

## Article

# Selective Removal of Arsenic and Antimony from Pb-Ag Sulfide Concentrates by Alkaline Leaching: Thermodynamic and Kinetic Studies

Walter Blanco-Vino <sup>1</sup>, Gerardo Zamora <sup>2</sup> and Javier I. Ordóñez <sup>1,\*</sup>

<sup>1</sup> Departamento de Ingeniería Química y Procesos de Minerales, Universidad de Antofagasta, Antofagasta 1271155, Chile; walter.blanco.vino@ua.cl

<sup>2</sup> Ingeniería Metalúrgica y Ciencia de los Materiales, Facultad Nacional de Ingeniería, Universidad Técnica de Oruro, Oruro 00591, Bolivia; gerardozamora@metalurgia.edu.bo

\* Correspondence: javier.ordonez@uantof.cl; Tel.: +56-552637507

**Abstract:** Arsenic and antimony are impurities that reduce the economic value of concentrates due to the environmental problems they cause. The removal of these impurities by hydrometallurgical means has been highly studied for sulfide copper concentrates using different leaching agents in an alkaline medium (NaClO, H<sub>2</sub>O<sub>2</sub>, NaOH, Na<sub>2</sub>S, NaHS, and S). For a lead–silver concentrate consisting of galena, sphalerite, and pyrite, it was possible to selectively reduce the arsenic content from 1.10% to 0.55% and antimony from 2.41 to 1.04% through the digestion-leaching technique that uses elemental sulfur as a leaching agent in alkaline medium. The adequate powdered sulfur and sodium hydroxide dosage were 336 and 342 kg/t, respectively. The process was carried out at 120 °C with a liquid/solid ratio of 2 in digestion and 5.67 in leaching; the appropriate digestion and leaching time were 20 and 30 min, respectively. The thermodynamics and kinetics of this process turned out to be very complex due to the great variety of simultaneous leaching and precipitation reactions. The digestion process exhibited a mixed kinetic control, where diffusion through the boundary layer and the chemical reaction were the controlling steps with an activation energy of 11.05 kcal/mol.

**Keywords:** lead–silver sulfide concentrate; arsenic; antimony; alkaline digestion–leaching; elemental sulfur



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## 1. Introduction

Arsenic (As) and antimony (Sb) are toxic and carcinogenic elements [1], which makes them harmful impurities for environments that are increasingly associated with sulfur concentrates. In conventional pyrometallurgical processes, these impurities volatilize, and gaseous discharges require high-cost treatment to comply with current environmental discharge regulations. Consequently, the problem begins when the presence of As and Sb in Bolivian lead (Pb)–silver (Ag) concentrates is increasingly recurrent and difficult to treat. It is possible to control the As and Sb content if these impurities are not closely associated with the element of economic interest in a mineralogical structure. However, if the Pb-Ag concentrate contains considerable amounts of jamesonite (Pb<sub>4</sub>FeSbS<sub>14</sub>) and geochronite (Pb<sub>5</sub>SbAsS), among other Pb-Sb-As complex minerals, it is not possible to control or reduce these impurities by flotation.

From an environmental point of view, in the pyrometallurgical processing of sulfide minerals, As and several of its compounds are highly volatile [1], the same for Sb and its compounds, mainly Sb<sub>2</sub>O<sub>3</sub>. This requires an expensive and very efficient gas-cleaning system. To minimize As and Sb contamination problems, the arsenic content in copper concentrates should generally be reduced to levels below 0.5% [1–3]. In the case of Pb concentrates, the maximum limits for As and Sb are <0.3% [4].

Various alternatives have been explored to remove arsenic and antimony from various materials containing them selectively. On the one hand, the use of the flotation process

for depressing arsenic species from chalcopyrite concentrates obtained an As reduction from 63 to 11%, using the oxidation of arsenopyrite with calcium hypochlorite and sodium humate [5]. The flotation processing is effective when the species are released and exposed to the environment through small particles. On the other hand, under a hydrometallurgical approach, the selective leaching of As and Sb oxidized compounds through using sodium hydroxide, present in copper anode sludge, has proven to be very efficient [6]. However, the reactions are more complex when As and Sb are found as sulfides. In the case of stibnite ( $\text{Sb}_2\text{S}_3$ ) leaching with NaOH, the reaction products are several soluble thioantimonites [2].

