{O}$  system and the  $\text{Bi}-\text{Cl}-\text{H}_2\text{O}$  system through predominance diagrams in the conditions of the eluate show that the appearance of oxychlorides begins at pH values close to 0.3 and the bismuth hydrolysis begins at pH values close to 1.5. Therefore, pH values between 0.25 and 1 were studied. For temperature, the range from 25 °C to 50 °C was selected in an effort to attain a compromise between the improvement in efficiency and the energy consumption. Antimony extraction efficiency, defined as the relationship between the antimony content in the liquid sample measured by ICP and the antimony content in the solid product measured by XRF, was selected as response as given in Eq. 3:

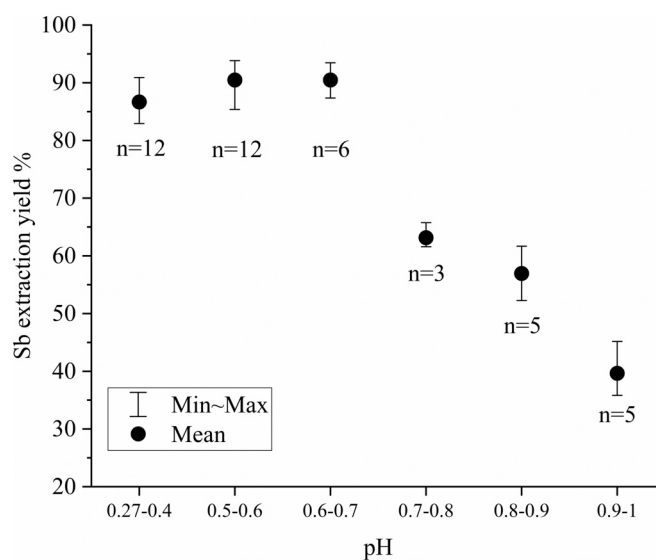
$$\text{Sb yield extraction}\% = \frac{\text{Sb content in hydrolysis product (g)}}{\text{Sb content in solution (g)}} \times 100 \quad (3)$$

Data obtained in the laboratory tests was adjusted using a quadratic model to ascertain whether there were any correlations between the response variable, antimony extraction yield, and the input variables, pH, and temperature.

### 3. Results and discussion

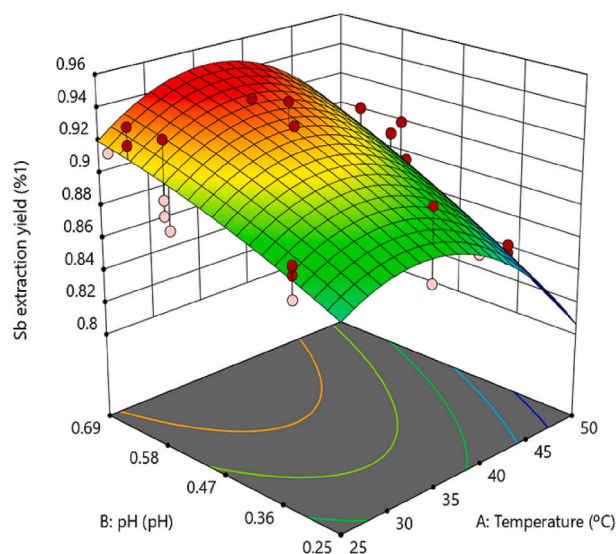
#### 3.1. Effects of pH and temperature

For an analysis of the effect of pH and temperature on the antimony extraction yield, it is important to consider that the eluate has a concentration of bismuth in the same range as that of antimony. It is well described (Smith et al., 1997; Tooth et al., 2013) that bismuth undergoes a hydrolysis reaction that follows the same mechanism as antimony, but occurring at different pH values, generally higher than 1 (Chunfa et al.,



**Fig. 2.** Effect of pH on the hydrolysis antimony extraction yield obtained in experimental tests using hydrolysis with water (temperature from 25 °C to 50 °C). The bars represent the maximum and minimum values.

