J. Min. Metall. Sect. B-Metall. 61 (2) (2025) 251 - 268

Journal of Mining and Metallurgy,
Section B: Metallurgy

# ANTIMONY RECOVERY BY HYDROMETALLURGY - EMPHASIS ON RECOVERY FROM LEACH SOLUTIONS

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*(Received 28 April 2025; Accepted 06 October 2025)*

***Abstract***

*Antimony (Sb) is listed as a critical raw material in both Europe and the USA. Pyrometallurgical and hydrometallurgical methods are used for its recovery from raw sources. Hydrometallurgy is considered a suitable technology when Sb sources are low-grade ores or technogenic waste. After a brief introduction to the Sb species present in pregnant leach solutions (PLS) obtained by using different leaching reagents, this paper presents various methods for recovering Sb from PLS produced in the leaching hydrometallurgical stage. The discussion covers antimony recovery by hydrolysis and conversion, selective precipitation, crystallization, electrowinning, replacement, liquid-liquid extraction and ion exchange. Factors affecting the effectiveness of these processes and the recent attempts to improve these technologies are presented. Finally, possible future research directions are outlined.*

**Keywords:** *Antimony recovery; Electrowinning; Hydrolysis and conversion; Precipitation and crystallization; Liquid-liquid extraction; Ion exchange*

## 1. Introduction

Antimony (Sb) is a metalloid, with an average abundance of 0.2 mg/kg in the Earth's crust. It is found in sulfur (S) containing minerals (sulfides and sulfosalts) of lead (Pb), copper (Cu), and silver (Ag). Antimony is present in over 100 minerals, with stibnite ($Sb_2S_3$) being the predominant and most important mineral from an industrial perspective. Other Sb-bearing minerals of industrial interest that contain S are jamesonite ($Pb_4FeSb_6S_{14}$), boulangerite ($Pb_5Sb_4S_{11}$), bindheimite ($Pb_2Sb_2O_6$(O,OH), zinkenite ($Pb_9Sb_{22}S_{42}$), tetrahedrite ($Cu_{12}Sb_4S_{13}$), berthierite ($FeSb_2S_4$), livingstonite ($HgSb_4S_7$), etc. Valentinite (rhombohedral $Sb_2O_3$), senarmontite (cubic $Sb_2O_3$), stibiconite ($H_2Sb_2O_5=Sb_2O_4 \cdot H_2O$), cervantite ($Sb_2O_4=Sb_2O_3 \cdot Sb_2O_5$), and kermesite ($Sb_2S_2O$) are oxide minerals that contain Sb of industrial interest [1, 2]. Antimony-containing Pb and gold (Au) ores are also sources of primary Sb [3].

Antimony trioxide ($Sb_2O_3$) is the most produced and widely used Sb compound [1, 4]. It is applied as flame retardant in plastics, rubbers, and coatings in different industries, such as electronics, textile, etc. Antimony compounds are used in the chemical industry - as stabilizers and catalysts. Adding antimony to lead alloys enhances their mechanical properties, making Pb - Sb alloys suitable for automotive lead-acid batteries and construction applications [2, 5-7].

Antimony and its compounds are considered suitable materials for thin-film and third generation solar cells [8-11]. Antimony based anodes have been suggested for lithium-ion batteries because of their good theoretical capacity, high electronic conductivities, and high reversible lithium storage capacity [12, 13]. One of the proposed and most studied materials for anode in the sodium-ion batteries is antimony trisulfide ($Sb_2S_3$) because of its high theoretical capacity [14, 15].

Pyrometallurgical and hydrometallurgical technologies are used to recover Sb from its primary resources. Pyrometallurgy is suitable for processing primary Sb-rich ores while hydrometallurgy is appropriate to treat low grade ores and residues (with relatively low and changeable Sb content) from industrial process recovering Sb and other metals.

Hydrometallurgy uses aqueous solutions and proper chemical reactions to dissolve valuable metals in the pregnant leach solution (PLS).

Further, the PLS is (most often) purified and the targeted metals are separated by different approaches, such as selective precipitation, solvent extraction, ion exchange, electrowinning. The present review is aimed to summarize and give an idea of the routes used to recover Sb from the PLS, and their

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***https://doi.org/10.2298/JMMB250428020P***

modifications proposed in the recent 10 years, with particular emphasis on antimony recovery from secondary nonmetal scrap resources. We aim to assist in selecting suitable approaches and process conditions for antimony recovery from the PLS obtained by leaching residues generated by mining and recovery processes in the nonferrous metals industries.

## 2. Methods

A careful search using suitable keywords was carried out in the Science Direct database and other databases (PubChem, DOAJ, BASE, RSCI, Mendeley, etc.) to identify appropriate articles and book chapters that were then cautiously reviewed for preparing a critical summary of the information and presenting it below in this article.

## 3. PLS type and dissolved Sb compounds

### *3.1. Acidic solutions*

In general, it is acknowledged that sulfuric acid ($H_2SO_4$) is not proper leaching reagent for Sb low grade ores and residues from industrial process [16, 17].

Industry uses acidic systems based on hydrochloric acid (HCl) solutions for Sb leaching from poor ores and Sb-bearing residues. Often ferric chloride ($FeCl_3$) is added and the following generalized reactions are processing [1, 18]:

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S \qquad (1)$$

$$6FeCl_3 + Sb_2S_3 \rightarrow 2SbCl_3 + 6FeCl_2 + 3S^0 \qquad (2)$$

The ferric chloride acts as an oxidizing and chloridizing agent that converts the antimony of the sulfide mineral into a chloride complex.

When the Sb is available as oxide in the system to be leached, $FeCl_3$ is not needed and the proceeding generalized reaction is:

$$Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O \qquad (3)$$

Figure 1 depicts a Pourbaix diagram of the $Sb_2S_3$–Cl–$H_2O$ system at room temperature, as an example of stibnite leaching. As it can be seen stibnite dissolves in hydrochloric acid based medium with formation of different species of $Sb^{3+}$ in dependence of medium pH and oxidation-reduction potential values [19]. Benabdallah et al., [20] propose the availability of the following main species depending on solution pH values: pH <-0.5–$SbCl^{4-}$ (the prevailing species) and $SbCl_3$; -0.5<pH<-0.25-$SbCl^{4-}$, $SbCl_3$, and $Sb(OH)^{2+}$; -0.25<pH<0-$SbCl^{4-}$, $SbCl_3$, and $Sb(OH)^{2+}$ (the prevailing species); 0<pH<0.5-$Sb(OH)_2^+$ and $Sb(OH)_3$; pH>0.5-$Sb(OH)_3$.

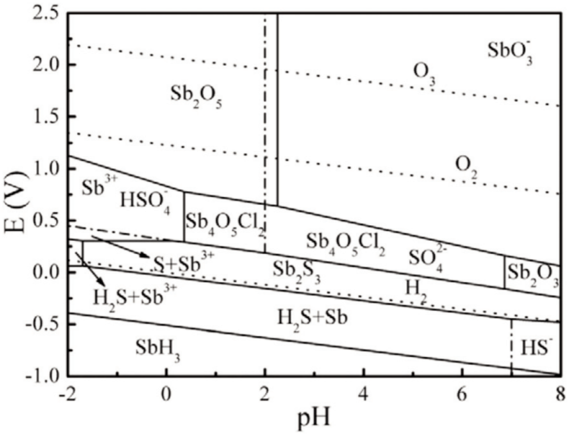

***Figure 1.*** *A Pourbaix diagram of the $Sb_2S_3$–Cl–$H_2O$ system at 25 °C ($[Sb^{3+}]$total = 0.1 mol/L, $[H_2S]$= 0.01 mol/L, $[Cl^-]$total = 4.5 mol/L) [19]*

The effect of chloride ions concentration in the leaching solution on the antimony species formed must also be considered. For example, Hernández-Pérez et al. [21] found the following order of species of $Sb^{3+}$ with increasing the chloride concentration: $SbCl^{2+}$, $SbCl_2^+$, $SbCl_3$, $SbCl_4^-$ , $SbCl_5^{2-}$ and $SbCl_6^{3-}$.

Increasing the amounts of antimony (V) complexes containing more chloride ions with increasing the total concentration of chlorides in the solution is described in depth by Li and coauthors [22].

Figure 2 shows a Pourbaix diagram of the Sb–$H_2O$ system at room temperature [23]. Possible transformations of antimony (III) oxide may serve as basis for understanding the leaching of oxide antimony minerals [23]. As it can be seen, antimony, antimony oxide and antimonate can exist steadily in the stable zone of water solution. Under strongly acidic conditions, they can be converted to $SbO^-$ and

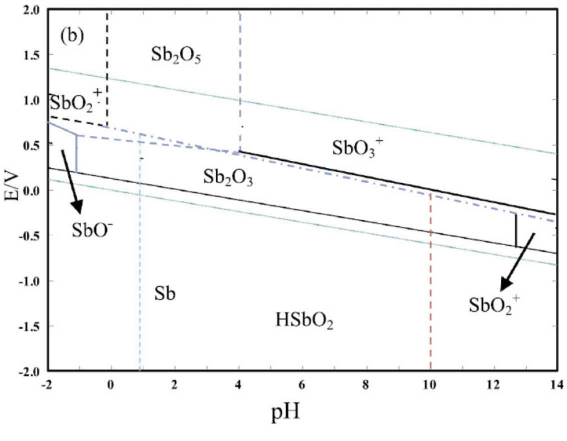

***Figure 2.*** *A Pourbaix diagram of the Sb–$H_2O$ system at 25 °C [23]*

$SbO_2^+$. Pentavalent antimony can be easily converted to $SbO_3^+$ under weakly acidic to alkaline conditions, whereas trivalent antimony $SbO_2^-$ reacts with $OH^-$ only under strongly alkaline conditions (see also below, point 3.2).