Another alternative for the hydrometallurgical treatment of copper concentrates with high As content is by using sodium hypochlorite [1,7,8]. These studies have shown that an oxidizing agent such as the hypochlorite ion allows the oxidation of the mineral containing As, forming soluble salts such as  $\text{Na}_3\text{AsO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and NaCl.

Another study demonstrated that the use of hydrogen peroxide is also presented as an alternative for the removal of As, Mo, and Zn from copper concentrates made up of chalcopyrite, tennantite, and molybdenite [9], eliminating more than 95% of Mo, 94% of As, and 94% of Zn under optimal conditions, dissolving only 1.7% of Cu. In the same way, hydrogen peroxide removed Bi efficiently in the flotation of a Mo-Bi-containing ore when it was used as a bismuthinite depressant in flotation, decreasing the levels from 50.1 to 4.6% in the product [10].

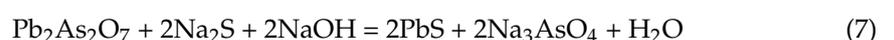
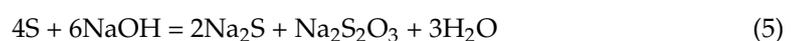
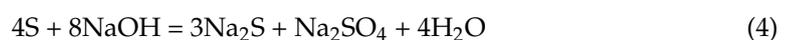
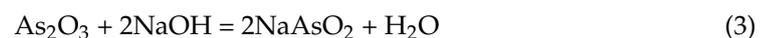
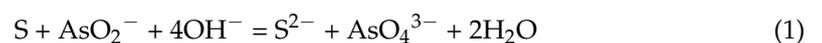
In the case of As leaching from Pb-Zn smelting ashes, where As is found as  $\text{As}_2\text{O}_3$  [11], As could be leached in more than 98%; however, Sb could not be leached due to the formation of  $\text{Na}_4\text{Sb}(\text{OH})_6$  that becomes insoluble under the conditions under which the process was carried out.

Predominantly the systems that include the sulfide ion in an alkaline medium are the most studied arsenic removal techniques, using sodium sulfide ( $\text{Na}_2\text{S}$ ) as a leaching agent [12,13], where the complex minerals containing these impurities can be leached due to the formation of soluble thiosals  $\text{Na}_3\text{AsS}_4$ ,  $\text{NaSbS}_2$ , and  $\text{Na}_3\text{SbS}_3$ .

Alternatively, sodium hydrosulfide ( $\text{NaHS}$ ) was also used as a leaching agent, mainly due to the highly reducing environment generated and with which the hydrolysis of the sulfur ions could be avoided [3,14]. This process allows the elimination of more than 90% of As by the formation of the soluble thiosal  $\text{Na}_3\text{AsS}_4$ .

Sulfur is a preferred leaching agent for As and Sb impurities due to its ability to improve solubility in a sulfurized medium. When sulfur is dissolved in a sodium hydroxide solution, the resulting  $\text{Sx}^{2-}$  polysulfides play a crucial role in the redox reactions of elemental sulfur. These inorganic polysulfides are ionic substances that contain di-anions in chain form  $\text{Sx}^{2-}$  [15], formed by the reaction between sulfur and the sulfide ion. The leachant used for leaching As and Sb typically involves dissolving elemental sulfur in a sodium hydroxide solution, resulting in a mixed solution of sodium sulfide, sodium thiosulfate, and sodium polysulfides [12,16].

Sulfur in sodium hydroxide can interact with a mineral complex of lead and arsenic to solubilize arsenic and precipitate lead; these reactions are shown in [17] with the following reactions:



To favor the kinetics of the formation of As and Sb soluble salts, a technique called “alkaline digestion” is used and described. Alkaline digestion is carried out by forming a pulp with a higher concentration of solids than conventional leaching to have a highly concentrated solution [18]. This technique allows the rapid formation of As and Sb thiosalts, followed by the dissolution of the salts formed by adding water to the concentrated pulp. Other leaching alternatives in an acid medium, using pressurized oxygen, ferric sulfate, or nitric acid, have also been effective for removing As from refractory gold concentrates [19].