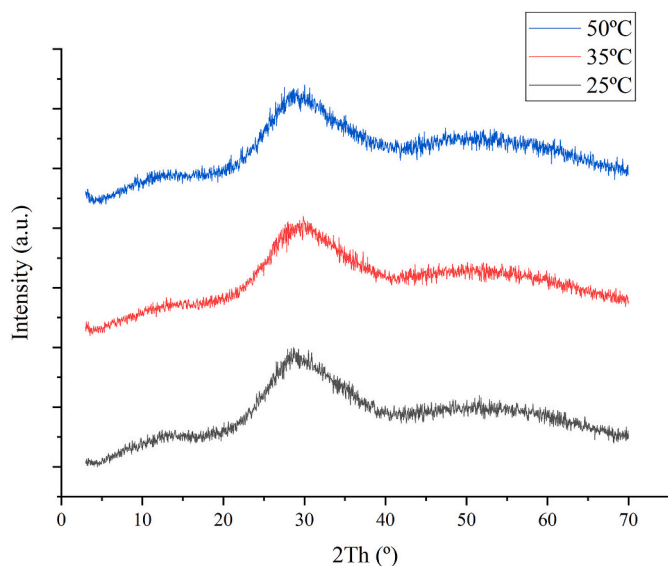
- Design points above predicted value
- Design points below predicted value
- 0.829337 ■ 0.943432



**Fig. 3.** Response surface obtained from pH from (0.25 to 0.7) and temperature (25 °C to 50 °C).

2020). According to the dominance diagrams generated under the eluate conditions (see the Supplementary Information Section S3) the bismuth oxychloride appears at pH values of approximately 2. The possible influence of the presence of bismuth on the antimony extraction yield is discussed in Section 3.3.

Fig. 1 shows the effect of temperature on antimony extraction yield. There are no differences between the results obtained at 25 °C and 35 °C; at 50 °C, the extraction yield decreased by 4%. Even though the maximum and minimum values overlap, the ANOVA analysis ( $p$ -value 0.008) and a subsequent TUKEY test confirm that the results show a significant difference in the case of the tests carried out at 50 °C with respect to those at 35 °C, with no significance in the results obtained at the rest of the temperatures tested. Similar results obtained by Ye et al.



**Fig. 4.** Representative diffractograms obtained for the hydrolysis products at various temperatures.

(2019), show a decrease in extraction yield which is attributed to the effect of temperature on the evaporation of the reagent and on the solubility of the hydrolysis products. The first factor decreases the reactant concentration, while the second increases the amount of antimony in the solution. In this work, the use of water as a reagent should minimise the effect of evaporation, since water is less volatile than ammonium hydroxide. By taking this into account, the small decrease in the extraction yield could be attributed solely to the temperature effect on solubility. Nevertheless, a larger study test campaign should be carried out to confirm this hypothesis.

The influence of pH in antimony extraction yield has two well-delimited trends (Fig. 2). For pH values between 0.25 and 0.7, the extraction yield is high, ranging between 80% and 94%, with a slight increase as pH increases. On the other hand, for pH values between 0.7 and 1, the trend is inverted, and the antimony extraction yield strongly decreases with an increasing pH in a linear trend.

In order to analyse the combined effect of temperature and pH, the response surface was generated using Design Expert software (Version 11) in the pH range between 0.25 and 0.7. Values were adjusted to a quadratic model. Statistical significance was analysed using the F test and ANOVA, and yielded an F value of 20.69 and an adequate precision of 14.650. As can be observed in Fig. 3, the model predicts a similar behaviour to that found in the analysis of the individual variables, that is, the antimony extraction yield increases with the increase in pH while the temperature improves the yield up to a maximum at 35 °C, and decreases as the temperature increases further. According to ANOVA, the effect of temperature on antimony extraction yield is not significant in the model. If the model is utilised to find the optimal conditions under which performance is maximised, then pH 0.645 and 34 °C offer the best results reaching 99.4%. The subsequent maximum yield point occurs at 25 °C and pH 0.56 with an antimony extraction yield of 93.4%, very close to the optimal conditions.