Thus, as a result of acidic leaching, the PLS contains mainly dissolved species of $Sb^{3+}$. However, acids also dissolve other metals that present in the ores. Considering the common associates of stibnite and senarmontite (https://www.mindat.org/min-3782.html), the other metal ions that most probably would enter the solution are those of calcium, barium and iron.

### 3.2. Alkaline solutions

Due to its selectivity for dissolving antimony from complex waste matrices and its lower corrosion risk for equipment - compared to strong acids and oxidising mixtures - alkaline sulfide leaching is often the industry choice.

A mixture of sodium sulfide ($Na_2S$) and sodium hydroxide (NaOH) is the lixiviant in the alkaline leaching system. When stibnite contacts with this solution sodium thioantimonite ($Na_3SbS_3$) is produced as shown by the following reactions [16]:

$$Na_2S + Sb_2S_3 \rightarrow 2NaSbS_2 \tag{4}$$

$$NaSbS_2 + Na_2S \rightarrow Na_3SbS_3 \tag{5}$$

The dissolution of naturally occurring elemental sulfur in minerals in NaOH produces sulfur species that can also serve as a lixiviant for antimony in the alkaline-sulfide leaching. Sulfide ($S^{2-}$), sodium thiosulfate ($Na_2S_2O_3$) and sodium polysulfides ($Na_2S_x$) are created, as shown by the following generalized reactions:

$$\begin{gathered} 4S^0 + 6NaOH \rightarrow 2Na_2S + \\ + Na_2S_2O_3 + 3H_2O \end{gathered} \tag{6}$$

$$\begin{gathered} (x-1)S^0 + Na_2S \rightarrow Na_2S_x \\ (where\ x = 2\ to\ 5) \end{gathered} \tag{7}$$

Thioantimonite is oxidized by polysulfides to sodium thioantimonate ($Na_3SbS_4$) that is the major species found typically in the solution:

$$\begin{gathered} Na_2S_x + (x-1)Na_3SbS_3 \rightarrow \\ \rightarrow (x-1)Na_3SbS_4 + Na_2S \end{gathered} \tag{8}$$

Normally, NaOH is added to prevent hydrolysis of $Na_2S$ by reactions [2]:

$$Na_2S + H_2O \rightarrow NaHS + NaOH \tag{9}$$

$$NaHS + H_2O \rightarrow H_2S + NaOH \tag{10}$$

In addition, NaOH also solubilizes the $Sb_2S_3$ by producing alkaline thioantimonides and oxothioantimonites [2]:

$$\begin{gathered} Sb_2S_3 + NaOH \rightarrow NaSbS_2 + \\ + NaSbOS + H_2O \end{gathered} \tag{11}$$

In alkaline solutions antimony oxide from minerals may be dissolved to form a mixture of thioantimonite, antimonate, and meta-antimonite species, the process described by the following generalized reactions [24, 25]:

$$\begin{gathered} Sb_2O_3 + 3Na_2S + 3H_2O \rightarrow Na_3SbS_3 + \\ + Na_3SbO_3 + 6H^+ \end{gathered} \tag{12}$$

$$Sb_2O_3 + 2NaOH \rightarrow 2NaSbO_2 + H_2O \tag{13}$$

Although selective for antimony, the alkaline leaching causes dissolution also of gold, arsenic, and mercury minerals. In addition, because $Sb_2S_3$ occurs with other sulphide minerals (PbS, ZnS, FeS, etc.), these minerals are leached by NaOH and soluble plumbite ($Na_2PbO_2$), zincate ($Na_2ZnO_2$) and iron hydroxide ($Fe(OH)_2$) are formed. This, not only results in reagents loss but also causes the presence of these metals in the PLS. Having in mind the common associates of stibnite and senarmontite (https://www.mindat.org/min-3782.html) ions of other metals such as bismuth and tin (if present in the ore), may also enter the solution.

Therefore, whether from acidic or alkaline PLS, Sb recovery requires application of different techniques.

## 4. Methods for Sb recovery from PLS

### 4.1. Hydrolysis and conversion by alkalization

#### 4.1.1. Antimony compounds obtaining from PLS

Hydrolysis, most often immediately followed by conversion with an alkalizing reagent, is widely used in industry to recover Sb from acidic PLS. Nonetheless, studies are still continuing to improve this treatment route. The total process usually involves different stages and reactions influenced by metal ions concentration, pH, temperature, and chloride ions concentration.

In the hydrolysis process the metal ion present in the leach solution reacts with water. In this case $Sb^{3+}$ (for example, from the $SbCl_3$ produced by acid leaching) reacts to form solid oxychlorides in two consecutive stages, according to Anderson [16]:

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \tag{14}$$

The produced SbOCl is further transformed to $Sb_4O_5Cl_2$:

$$4SbOCl + H_2O \rightarrow Sb_4O_5Cl_2 + 2HCl \tag{15}$$

Some authors consider direct production of $Sb_4O_5Cl_2$ [19, 20]:

$$4SbCl_3 + 5H_2O \rightarrow Sb_4O_5Cl_2 + 10HCl \tag{16}$$

Thermodynamic simulations have been conducted and predominance diagrams constructed to predict the behavior of the Sb(III)-Cl-$H_2O$ system at different pH values [26-28].

Hashimoto and coauthors found that $Sb_4O_5Cl_2$ is the solid product resulting from the hydrolysis in the Sb(III)-HCl–$H_2O$ system at 25 °C at higher acidity (HCl > 0.12 mol/L, i.e. pH < 1), while at lower acidity (HCl < 0.1 mol/L, pH > 1) $Sb_2O_3$ is formed [29].

According to findings of Hashimoto et al. [29], at pH around 2 crystalline $Sb_8O_{10}(OH)_2Cl_2$ is formed while at pH around 4 - 4.5, initially $Sb_8O_{10}(OH)_2Cl_2$ precipitated is arbitrarily converted into $Sb_2O_3$. The following reactions describe the processes:

$$Sb_4O_5Cl_2 + 3H_2O \rightarrow 4HSbO_2 + 2HCl \tag{17}$$

$$\begin{aligned} &8HSbO_2 + 2HCl \rightarrow \\ &\rightarrow Sb_8O_{10}\left(OH\right)_2Cl_2 + 4H_2O \end{aligned} \tag{18}$$

$$Sb_8O_{10}\left(OH\right)_2Cl_2 \rightarrow 4Sb_2O_3 + 2HCl \tag{19}$$

At that pH value and higher, the hydrolysis reaction proceeds very slowly. The presence of chloride ions retards the hydrolysis reaction, with a more pronounced effect as the pH value increases.

Even more, Tian et al. [28] reported that in system containing $Sb^{3+}$ species and chloride concentrations of 1 and 3 mol/L, SbOCl could be found only in very acidic system (pH= -2 to -0.2), if the thermodynamically favorable transformation process of SbOCl to $Sb_4O_5Cl_2$ has not occurred, i.e. only theoretically. However, in real systems SbOCl is spontaneously transformed to $Sb_4O_5Cl_2$ and solid SbOCl is not found in the pH range -2 to 6.3 where $Sb_4O_5Cl_2$ is the predominating stable solid compound. Thus, $Sb_4O_5Cl_2$ could be obtained directly or by transformation, when the pH of the PLS is less than 6.3.

According to the same authors at low pH (0 - 2) monoclinic $Sb_4O_5Cl_2$ (JCPDS No. 30−0091) precipitates, while at higher pH values (2 - 4) orthorhombic $Sb_4O_5Cl_2$ is formed. In addition, in the pH range 2-4 orthorhombic transition material $Sb_8O_{11}Cl_2 \cdot 6H_2O$ (JCPDS No. 77−1584) is detected, most probably produced by the reaction:

$$8SbCl_3 + 11H_2O \rightarrow Sb_8O_{11}Cl_2 + 22HCl \tag{20}$$

At pH value equal to or higher than 4.0 orthorhombic $Sb_2O_3$ (JCPDS No. 11−0689) could be formed spontaneously.

$$\begin{aligned} &Sb_8O_{11}Cl_2 \cdot 6H_2O \rightarrow 4Sb_2O_3 + \\ &+ 2HCl + 5H_2O \end{aligned} \tag{21}$$

The oxychlorides are converted to $Sb_2O_3$ not only by hydrolysis but also by medium alkalization - often by ammonia water addition [16].

$$\begin{aligned} &2SbOCl + 2NH_4OH \rightarrow Sb_2O_3 + \\ &+ 2NH_4Cl + H_2O \end{aligned} \tag{22}$$

$$\begin{aligned} &Sb_4O_5Cl_2 + 2NH_4OH \rightarrow 2Sb_2O_3 + \\ &+ 2NH_4Cl + H_2O \end{aligned} \tag{23}$$

Other reagents proposed for oxychlorides conversion to $Sb_2O_3$ are NaOH and $Na_2CO_3$ - reactions (24) - (25):

$$\begin{aligned} &Sb_4Cl_2O_5 + 2NaOH \rightarrow 2Sb_2O_3 + \\ &+ 2NaCl + H_2O \end{aligned} \tag{24}$$

$$\begin{aligned} &Sb_4Cl_2O_5 + Na_2CO_3 \rightarrow 2Sb_2O_3 + \\ &+ 2NaCl + CO_2 \end{aligned} \tag{25}$$

Tian and coauthors [28] proved experimentally that $Sb_2O_3$ is generated by conversion and the process starts when pH is higher than 1.9. The transition material $Sb_8O_{11}Cl_2 \cdot 6H_2O$ is converted at pH higher than 4:

$$\begin{aligned} &Sb_8O_{11}Cl_2 + 2NaOH \rightarrow 4Sb_2O_3 + \\ &+ 2NaCl + H_2O \end{aligned} \tag{26}$$

From the other hand, a recent study, based on Density functional theory, experimental work and infrared spectroscopy proved existence of SbOCl at pH 0 [30].