The most convenient As and Sb removal alternative for a concentrate depends on its selectivity with metals of economic interest. In terms of toxicity, it should be considered that arsenic compounds have different levels and follow the following order (from highest to lowest): arsines > inorganic arsenites > trivalent organic compounds (arsenoxides) > inorganic arsenates > organic pentavalent compounds > arsonium compounds ( $\text{AsH}_4^+$ ) > elemental arsenic. As(III) compounds are almost 70 times greater than the organic forms of As and 10 times greater than that of As(V). Arsenite is more soluble, mobile, and more toxic than arsenate compounds [20].

This article delves into the hydrometallurgical alternatives for the elimination of arsenic (As) and antimony (Sb) from a lead–silver (Pb–Ag) concentrate. The research is novel since other available studies have addressed the treatment of sulfide copper concentrates with dissimilar mineralogy, and therefore, chemical interaction levels among valuable species and leachants are not extrapolable. The primary focus is on analyzing the selectivity of different leaching alternatives and presenting the most suitable option for the As and Sb removal, ensuring that the content of Pb and Ag remains steady. Additionally, a detailed interpretation of the thermodynamic and kinetic aspects of this alternative is proposed. The findings of the study are expected to promote the development of more efficient hydrometallurgical processes for the extraction of valuable minerals from sulfide concentrate ores.

## 2. Materials and Methods

### 2.1. Sulfurous Pb–Ag Concentrate

The research was carried out using a Pb–Ag concentrate obtained from an actual metallurgical operation in Oruro, Bolivia, which beneficiates sulfide ores. The As and Sb levels in the concentrate were higher than the permissible limits for its commercialization, i.e., <0.5%. This concentrate was dried in an oven at 105 °C for 24 h and subsequently characterized physically, chemically, and mineralogically. The concentrate exhibited a specific weight of 4903 g/cm<sup>3</sup> and a D<sub>80</sub> of 128 μm. The chemical composition of the concentrate is shown in Table 1.

**Table 1.** Chemical composition of concentrate. Concentrations in %.

Pb	S	Ag	Fe	SiO <sub>2</sub>	Zn	Sb	Sn	As	Bi
41.4	18.93	0.32	6.98	8.94	7.65	2.48	1.29	1.15	0.02

A mineralogical analysis by X-ray diffraction (Figure 1) determined that the mineralogical matrix is mainly composed of galena, blende, pyrite, and quartz.

### 2.2. Hydrometallurgical Treatment of Concentrate

The study on the hydrometallurgical treatment of the Pb–Ag concentrate was performed in two phases. In the first, exploratory trials were conducted with the objective to choose the best leachant. Subsequently, and considering the results of the first step, the analysis was focused on the effect of several variables on impurities dissolution. In both stages, leaching tests were performed in a 1 L glass reactor agitated magnetically at 300 rpm (Figure 2). The temperature was monitored continuously. After leaching, the residues were washed with distilled water and analyzed by X-ray fluorescence (XRF) to compare the effect of the different leaching systems.