### 3.2. Characterisation

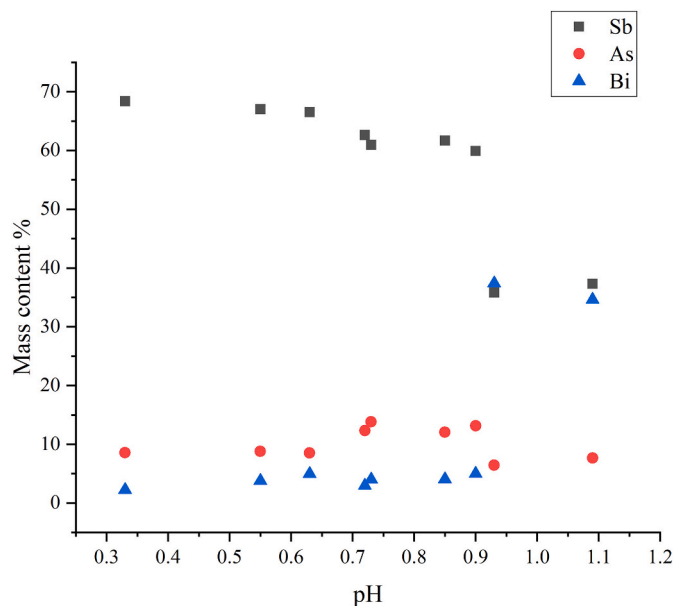
#### 3.2.1. XRD

As can be observed in Fig. 4, no crystalline structure was detected for the products obtained in the hydrolysis of process eluates under any of the pH values and temperature conditions tested. These results are not consistent with the identified species (crystalline  $\text{Sb}_4\text{O}_5\text{Cl}_2$  JCPDS No. 30-0091) reported in other studies (Ye et al., 2019; Tian et al., 2016b),

**Table 3**

Mass percent average compositions of the products obtained in the hydrolysis.

Element	Sb	Cl	O	As	Bi	Others
Average	64.75 ±	4.01 ±	16.32 ±	10.90 ±	2.93 ±	<1
± SD	3.59	2.46	1.81	2.04	1.73	



**Fig. 5.** Evolution of main elements present in the solid product with the value of pH (temperature from 25 °C to 50 °C).

under equivalent conditions. This may be explained in terms of eluate composition. As stated previously, a large part of the literature reported that experimental tests have been carried out from synthetic solutions. The presence of other elements in this work may affect crystallisation. Future work is needed to go into greater depth with this issue.

#### 3.2.2. XRF

Table 3 shows the results of XRF analysis of hydrolysis products. An average content of 65% Sb, 4% Cl, and 16% O was measured. Moreover, significant amounts of up to 10% As and 3% Bi were also observed. Furthermore, variable content of other impurities such as Zn, Cr, Fe, Ca, Al, and Mo were detected. Although the precipitated products could not be identified by X-ray diffraction (XRD), Sb, Cl, and O contents are compatible with the stoichiometry of oxychloride compounds. However, at the present research stage, no clear evidence is available on how identified amounts of As and Bi enter the constitution of the products. Regarding the evolution of the composition with pH, antimony content decreases slightly as pH increases. This behaviour is accentuated at pH values closer to 1, probably due to the increase in the formation of bismuth oxychlorides: a hypothesis that is reinforced considering the evolution of bismuth composition. Arsenic contained in the eluate is incorporated into the solid in percentages of approximately 10%, and this percentage does not vary with the value of pH (Fig. 5).

#### 3.2.3. SEM

Solids generated due to the hydrolysis were studied by scanning electron microscopy using a high-resolution microscope equipped with an EDS analyser. The morphology and composition of the hydrolysis products have been studied.

Samples prepared directly from the filtered and dried product cake appear as variable-size flakes of up to 100 μm (Fig. 6). The EDS point analysis shown in Table 4 reveals a difference between the particles in