Figure 3 visualizes findings of different authors

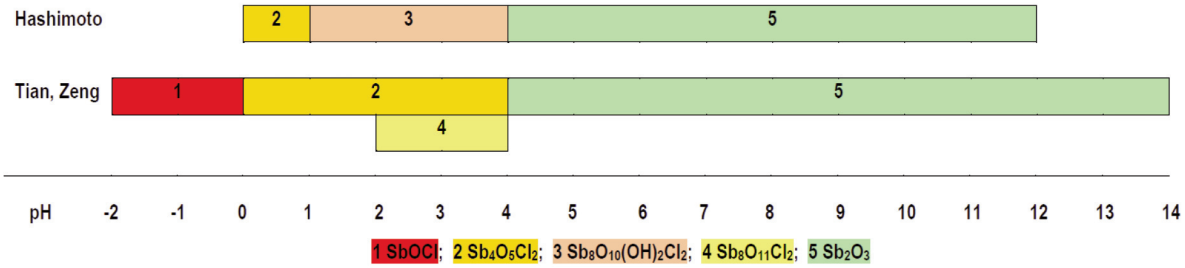

***Figure 3.*** *Antimony species formed as a result of hydrolysis, alkalization and precipitation from acidic PLS, according to different authors*

from studies on the antimony species formed as a result of hydrolysis, alkalization and precipitation from acidic PLS. As it can be seen, there is an agreement that at pH over 4 the produced material is $Sb_2O_3$.

Ibrahim and coauthors studied the effect of the used alkalizing reagent ($NH_4OH$ and NaOH), pH (1.5, 2, 2.5, and 3), temperature (50, 60, 70, and 80 °C), and stirring speed (100, 200, 300, and 400 rpm), on the precipitation (by hydrolysis and immediate conversion) of Sb ions from the PLS produced by leaching of slag (generated in an antimony smelting plant) with HCl based solution. The aim was to obtain high purity Sb-containing solid product at high precipitation rates, with no iron (Fe) presence in the product [31]. By using the Taguchi approach and ANOVA analysis the authors showed that the solution pH and stirring speed strongly influence the precipitation rate of Sb, while alkali type and reaction temperature are less influential factors.In contrast, all studied parameters influenced considerably the precipitation rate of Fe. Another finding was that in order to obtain Sb-precipitate with high recoveries, the hydrolysis process has to be conducted using NaOH at 70 °C, the solution pH to be 3 and the PLS to be stirred at 100 rpm. However, a higher precipitation rate is accompanied by the production of higher amount of Fe-bearing precipitate, resulting in contaminated Sb compounds. The use of $NH_4OH$ as the hydrolyzing and converting reagent led to the formation of Sb-bearing precipitates with higher purity. The final material produced under the optimal conditions (use of $NH_4OH$ to reach pH 1.5, 50 °C and 100 rpm) was composed of 81.43% Sb, 16.23% O, and 2.34% Fe. The material was identified as antimony oxide ($Sb_2O_3$) by XRD analysis.

Most authors study the hydrolysis of $Sb^{3+}$ ions. However, when during the leaching process highly oxidizable conditions are established, the $Sb^{5+}$ ions present in the acidic PLS. In this case (i.e. $Sb^{5+}$–$H^+$–$Cl^-$ system), according to Meng et al., the hydrolysis leads to the formation of $Sb_2O_5$ [32]:

$$2Sb^{5+} + 5H_2O \rightarrow Sb_2O_5 + 10H^+ \tag{27}$$

$$Sb^{5+} + iCl^- \rightarrow \left[SbCl_i\right]^{5-i}, i = 1, 2, \ldots 6 \tag{28}$$

The authors studied the effects of aging time (0, 3, 5 and 7 days) and hydrolysis ratio (0.5, 1, 1.5 and 2) on the Sb recovery. A hydrolysis ratio of 1.5 and aging time of 7 days are found as optimal when the recovery rate of 97 % is achieved.

Leaching Sb-bearing solid material with acids inevitably brings into the PLS other metals that present in that material, such as Al, K, Mg, Na, Mn, Fe, etc. These impurities available in the PLS do not decrease the purity of the Sb precipitate produced by the hydrolysis because, at the pH levels of Sb hydrolysis, they stay in an ion form in the PLS. The exception is $Fe^{3+}$ ions that (depending on their concentration) begin to precipitate within the pH range where Sb precipitates by hydrolysis, i.e. pH 1 – 4 [33].

Ye et al. suggested hydrolysis (from Sb-Fe solution) under strictly controlled pH value as a way to recover Sb containing precipitate $Sb_4Cl_2O_5$ with very low amount of Fe impurities [26]. Their work is based on the fact that $Sb^{3+}$ and $Sb^{5+}$ hydrolyze at pH above 0, while the hydrolysis of ferric iron starts at pH above 1. They studied the effects of temperature (in the range 30 - 70 °C) and the final pH of the treated PLS. Controlled pH values were achieved by hydrolysis carrying out through the addition of $NH_4OH$ solution.

Hydrolysis ratio of Sb and Fe, as well as separation coefficient were calculated using formulas: (29), (30), (31):

$$\begin{aligned} &Hydrolysis\ ratio\ of\ Sb, \% = \\ &= \left[\left(c_1 \cdot V_0 - c_3 \cdot V\right) / \left(c_1 \cdot V_0\right)\right] \cdot 100 \end{aligned} \tag{29}$$

$$\begin{aligned} &Hydrolysis\ ratio\ of\ Fe, \% = \\ &= \left[\left(c_2 \cdot V_0 - c_4 \cdot V\right) / \left(c_2 \cdot V_0\right)\right] \cdot 100 \end{aligned} \tag{30}$$

$$\begin{aligned} &Separation\ coefficient\ of\ Sb - Fe = \\ &= \left[\left(c_1 / c_3\right) / \left(c_2 / c_4\right)\right] \cdot 100 \end{aligned} \tag{31}$$

where $c_1$ and $c_2$ are the Sb and Fe contents in the solution before hydrolysis, g/L; $c_3$ and $c_4$ are the Sb and Fe contents in the solution after hydrolysis, g/L; $V_0$ and V are the volumes of the solution before and after hydrolysis, L. It was found that the optimal hydrolysis conditions are 30 °C, final pH 0.5, and an $NH_4OH$ addition rate of 1.33 mL/min under which the antimony hydrolysis ratio exceeds 99.0% and the Fe hydrolysis ratio was lower than 0.1% and the separation coefficient was 285. The authors investigated the effect of different reagents ($NH_4OH$, NaOH and $Na_2CO_3$) on the $Sb_4Cl_2O_5$ conversion. It is found (by SEM images analysis) that when $NH_4OH$ and $Na_2CO_3$ were used the obtained $Sb_2O_3$ exhibited better crystallinity, uniform particle size and a cubic structure meeting the requirements for products used in flame retardants. When NaOH was used, the obtained $Sb_2O_3$ consisted of a crystal clutter and fine particles, which hindered filtration. Thus, the authors' concluded that $NH_4OH$ and $Na_2CO_3$ are reagents suitable for the transformation of antimony oxychloride. Following Cai et al. [34], Ye and coauthors suggested the PLS left after $Sb_4Cl_2O_5$ precipitation to be subjected to solvent extraction with N,N,N′,N′-tetra-2-ethylhexyldiglycolamide (T2EHDGA) to recover pure iron products. Ye et al. proposed the described separation process to be used to recover Sb from a Sb post-electrowinning solution producing pure $Sb_2O_3$ and Fe-bearing products, while also addressing the problem of Sb and Fe accumulation in the process.

### *4.1.2. Antimony compounds obtaining from eluate from copper electrolyte purification*

The depletion of rich copper ores necessitates the use of poorer ores containing various impurity minerals, e.g. enargite ($Cu_3AsS_4$), tennantite ($Cu_{12}As_4S_{13}$) and tetrahedrite ($Cu_{12}Sb_4S_{13}$) which are associated with the main copper sulfide minerals in the ore bodies [35]. Flotation produces copper concentrates that bear Sb and As. These impurities cause difficulties in further materials' processing for copper recovery both by smelting and electrowinning. To purify copper containing solutions before Cu electrowinning often ion exchange is applied. The eluate from resins recovery can be used as a secondary source of antimony.

Hydrolysis and subsequent conversion are used to recover Sb from the eluate of a preliminarily loaded ion exchange resin used to purify copper electrolyte before Cu electrowinning at an industrial facility. Elution is conducted with an HCl solution. The eluate typically contains, in g/L - Sb 9-10, Bi 8-10, As 2-5 and Cl - 170. Different reagents that cause hydrolysis of $SbCl_3$ to $Sb_4O_5Cl_2$ have been studied at 25 °C, namely distilled water, $NH_4OH$ (30% w/w) and NaOH (10% w/w) [27]. It was found that the Sb recovery by hydrolysis is higher when $NH_4OH$ or NaOH were used, in comparison to water. At the optimal pH = 0.5 level for water and pH = 1 for $NH_4OH$ and NaOH, the average antimony extraction yields were correspondingly 90.4%, 96.1%, and 96.7%. However, with respect to impurities, and especially As in the solids formed, the lowest amount (8%) was included in the Sb precipitate that was produced by using water as hydrolyzing reagent. The bismuth amount in all formed Sb precipitates was low (less than 2%) and generally was not affected by pH levels. In terms of the reagents employed, the best results were obtained when $NH_4OH$ was used - antimony extraction values > 90% at all the pH levels tested (from 0.25 to 1.0), highest product crystallinity and the lowest amount of the reagent needed. Overall, the study has showed that hydrolysis conducted with $NH_4OH$ is the most efficient means for antimony extraction from this solution.

Another research group also studied the hydrolysis and further conversion as means to recover antimony from the above-mentioned type of eluate (containing bismuth and arsenic) from the copper electrorefining [36]. In order to avoid inclusion of high amounts of As in the Sb and Bi bearing precipitates, it is proposed that the eluate be pretreated with $SO_2$(g) or $NaHSO_3$(s) - the latter being an alternative. This reduces $As^{5+}$ and $Sb^{5+}$ ions that present in the solution:

$$SO_{2(g)} + H_3AsO_4 + H_2O \rightarrow 2H^+ + \\ + SO_4{}^{2-} + H_3AsO_3 \tag{32}$$

$$NaHSO_{3(s)} + H^+ \rightarrow Na^+ + H_2O + SO_{2(g)} \tag{33}$$

The eluate ORP value decreased from an initial value of 500 mV to 300 mV when $SO_2$ was used as the reducing reagent, and from 489 mV to 385 mV when $NaHSO_3$(s) was utilized. Different reagents, namely $Ca(OH)_2$(s), $CaCO_3$(s) or NaOH(l), were tested in the experiments on Sb hydrolysis and further conversion with the aim to increase the solution pH from -0.6 to 3.2 at 22 °C. Precipitation of calcium sulfates was observed when Ca-bearing reagents were used, causing contamination of the Sb and Bi-bearing precipitates obtained. That is why further studies were conducted with 5M NaOH. It was found that at pH 0.2, the precipitated solid was $Sb_4O_5Cl_2$(s) with a purity higher than 93%. At pH 1.0 the solid material formed was a mixture of SbOCl(s) and BiOCl(s), with low content of As (<0.85%). The material precipitated at pH 2.00 was mostly BiOCl(s) with a purity higher > 95%. Results showed that when $As^{5+}$ was reduced completely to $As^{3+}$, the precipitation of $SbAsO_4$(s) was avoided. The authors proposed an eluate treatment scheme for Sb and Bi recovery: Initially $NaHSO_3$ solid to be used to reduce $As^{5+}$ in the eluate to $As^{3+}$. Further, 5M NaOH to be added to pH 1 and $Sb_4O_5Cl_2$(s) allowed to precipitate. Next, the pH is raised to 2.5 to obtain BiOCl(s). In the next step the eluate pH is increased to 4, solid $Fe_2(SO_4)_3$ is added and As precipitated and stabilized as scodorite ($FeAsO_4 \cdot 2H_2O$(s)).

The same research group studied the effect of the concentration of the added alkalizing reagent (from 5 g/L to 50 g/L) on the content of As in the solid Sb-bearing materials produced [37]. They found that increasing the concentration of NaOH decreased the As content in the solid sample - to 0.1 % for 50 g/L NaOH. Studies on the effect of temperature (25 and 75 °C) showed that conversion at higher temperature may enhance the purity of the obtained $Sb_2O_3$(s). The authors proved that under optimal conditions (preliminary treatment of eluate with $SO_2$(g), hydrolysis and conversion with 100 g/L NaOH at 25 °C for 2 h), a commercial grade $Sb_2O_3$(s) it produced, with purity of 97.4%.

Based on the above-described studies, it can be summarized that $NH_4OH$ and NaOH are suitable reagents for Sb recovery from the PLS by hydrolysis and conversion. Generally, moderate heating (30-50 °C) increases the Sb recovery and the purity of the produced $Sb_2O_3$.

### 4.2. Precipitation and crystallization

A solid from an aqueous solution is obtained via both precipitation and crystallization processes. The main differences between these processes are the fineness of the final products and the duration of the process. Crystallization is a relatively slow process and the obtained product is with shaped crystals, while the precipitation is usually faster process and the product can be in amorphous or crystal form [38].

#### 4.2.1. Recovery from alkaline - sulfide PLS

Wikedzi et al. proposed Sb recovery from PLS obtained by alkaline sulfide leaching by hydrogen peroxide ($H_2O_2$) facilitated process [39]. Hydrogen peroxide oxidizes $Sb^{3+}$ and $S^{2-}$ ions that present in the PLS and antimony is precipitated as $NaSb(OH)_6$, as described by the reactions (34) and (35):

$$Na_3SbS_3 + 13H_2O_2 + 4NaOH \rightarrow \rightarrow NaSb(OH)_6 + 3Na_2SO_4 + 12H_2O \quad (34)$$

$$Na_2S + 4H_2O_2 \rightarrow Na_2SO_4 + 4H_2O \quad (35)$$

$$Na_3AsS_3 + 13H_2O_2 + 6NaOH \rightarrow \rightarrow Na_3AsO_4 + 16H_2O + 3Na_2SO_4 \quad (36)$$

It is found that the Sb recovery depends on both time and $H_2O_2$ dosage. Use of nearly 100% of stoichiometric hydrogen peroxide is required to achieve complete oxidation of the total quantity of $Sb^{3+}$ and $S^{2-}$ in the solution. Nearly 99% of the antimony that present in the PLS is precipitated in 3 hours at 25 °C and at 1:1 (w/w) ratio of PLS to 30% $H_2O_2$. However, it should be borne in mind that the presence of residual $Na_2S$ and the As species in the PLS also can consume $H_2O_2$ via reactions (35) and (36). Sodium thioantimonite is oxidized and precipitated as sodium antimonate. Sodium thioarsenite is oxidized to soluble sodium arsenate. Fortunately, the difference in the solubility of produced compounds enables their separation [40].

The same study also describes another way to recover Sb from the PLS resulting from alkaline leaching, namely crystallization of sodium thioantimonate formed by the reaction (8) by solution cooling. About 59% of Sb that present in the PLS (initial concentration of 45 g/L) is precipitated in 12 hours when the solution was kept at 30 °C. The temperature decreases to 25 and 10 °C, lead to precipitation of 71% and 76% respectively of the antimony that is present in the PLS.

Yang et al. proposed pressure oxidation of the PLS that contains sodium thioantimonite, in order to transform it to sodium pyroantimonate [41]. After completing the leaching, the PLS is transferred to an autoclave, oxygen is added and a reaction described by the equation (37) proceeds:

$$2Na_3SbS_3 + 7O_2 + 2NaOH + 10H_2O \rightarrow \rightarrow 2NaSb(OH)_6 + 3Na_2S_2O_3 + 5H_2O \quad (37)$$

The treated solution is concentrated by heating, hot filtered and then cooled. Under optimal conditions (oxygen partial pressure 0.4 MPa, reaction time 2 h, sodium hydroxide concentration 20 g/L, stirring speed 800 rpm, and reaction temperature 90 °C), the antimony precipitation ratio exceeded 99.80%, and the antimony concentration in the treated PLS was <0.092 g/L. The produced sodium pyroantimonate showed a regular tetragonal morphology.

Han et al. recovered Sb from alkaline $Na_2S$ leaching solution, where Sb was present as liquid sodium thioantimonate, by precipitation of $Na_3SbS_4(H_2O)_9$ crystals via evaporation-crystallization [42]. The achieved recovery of antimony was 93.83%.

#### 4.2.2. Recovery from acidic PLS

Multani and coauthors also studied $H_2O_2$ facilitated precipitation (in the form of tripuhyite, i.e. ferric antimonate - $FeSbO_4$) as a means for the Sb recovery from solution, specifically from acidic solution containing 6 g/L of Sb [43]. Under the optimum conditions (use of 10 % $H_2O_2$, pH 5.3, 95 °C, 3.5 h) $FeSbO_4$ with poor crystallinity was formed. The resulting material was then treated in two ways with the aim to increase its stability in water: (i) Hydrothermal treatment in water at pH 1, 200 °C for 12 h, and (ii) calcination at 950 °C for 12 h. The stability / leachability tests carried out pointed that pseudo-equilibrium was reached in ≈ 15 days. The hydrothermally treated precipitate showed higher stability (the lowest amount of released Sb ions in contact with water).