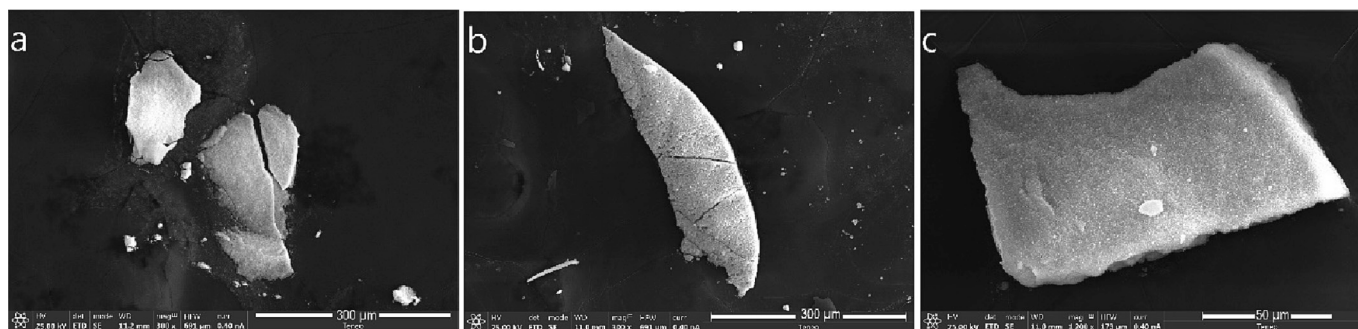


Fig. 6. SEM images of dry filter cake samples.

Table 4  
Mass percent EDS point analysis results.

Particle image	Mass percent of elements				
	As	Bi	Sb	Cl	O
Image 6a	6.66	3.18	64.29	3.18	22.69
Image 6b	6.71	3.27	70.66	2.61	16.75
Image 6c	5.13	1.12	47.03	2.09	44.63
Image 7a	12.64	3.86	57.55	0.60	25.34
Image 7c	10.61	3.29	52.72	3.66	29.71

images 6a and 6b and the particle shown in Fig. 6c. The smaller particles show antimony percentages of between 64% and 70%, whereas the average Cl and O content is around 3% and 20%, respectively. Arsenic content is 6% and bismuth content is around 3%. On the other hand, in larger particles, the content of Sb, As, Bi, and Cl are lower while the oxygen content reaches 40%. It should be noted that the decrease in percentages of Sb, Cl, and As is similar and at approximately 30% while the bismuth content is up to 60% lower than in small particles.

A simple mechanical disaggregation of the particles was carried out to observe the possible segregation of the compounds that form the observed agglomerates. Indeed, the size of the particles is considerably reduced to between 10 and 50 μm, whereby geometries like those found in the previous samples appear, as do other irregularly shaped particles that have a granular or arborescent appearance. It should be noted that particles with a marked spherical geometry have been found (Fig. 7a). The EDS point analyses of these particles reflect similar contents of antimony (55%), arsenic (11%), and bismuth (3.5%), while the chlorine content in the spherical particle is <1% compared to 3.66% in the agglomerate (Table 4).

### 3.3. Effect of bismuth and arsenic

The presence of arsenic and bismuth in the hydrolysis products is generalised to all the conditions tested. However, their behaviour and influence are dissimilar. As can be observed in Fig. 8, the arsenic content

is maintained in values of approximately 10% without any notable effect on antimony extraction, across the whole pH range. On the other hand, bismuth remains at values below 10% for up to a pH value of 0.9, increasing to values close to 35% at higher pH levels. The relationship with the extraction yield must be considered, which experiences a steep drop to values of 40%.

Although the results show that arsenic is incorporated into the hydrolysis product, it has not been possible to identify the cause of this phenomenon, partly due to the lack of crystallinity of the product, which can also be attributed to the presence of arsenic, since other authors (Hashimoto et al., 2005; Tian et al., 2016a; Tian et al., 2016b) who have tested conditions similar to that studied in this work, without the presence of this element, report crystalline species of antimony in all cases.

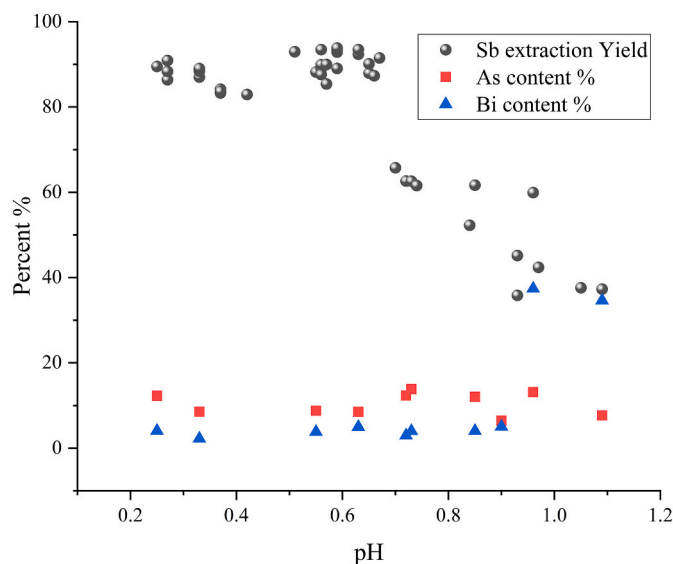


Fig. 8. Evolution of arsenic and bismuth content vs. antimony yield extraction.