Based on the above presented studies it seems that the use of oxidizing reagents facilitates Sb recovery from the PLS by precipitation, but this requires (i) the implementation of enhanced work-place safety measures and (ii) the use of equipment with high corrosion resistance.

### *4.3. Methods based on oxidation-reduction processes*

Antimony ions present in PLS can be reduced to solid metal or compound and thus be recovered from the PLS. In the replacement and cementation process electrons are transferred from less noble metal to Sb ions. In the electrowinning process a rectifier is the electrons source.

#### *4.3.1. Replacement and Cementation*

Ye and coauthors [18] used an iron plate to replace $Sb^{3+}$ ions from PLS. The process generally is described by the reaction (38). A total of 96.86% of the Sb available in PLS was recovered in a two- stage process, and pure $FeCl_2$ solution was obtained that was further treated to produce $FeCl_3$ as leaching solution and Fe plate. The amount of Fe used was 1.2 times higher than the stoichiometrically needed because it was consumed to neutralize the acid to pH 0.8 that was more favorable for Sb recovery. The produced Sb powder morphology was represented by small and uniform particles and its purity reached 97.65 %.

Tian et al. used Fe powder as a reducing reagent to selectively recover Sb from chloride based PLS [44]. Both $Sb^{3+}$ ions and $Sb^{5+}$ ions (in two stages) can be reduced to solid metal. The processes are spontaneous as indicated by the changes in the Gibbs free energy.

$$3Fe^0 + 2SbCl_3 \rightarrow 3Fe^{2+} + 2Sb + 6Cl^-, \Delta G = -378.510\, kJ/mol \tag{38}$$

$$Fe^0 + SbCl_5 \rightarrow Fe^{2+} + SbCl_3 + 2Cl^-, \Delta G = -134.561\, kJ/mol \tag{39}$$

In the pH range of the PLS arsenic is present. Authors found that the processes of As species reduction by iron are also thermodynamically favorable:

$$3Fe^0 + 2HAsO_2 + 6H^+ \rightarrow 3Fe^{2+} + 2As^0 + 4H_2O, \Delta G = -379.497\, kJ/mol \tag{40}$$

$$5Fe^0 + 2H_3AsO_4 + 10H^+ \rightarrow 5Fe^{2+} + 2As^0 + 8H_2O, \Delta G = -758.786\, kJ/mol \tag{41}$$

It is established that the reduction efficiency of antimony raised with the raising iron dosage, stirring speed and time. At temperature over 65 °C antimony recovery efficiency was 99 % in 12 min, while under the same conditions the As recovery was only 12 %. At higher Fe dose, at 25 °C, antimony recovery of 99% was achieved, with less than 5.9% recovery of As. Antimony was recovered as metal with rhombohedral structure (card PDF#85-1323). It is found that antimony was extracted from the PLS prior to arsenic due to the difference in the reduction rate - that of antimony was higher than that of arsenic. In addition, it was proved that when nano iron powder was applied as the reductant the reduction process rate was higher compared to the case when iron powder with bigger particles was used.

In another approach Wu and coworkers recovered (in laboratory experiments) Sb from the hydrochloric acid based PLS by producing directly solid $Cu_2Sb$ which is one of the promising materials for preparing anodes for lithium and sodium ion batteries [45]. The authors pointed that in HCl solutions with different concentrations (3-7 mol/L) the calculated redox potential of $Cu^+/Cu$ couple is considerably more negative than that of the $Sb^{3+}/Sb$ redox couple. The potential difference of over 400 mV between these redox couples suggests that the reaction between antimony ions and copper powder (reaction 42) is thermodynamically favorable and cementation of antimony on copper is spontaneous process at room temperature.

$$SbCl_3 + 5Cu \rightarrow 3CuCl + Cu_2Sb \tag{42}$$

During reduction and cementation process stibine is not generated and the produced CuCl is used as catalyst for cellulose denitration and desulfurizing agent in the petrochemical industry.

#### *4.3.2. Electrowinning*

Antimony recovery from PLS by electrodepositing is widely used process. Antimony can be electrowon both from alkaline and acidic PLS

[1, 46].

#### 4.3.2.1. Electrowinning from alkaline PLS

The antimony electrodeposition as metal on the cathode from the alkaline-sulfide PLS is carried out more often in diaphragm cells. Antimony metal with purity over 99.5% can be obtained after washing [16].

In the primary cathode reaction antimony ions from $Na_3SbS_3$ obtained in alkaline sulfide leaching are reduced [1, 46]:

$$SbS_3^{3-} + 3e^- \rightarrow Sb^0 + 3S^{2-}, E = -0.900\, V_{SHE} \quad (43)$$

Eventually, available $SbS_4^{3-}$ ions may also be reduced [2]:

$$SbS_4^{3-} + 5e^- \rightarrow Sb^0 + 4S^{2-} \quad (44)$$

The undesired side reactions that can proceed on the cathode and decrease the current efficiency are [46]:

$$H_2O + e^- \rightarrow 0.5\, H_{2(g)} + OH^-, E = -0.828\, V \quad (45)$$

$$SbS_4^{3-} + 2e^- \rightarrow SbS_3^{3-} + S^{2-}, E = -0.660\, V_{SHE} \quad (46)$$

$$S_2O_3^{2-} + 2e^- \rightarrow S^{2-} + SO_3^{2-}, E = -0.631\, V_{SHE} \quad (47)$$

The formation of hydrogen gas in alkaline solutions can be inhibited when the Sb concentration in the solution is higher than 25 g/L [47].

Thiosulfate that presents in the solution facilitates oxidation of trivalent Sb to pentavalent Sb in solution [46]:

$$S_2O_3^{2-} + SbS_3^{3-} \rightarrow SbS_4^{3-} + SO_3^{2-} \quad (48)$$

The primary anode reactions proceeding in the PLS obtained by sulfide alkaline leaching are [1, 46]:

$$4OH^- \rightarrow 4e^- + 2H_2O + O_2, E = -0.401\, V \quad (49)$$

$$S^{2-} \rightarrow 2e^- + S^0, E = -0.476\, V \quad (50)$$

The oxygen gas evolution is the desired reaction because no oxidation of sulfur occurs.

The possible to proceed side reactions are described by equations (51) - (54) [47]:

$$2S^{2-} + 2O_2 + H_2O \rightarrow S_2O_3^{2-} + 2OH^- \quad (51)$$

$$S^{2-} + S^0 \rightarrow S_2^{2-} \quad (52)$$

Formed polysulphides are able to dissolve deposited antimony:

$$3S_2^{2-} + 2Sb^0 \rightarrow 2SbS_3^{3-} \quad (53)$$

or are oxidized and produce $S_2O_3^{2-}$ ions in the electrolyte:

$$\begin{aligned} &S_2^{2-} + 4OH^- \rightarrow S_2O_3^{2-} + 2H_2O + 4e^- \\ &E = -0.353\, V \end{aligned} \quad (54)$$

Further alkalizing the solution is proposed as one of the ways to suppress polysulfides and thiosulfate formation [47]:

$$\begin{aligned} &S^{2-} + 6OH^- \rightarrow SO_3^{2-} + 3H_2O + 6e^- \\ &E^0 = -0.598\, V \end{aligned} \quad (55)$$

$$\begin{aligned} &S^{2-} + 8OH^- \rightarrow SO_4^{2-} + 4H_2O + 8e^- \\ &E^0 = -0.679\, V \end{aligned} \quad (56)$$

$$2S^{2-} + 2O_2 + H_2O \rightarrow S_2O_3^{2-} + 2OH^- \quad (57)$$

$$\begin{aligned} &10OH^- + S_2O_3^{2-} \rightarrow 2SO_4^{2-} + 5H_2O + 8e^- \\ &E^0 = -0.799\, V \end{aligned} \quad (58)$$

$$\begin{aligned} &SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \\ &E^0 = -0.920\, V \end{aligned} \quad (59)$$

The overall reaction of Sb electrodepositing can be presented as [47]:

$$\begin{aligned} &8SbS_3^{3-} + 24OH^- \rightarrow 8Sb^0 + 21S^{2-} + \\ &+ 21S^{2-} + 3SO_4^{2-} + 12H_2O \end{aligned} \quad (60)$$

Reactions (55) - (59) are not thermodynamically favorable due to their low oxidation potentials. If they proceed, they can increase the efficiency of antimony electrodeposition. It is found that increasing the anodic current density over 1000 A/m$^2$ causes these reactions and decreases polysulfides formation thus increasing current efficiency with respect to Sb electro-deposition [47].

In order to avoid the negative effect of polysulfides and thiosulfate of the Sb deposition efficiency, the industry mainly uses diaphragm-cell electrolysis. In these electrolyzers the anolyte and catholyte are separated into different compartments by a diaphragm that hinders the sulfur species migration from the anode to the cathode surface. However, the high cost of diaphragm electrolysis cells and maintenance problems lead to focusing the research to non-diaphragm cell electrolysis.

Preventing the formation of polysulfides and thiosulfate hinders undesired antimony oxidation, and as a result Sb deposition efficiency is increased. In order to defeat these species formation, various salts were tested as precipitating reagents for the generation of metal sulphates and sulphites. The salts used in the experiments were $BaCl_2$, $CaCl_2$, $Ba(OH)_2$, $Ca(OH)_2$ [46]. A decrease in sulfate concentration by precipitation will cause the reaction (60) to proceed to the right, as stated by the Le Chatelier's principle.

The Taguchi experimental design was applied to study the the effects of different factors (Sb concentration, electrowinning time, temperature and amount of NaOH and $Na_2S$ in the PLS) on the Sb deposition. Minitab software was used [46]. The authors [46] found that current efficiency is higher when chlorides were used in comparison with the hydroxide compounds of the given metal. When chlorides are added to the solution with high pH value, metal hydroxides are precipitated, $Cl^-$ ions remain in the solution and their concentration increases in the solution. This creates an opportunity for another oxidation reaction to take place on the anode surface:

$$\begin{aligned} &Cl^-{}_{aq} + OH_{aq}{}^- \rightarrow OCl_{aq}{}^- + H_2O + 2e^- \\ &E^0 = -0.89\,V \end{aligned} \tag{61}$$

The formation of chlorine gas is avoided in the alkaline medium, so chloride ions indirectly contribute to the current efficiency increasing. Moreover, corrosion of the 316 stainless-steel electrodes (anode and the cathode) was not observed. Thus, the best results were obtained when $BaCl_2$ salt was used. The use of $BaCl_2$ salt increased the current efficiency by 31.1% and Sb deposition of 96.9% was achieved. The use of $BaCl_2$ salt as a useful additive in the antimony alkaline PLS for Sb electrowinning is proposed. The effect of $BaCl_2$ addition is more pronounced at higher concentrations of sulphur ions in the PLS. The Taguchi experimental design pointed the time as the most influential process parameter in terms of Sb deposition efficiency. It is found that the current efficiency decreased with time increasing. The optimal electrowinning temperature was 40 °C.

Another researcher also found that increasing the time (in the range of 1- 6 h) and temperature (in the range of 45-65 °C) leads to a decrease in the current efficiency of Sb electrowinning [48]. Per one kilogram of deposited antimony the energy consumed was from 1.35 at 45 °C to 2.28 kWh at 65 °C. At 45 °C the maximum energy efficiency was 70% after 6 h electrodeposition, while after one hour electrodeposition it was 90 %.

### *4.3.2.2. Electrowinning from acidic PLS*

Concerning the acidic PLS, the solubilized antimony can be electrodeposited on cathode in diaphragm cells. The process regenerates the lixiviant at the anode [16].

The main cathodic reaction is Sb deposition:

$$Sb^{3+} + 3e^- \rightarrow Sb \tag{62}$$

while the secondary reaction that proceeds is hydrogen evolution:

$$2H^+ + 2e^- \rightarrow H_2 \tag{63}$$

The main anodic reactions are:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{64}$$

$$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^- \tag{65}$$

Zhang et al. proposed using slurry electrolysis for extracting and recovery of Sb from high arsenic and gold-containing stibnite ore [7]. The slurry electrolysis combines leaching, partial solution purifying, and electrowinning. Sulfide ore is leached on the anode by oxidation and Sb is deposited on cathode. Electricity consumption is decreased and generation of $SO_2$ is prevented. The recovery of Sb metal on cathode was above 98% (with arsenic impurity less than or equal to 0.21%) under optimal conditions: 60 °C, 6 h, HCl - 30 g/L, Sb - 30 g/L and anodic current density of 80 $A/m^2$.

Recently Sajadi et al. compared Sb recovery by electrowinning from alkaline and acidic leaching solutions of low-grade antimony ore [49]. They investigated the applicability of different materials as cathode (silver, graphite and steel - the latter in three electrode system) and found that use of the double cathode made of steel ensured 20% higher current efficiency compared to single cathode. The electricity consumption per ton electrowon Sb was $8.577 \times 10^5$ Ah. The highest Sb electrowinning yield of 89% from acidic PLS was achieved at 30 °C and current density of 2.5 $mA/cm^2$. The highest Sb electrowinning yield of 97% from alkaline PLS was achieved at 80 °C and current density of 12.5 $mA/cm^2$. The study concluded that the alkaline process is preferable due to the high corrosion of electrodes used in the acidic system.

Antimony can also be recovered from chloride electrolytes which are a byproduct of the copper extraction process and can be used as a secondary source. Thanu et al. found that from such electrolyte (containing Sb, Bi, Cu and Fe, respectively - 4, 6, 1.5 and 0.1 g/L) Sb can be successfully recovered at ambient temperatures, potential of −0.5 V, current density of 5 $A/dm^2$ [50]. It is found that the deposition under galvanostatic conditions yielded higher recovery than under potentiostatic conditions.

However, Sb recovery under potentiostatic regime resulted in more uniform and compact deposits compared to those obtained under galvanostatic regime. The electrochemical metal recovery decreased with increasing the solution temperature.

Hernéndez-Pérez et al. also studied the process of Sb recovery from HCl-containing waste electrolyte from the copper electrorefining industry [21]. Experiments were conducted in both galvanostatic and potentiostatic modes. Under both regimes compact and adherent antimony deposits are produced at operating under lower current densities that minimize the hydrogen evolution. An increase in hydrochloric acid concentration was found to enhance e the antimony deposition of, although the high concentration of acid in the electrolyte usually facilitates proceeding of the side hydrogen evolution reaction. This finding implied that metallic Sb acts as an inhibitor of the hydrogen evolution. The study concluded that antimony deposition is a mass transfer-controlled process.

Considering the works described, it can be summarized that replacement and cementation may be used to recover Sb from acidic PLS. The electrowinning process is applicable both to acidic and alkaline PLS. Use of diaphragm cells is a technology widely employed in industry for Sb electrowinning from alkaline PLS. Scientific efforts focus on finding conditions for high recovery of Sb at high current efficiency without use of expensive diaphragm cells. Diaphragm cells are also used to recover Sb from acidic PLS. Here equipment corrosion is an additional task to be solved.

### *4.4. Liquid-liquid solvent extraction*

Liquid-liquid solvent extraction (SE) is a widely applied method for recovering metals from solutions, including from PLS [2]. It uses different organic compounds, dissolved in proper diluents, to form specific stable compounds with the metal that is extracted. However, with respect to Sb, SE is mainly applied to remove Sb from electrolytes from which other valuable metals (mainly copper) are electrowon or electro-refined. These electrolytes are actually secondary sources of antimony.

For example, $Sb^{3+}$ and $Bi^{3+}$ ions that present in acidic $HCl/H_2SO_4$ aqueous solutions of $Cu^{2+}$ were efficiently removed from the solution by using supported liquid membrane (a polyvinylidene fluoride microporous membrane impregnated with Cyanex 921) [51]. The extraction rate for Sb was 95.4%, the recovery rate at striping with 0.5% tartaric acid solution was near to 99%.

Artzer et al. studied the opportunity to use two types of phosphonic acid ester extractants (REX-1 and REX-2 - BASF Mining Chemicals) to remove antimony and bismuth from copper electrorefining electrolytes [52]. Different mixtures of the extractants, dissolved into Orfom SX-12 diluent, were investigated (100 wt.% REX-1, and 25 wt.%, 50 wt.%, 75 wt.% and 100 wt.% REX-2), at different aqueous to organic ratios. It is found that REX-2 is a better extractant than REX-1 for antimony and bismuth at A:O ratio = 1:1. The 100 wt.% REX-2 extractant extracted 85–95% of the Sb and 60–70% of the Bi from the electrolyte. A synergistic effect between REX-1 and REX-2 on extraction efficiency was not observed. The higher percentage REX-2 solutions showed the best extraction efficiency for Sb, but poor stripping efficiencies with 400 g/L $H_2SO_4$ solution. When the extraction and stripping data were combined, the overall removal efficiency was calculated. The investigators found that 25 wt.% REX-2 solution possessed the highest Sb overall removal efficiency due to its better stripping efficiency. A synergistic effect between REX-1 and REX-2 was found with respect to strippability. It is observed that while practically entirely extracting Sb from copper electrorefining electrolytes, the studied mixture extracts also Cu and As (generally < 10% from their initial amount in the electrolyte). However, because the amounts of these elements in the solutions are two orders of magnitude higher than Sb, the extracted amount of As and Cu are not insignificant. That is why organic scrubbing or other additional purification step will be necessary to remove Cu and As from the raffinate in order to obtain a saleable product bearing Sb and or Bi. Benabdallah et al. studied the recovery of Sb (1.9 g/L) and Bi (2.6 g/L) from HCl solution (180 g/L) produced during copper electro-refinery processes and contaminated with As (3.2 g/L) [20]. The extractant used was Cyanex 923 - liquid mixture of four trialkyl phosphine oxides with an average molecular weight of 348 g/mol, dissolved in kerosene (fraction 160–220 °C) and 1-decanol (10 %). The analysis performed with the Hydra/Medusa and PHREEQC code software showed that in the studied media $Sb^{3+}$ is present as a mixture of $SbCl_4^-$ and $SbCl_3$, $Bi^{3+}$ is mainly under the form of $BiCl_4^-$ and $As^{5+}$ is present as $H_3AsO_4$. The extraction of these three species from HCl solutions is described by the following reactions:

$$MCl_4^- + H^+ + mS_{org} \rightarrow MCl_4H \cdot mS_{org} \qquad (66)$$

where M = Sb and Bi

$$H_3AsO_4 + mS_{org} \rightarrow H_3AsO_4 \cdot mS_{org} \qquad (67)$$

The extraction efficiency (% E) was found by using equation (68):

$$\%E = \left[\left(c^0_{i,aq} - c_{i,aq}\right) / c^0_{i,aq}\right] \cdot 100 \qquad (68)$$

where $c^0_{i,aq}$ is the total initial concentration of the solute i in the aqueous phase (mol/L) and $c_{i,aq}$ is the total equilibrium concentration of the solute i in the aqueous phase (mol/L). The concentration of the solute i in the organic phase can be found from the solute mass balance and considering the aqueous to organic volume ratio ($V_{aq}/V_{org}$) by applying equations (69) and (70):

$$\left(c^0{}_{i,aq} - c_{i,aq}\right) \cdot V_{aq} = \left(c_{i,org} - c^0{}_{i,org}\right) \cdot V_{org} \tag{69}$$

$$c_{i,org} = \left(c^0{}_{i,aq} - c_{i,aq}\right) \cdot \left(V_{aq} / V_{org}\right) \tag{70}$$

where $c^0_{i,org}$ is the total initial concentration of the solute i in the organic phase (mol/L) and $c_{i,org}$ is the total equilibrium concentration of solute i in the organic phase (mol/L), $V_{aq}$ is the volume of the aqueous phase (L) and $V_{org}$ is the volume of the organic phase (L). The solute stripping percentage (% S) was found by using Eq. (71):

$$\%S = \left[\left(c_{i,org} - c^0{}_{i,org}\right) / c_{i,org}\right] \cdot 100 \tag{71}$$

The distribution coefficient ($D_i$) of solute i, which is representative for the solute i transfer from aqueous to organic phase, is given by:

$$D_i = \Sigma\left[i\right]_{org} / \Sigma\left[i\right]_{aq} \tag{72}$$

where $[i]_{org}$ is the total concentration of the solute i in the organic phase, (mol/L) and $[i]_{aq}$ is the total concentration of solute i in the aqueous phase (mol/L).

The authors found that Cyanex 923 dissolved in kerosene possessed capability to extract selectively $Sb^{3+}$ and $Bi^{3+}$ from HCl solutions containing As in elevated concentrations. Under optimal conditions (Cyanex 923 - 0.10 mol/L, A/O ratio of 1/3, 22 °C) a quasi-selective extraction of $Sb^{3+}$ and $Bi^{3+}$ can be achieved from real industrial solution - 78% Sb and 39% Bi were extracted at < 2.5% As extraction. Decreasing the Cyanex 923 concentration to 0.10 M (and using 3 extraction stages) increases selectivity with respect to Sb. Stripping with 8M $HNO_3$ ensures efficiencies of 95.6 ± 5.4% for $Sb^{3+}$ and of 87.2 ± 1.8% for $Bi^{3+}$.

Further, the authors proposed adding NaOH to recover oxides ($Sb_2O_3$(s) and $BiO_3$(s)) and /or oxychlorides (SbOCl(s) and BiOCl(s)). Adding a mixture of $FeSO_4$(s) and CaO(s) to the raffinate from extraction stabilizes arsenic as scorodite ($FeAsO_4 \cdot 2H_2O$(s)).

Based on the above-described work, it can be said that although successful results are achieved in applying SE to remove Sb from Cu electrorefining electrolytes, the method is understudied specifically for Sb recovery from solutions obtained by Sb raw materials leaching. However, experience gathered in developing the liquid-liquid extraction schemes for antimony recovery from electrorefining electrolytes can serve as a basis for developing SE technology for antimony gaining from PLS produced by leaching antimony ores.

### *4.5. Ion exchange*

In the ion-exchange (IX) process different types of resins are used to extract metal ions from solution. The use of the ion exchange method for extracting Sb from PLS solution is not widely applied or investigated [2]. Antimony extraction by IX from copper electrolyte, with the aim of purifying the electrolyte, is mainly described in the literature. These electrolytes can serve as secondary sources of antimony.

Arroyo-Torralvo et al. proposed the use of Lewatit MP TP-260 resins to remove of Sb (150 - 450 mg/L) and Bi (150 - 350 mg/L) impurities from the copper refinery electrolyte [53]. TP-260 is a weakly acid macroporous cation exchange resin containing chelating aminomethylphosphonic acid groups. The resin is selective with respect to Sb and Bi and the average (from 10 cycles) Sb retention is 70 %, while the average Bi retention is 90 %. A mixture of 6.7 M HCl and 1 g/L of thiourea was selected as the regenerating solution, since thiourea in concentrated HCl solution reduces $Sb^{5+}$ to $Sb^{3+}$, allowing for the conventional elution of $Sb^{3+}$ with HCl.

González de las Torres et al. also used Lewatit TP 260 ion exchange resin for selective removal of Sb and Bi from Cu electrolyte at both laboratory and industrial scale pilot plants [54]. They initially pretreated the electrolyte with copper shavings to promote the reduction of $Fe^{3+}$ to $Fe^{2+}$, thereby preventing potentional poisoning of the ion exchange resin with $Fe^{3+}$ ions. In the laboratory-scale pilot plant nearly 100% of $Sb^{3+}$ and 50% of $Sb^{5+}$ were successfully immobilized from the industrial copper electrolyte. The industrial pilot plant removed 50% of $Sb^{3+}$ and 36% of $Sb^{5+}$ resulting in the overall decrease by 45% of Sb concentration in the electrolyte.

Furthermore, Luo et al. used amino-phosphonic IX resin TP260 for selective elimination of Sb and Bi from copper electrorefining $H_2SO_4$ - based electrolyte [36, 37]. They found that $Sb^{3+}$ and $Bi^{3+}$ are present as $SbO^+$ and $BiO^+$ that can be selectively retained by the amino-phosphonic groups. Resin regeneration with 6M HCl generates eluate containing Sb, Bi (7–14 g/L each), as well as As (1–4 g/L). Other metal ions that present in the electrolyte (Cu, Zn, Al, Fe, Cd, Pb, Ni, Ca, and Sn) are not ion exchanged and present in the eluate at μg/L concentrations. Further, the eluate is treated with $SO_2$(g) or $NaHSO_3$ to reduce $As^{5+}$ and

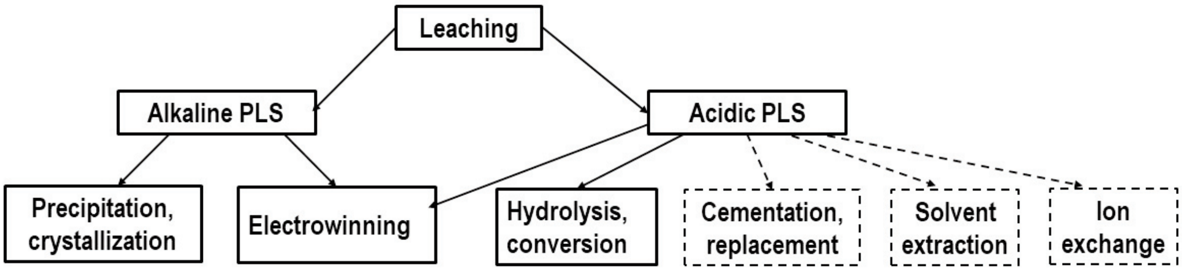

***Figure 4.*** *Technologies for Sb and Sb compounds recovery from PLS: solid lines – industrial level processes, dashed lines – laboratory level*

***Table 1.*** *Comparison of different methods applicable for Sb recovery from acidic and alkaline solutions*

| Method | Applicability | Recovery; (Product purity) | Readiness stage | Produced material |
|---|---|---|---|---|
| Hydrolysis and conversion by alkalization | From acidic - HCl based PLS | 97 – 99 %; (97 – 98 %) | Industrial use | $Sb_4O_5Cl_2$<br>$(0<pH<4)^a$<br>$Sb_2O_3$ (pH>4)<br>$Sb_2O_5^b$ |
| | Eluate from copper electrolyte purification | 96 – 97 %; (93-97.5) | Advanced laboratory for eluate | |
| Precipitation and crystallization | From alkaline - sulfide PLS | Precipitation 94-98 %; (95-98 %), Crystallization 71-76 %; (88-90 %) | Industrial use - from alkaline solutions | Precipitation -$NaSb(OH)_6$, $Na_3SbS_4(H_2O)_9$; crystallization - $(x–1)Na_3SbS_4$ |
| | From acidic PLS | 70-90 %; (60-80 %) | Laboratory scale | precipitation - $FeSbO_4$ |
| Replacement and cementation | From acidic - HCl based PLS | 97-99 %; (94.1-97.6%) | Laboratory scale | Sb metal powder or Sb metal on metal sheet |
| Electrowinning | From alkaline - sulfide based PLS | 98%; (99.5 % (after washing) | Industrial use | Sb metal |
| | From acidic - HCl based PLS | 87-89 %; (73-76 %) | Industrial use | Sb metal |
| | | [c]79.9 %;(>98%) | Laboratory scale | |
| Liquid-liquid solvent extraction | From acidic waste electrolytes generated in copper electrorefining | Extraction rate 80-95%; Stripping rate 95-99 %, both rates depend on the system, reagents, number of stages | Laboratory scale | $MCl_4H\cdot mS_{org}$, where Sorg = Cyanex 921, Cyanex 923, REX-1 and REX-2; After re-extraction - HCl-based solution containing $Sb^{3+}$ |
| Ion-exchange | From acidic waste electrolytes from copper electrorefining | 70-99% retention – lab scale | Laboratory scale | After elution - HCl-based solution containing $Sb^{3+}$ |
| | | 45 % retention – industrial pilot scale; Elution 83 – 98 % | Industrial pilot scale | |