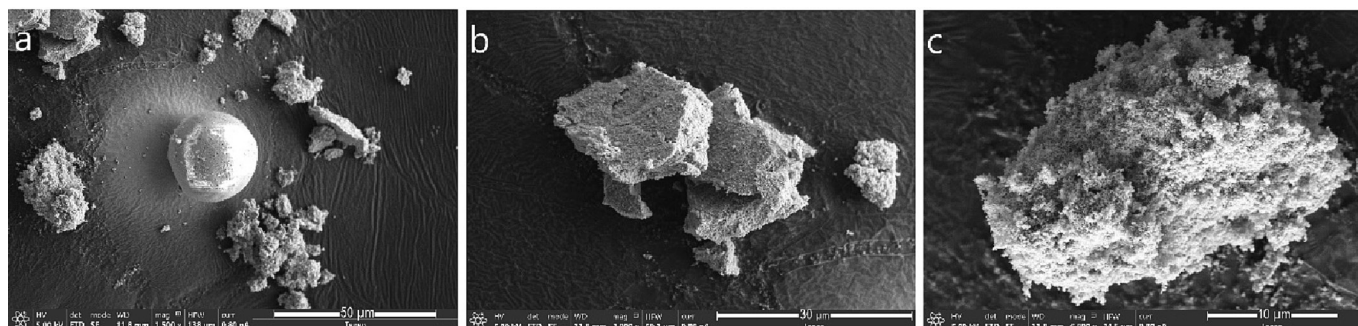


Fig. 7. SEM images of the morphology of the particles after the disaggregation of the filter cake.

However, to the best of our knowledge, no results have been attained in the literature. Consequently, understanding the incorporation of As in the precipitate is essential, since this element harms the quality of the hydrolysis products and will therefore be addressed in future studies.

Regarding the presence of bismuth, the hydrolysis of trichloride occurs at pH values above 1 and the equilibrium equations that describe the hydrolysis of bismuth (Chunfa et al., 2020) and antimony trichlorides are similar (Tian et al., 2016b). Therefore, it seems reasonable to propose that at pH values of approximately 1, both processes can occur simultaneously and competitively, and causing the decrease in antimony extraction yield.

#### 4. Conclusions

- (1) Optimal conditions for the hydrolysis of antimony(III) in a hydrochloric acid stream from an industrial process are recommended as 34 °C for a pH value of 0.645. For these values, the antimony extraction yield as a precipitated product reaches 94.4%.
- (2) The solids obtained are amorphous, with Sb, Cl, and O contents close to  $Sb_4O_5Cl_2$  stoichiometric ratios (i.e.  $Sb_2O_3 \cdot 2SbOCl$ ). However, this solid incorporates impurities such as As and Bi. Bismuth content increases as the pH increases and affects the antimony extraction yield. The effect is minimum at optimum pH values. Arsenic appears in amounts below 10% and shows no direct relationship with pH.
- (3) The presence of arsenic is detrimental to the possible marketing of the products obtained. Furthermore, it is possible that it plays a major role in the amorphisation of the final product. However, this requires further study and is proposed as a research line in future work.

#### CRedit authorship contribution statement

**E. Díaz:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Project administration. **José A. Maldonado Calvo:** Conceptualization, Validation, Resources, Writing – review & editing, Visualization, Supervision, Project administration. **J.M. Gallardo:** Conceptualization, Validation, Writing – review & editing, Supervision, Project administration. **A. Paúl:** Conceptualization, Validation, Writing – review & editing, Supervision, Project administration.

#### Declaration of Competing Interest

This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.hydromet.2023.106076>.

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