Table 1 continues on the next page

Table 1 continues from the previous page

| Method | Environmental and safety considerations | Advantages | Disadvantages |
|---|---|---|---|
| Hydrolysis and conversion by alkalization | Eventual release of acidic wastewater containing heavy metals; Antimony containing sludge that needs handling; Fine antimony oxide particles emission during dehydration to produce $Sb_2O_3$. | Relatively easy to conduct process | Slow process, Need of strict control of pH of the PLS |
| Precipitation and crystallization | Eventual release of wastewater containing arsenic; Antimony containing sludge that needs handling; Fine antimony oxide particles emission during dehydration to $Sb_2O_3$ | Crystallization - easy to conduct process; shaped crystals | Crystallization - relatively slow process |
| | | Precipitation - fast and easy to conduct process | Precipitation - poor crystallinity |
| Replacement and cementation | Toxic residues generated (unreacted cementing reagents, metal oxides/hydroxides) that need handling, Expose of workers to Sb powder | Separation of Sb from As; easy to conduct process | Need to use over stoichiometric amount of reductants |
| Electrowinning | Spent electrolyte may carry Sb and heavy metals, anode slimes contain concentrated toxic compounds – both waste streams need further management; Inhalation of Sb dust during electrodes handling | Pure Sb - low amounts of impurities (As, Bi) (Addition of $BaCl_2$ to PLS increases current efficiency) | From alkaline: Electricity price, Problems with sodium polysulfides species formation |
| | | | From acidic: Electricity price; possibility for electrodes corrosion |
| Liquid-liquid solvent extraction | Spent solvents and raffinates will need further handling; Extractants and solvents used may be toxic | Fast process, efficient separation of Sb from Bi and As | Need of additional steps to recover Sb metal or Sb compounds |
| Ion-exchange | Spent resins and washing/regenerating solutions are loaded with Sb and other pollutants and need further handling; Water consumption for resins' washing | Fast process, efficient separation of Sb from Bi and As | Problems with elution; Need of additional steps to recover Sb metal or Sb compounds |

[a] Intermediate products detected in the corresponding pH intervals $Sb_8O_{10}(OH)_2Cl_2$ ($1<pH<4$) or $Sb_8O_{11}Cl_2$ ($2<pH<4$)

[b] From PLS obtained under highly oxidizable conditions; [c] Slurry electrolysis

$Sb^{5+}$ to $As^{3+}$ and $Sb^{3+}$ and high purity $Sb_4O_5Cl_2$(s) and BiOCl(s) are precipitated, as described above in section 4.1.

Moghimi et al. studied the ability of Purolite S957 (a weakly acidic cationic ion-exchange resin possessing $H^+$ ions in its structure) to retain $Sb^{3+}$ ions in the presence of $Fe^{2+}$ ions [55]. They established that the $Sb^{3+}$ adsorption mechanism comprises competition for adsorbent sites with $Fe^{2+}$ ions. Practically, no competition was observed with $Cu^{2+}$ ions despite their considerably higher concentration compared to other ions. The kinetic model best describing the $Sb^{3+}$ uptake was found to be the pseudo-first-order, pointing that mainly physical adsorption takes place. It is found that the $Sb^{3+}$ uptake increases with increasing the contact time until resin surface sites are saturated. The solution pH value has a noticeable effect, good results are obtained in the pH range 5 - 8 with the best results at pH around 8. Increasing the mass of resin in contact with the solution also effects positively the process, since more active sites are available. Under optimum conditions

88.8% extraction of Sb is achieved. Complete recovery of $Sb^{3+}$ was achieved under optimum conditions for resin elution - HCl - 7 M and 60 °C.

As with the SE, the application of IX for Sb recovery from solutions obtained by Sb raw materials leaching is understudied, despite good results in using IX for Sb removal from Cu electrorefining electrolytes. Nevertheless, knowledge gathered in developing the IX methods for antimony recovery from electrorefining electrolytes can help in developing IX technology for antimony recovery from PLS produced by leaching of antimony ores. Recovering antimony from process solutions with ion exchange resins is an attractive alternative method because it can be operated in a closed loop, generates little volatile emissions, and offers high selectivity when the right functional groups are chosen.

Figure 4 presents schematically the ways for Sb and Sb compounds recovery from PLS. Table 1 summarizes different methods that may be applied for Sb recovery from PLS, giving an opportunity to compare them.

## 5. Conclusions

Different methods have been proposed for the recovery of Sb from PLS.

Generally, the method proposed as the most feasible depends on the type of the PLS, Sb and other metals concentrations (especially those with similar to Sb properties) in the PLS, and the final product aimed.

Research continues to focus on increasing the Sb recovery efficiency, improving the quality of Sb recovered from the PLS, and adapting existing technological schemes for complex PLS containing Sb.

Electrowinning is frequently used in industry to recover Sb from alkaline-sulfide PLS. However, sodium polysulfides species generation decreases the process efficiency. Studies aimed at hindering these species creation and avoiding the use of more expensive diaphragm cells are carried out, with further research still needed. Electrowinning from acidic PLS in addition requires solving the problem with electrodes' corrosion.

Hydrolysis and conversion by alkalization, as well as crystallization are relatively slow processes and to obtain metal Sb further treatment is needed. Precipitation often results in poor crystallinity of the product obtained. Studies continue on those processes' optimization.

Liquid-liquid solvent extraction and ion exchange remain underused and understudied technologies for Sb-bearing PLS purification and Sb recovery from PLS. The application of extraction processes, especially using green solvents, may be suitable for PLS purification preceding the Sb electrowinning process. With respect to ion exchange, resins suitable to extract $Sb^{3+}$ and $Sb^{5+}$ from acidic waste electrolytes from copper electrorefining are available, but the problems with the quantitative elution of Sb species still remain unresolved. In addition, these waste electrolytes generally differ in composition from the PLS obtained by leaching Sb containing primary and secondary raw materials. Further research should focus on identifying suitable ion exchangers for Sb extraction from PLS. The identification and optimization of suitable green solvents, as well as the development of ion-exchange resins appropriate for Sb recovery from acidic and base PLS, obtained by direct leaching of Sb bearing solid materials, represent specific knowledge and development gaps that need further enhanced studies.

Upscaling the developed laboratory methods to industrial processes remains a general problem. In order to determine the most robust and flexible methods, further work on semi-pilot and pilot scale is necessary, taking into account the changing composition of PLS (depending on the solid raw material leached).

Additionally, to identify the most promising methods for industrial-scale Sb recovery from PLS without creating environmental problems, economic feasibility studies and life cycle assessments need to be conducted.

## Acknowledgements

*This work has been carried out in the framework of the National Science Program "Critical and strategic raw materials for a green transition and sustainable development", approved by the Resolution of the Council of Ministers № 508/18.07.2024 and funded by the Ministry of Education and Science (MES) of Bulgaria.*

## Author Contributions

*Conceptualization and original draft preparation M. P.; writing - review V. P. All authors have read and agreed to the published version of the manuscript.*

## Data availability

*Data sharing not applicable – no new data generated.*

## Declarations on conflict of interest

*The authors declare no conflict of interest.*

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# HIDROMETALURŠKO IZDVAJANJE ANTIMONA – FOKUS NA IZDVAJANJE IZ RASTVORA DOBIJENIH LUŽENJEM

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***Apstrakt***

*Antimon (Sb) je naveden kao kritična sirovina i u Evropi i u SAD-u. Za njegovo dobijanje iz sirovina koriste se pirometalurške i hidrometalurške metode. Hidrometalurgija se smatra pogodnom tehnologijom kada su izvori Sb rude niskog kvaliteta ili tehnogeni otpad. Nakon kratkog uvoda u vrste Sb prisutne u bogatim rastvorima dobijenim luženjem (PLS) uz korišćenje različitih reagensa za luženje, ovaj rad predstavlja različite metode za dobijanje Sb iz PLS-a proizvedenog u fazi hidrometalurškog luženja. Diskusija pokriva dobijanje antimona hidrolizom i konverzijom, selektivnim taloženjem, kristalizacijom, elektroekstrakcijom, zamenom, tečno-tečnom ekstrakcijom i jonskom izmenom. Predstavljeni su faktori koji utiču na efikasnost ovih procesa i nedavni pokušaji poboljšanja ovih tehnologija. Na kraju su naznačeni mogući budući pravci istraživanja.*

**Ključne reči:** *Dobijanje antimona; Elektroekstrakcija; Hidroliza i konverzija; Taloženje i kristalizacija; Tečno-tečna ekstrakcija; Jonska izmena*