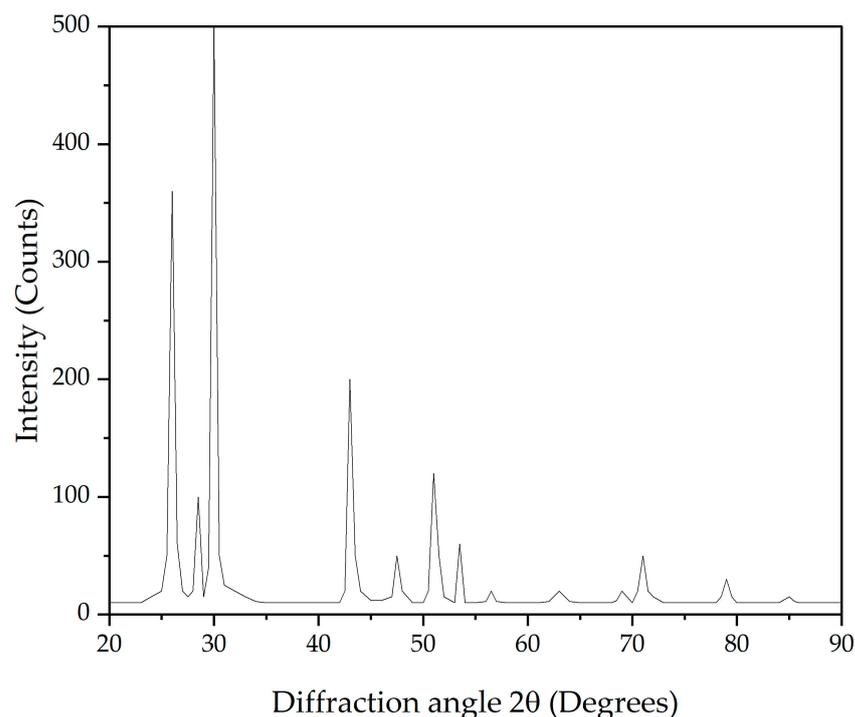


Figure 1. XRD spectrum of Pb-Ag concentrate.

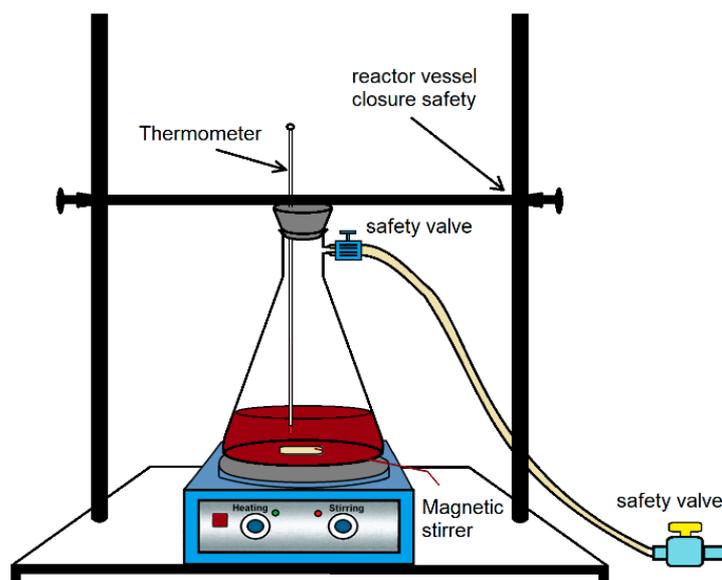


Figure 2. Scheme of the experimental equipment for the leaching of As and Sb from a Pb-Ag sulfur concentrate.

### 2.2.1. Exploratory Tests of Leaching Agents

To explore different alternatives for removing As and Sb from the concentrate, the conducted leaching experiments considered the stages of digestion (curing) and leaching using four different leachants:  $\text{NaClO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{S}$ , and S. The working conditions in these experimental tests were based on the information available in the literature and stoichiometry. In these tests, leaching was carried out at an S/L ratio of 15% and in the digestion stage 33.3%. The digestion and leaching conditions are listed in Table 2. The digestion was a pretreatment that was performed in several experiments in order to evaluate the contribution of a previous curing stage to improve the leaching performance.

In those experiments, the digestion time was 0.33 h, followed by the leaching stage of 1 h. In the non-digested experiments, the leaching time was 4 h.

**Table 2.** Experimental set of exploratory Pb-Ag sulfide concentrate leaching. S/L equals to 15%.

Test	Leachant	Leachant Dosage (kg/t Concentrate)	NaOH Dosage (kg/t Concentrate)	Temperature (°C)	Digestion Time (h)	Leaching Time (h)
1	NaClO	1.42	137	60	0	4
2	NaClO	1.42	7 mL H <sub>2</sub> SO <sub>4</sub> /100 g	60	0	4
3	H <sub>2</sub> O <sub>2</sub>	1.44	137	60	0	4
4	Na <sub>2</sub> S	505	137	90	0	4
5	Na <sub>2</sub> S	505	137	90	0.33	1
6	S (solution)	112	228	120	0	4
7	S (solution)	224	228	120	0	4
8	S (solution)	224	228	120	0.33	1
9	S (solid)	224	228	120	0	4
10	S (solid)	224	228	120	0.33	1

The thermodynamic interpretation of the processes studied in this article was based on thermodynamic data available in the HSC v6.0 software (Metso, Helsinki, Finland). The possible reactions of the concentrate components and the aqueous phase were studied based on their chemistry and Eh-pH diagrams reported in the literature.

### 2.2.2. Study of Leaching Operating Conditions

The study of the digestion–leaching technique was carried out, taking into account the leachant that obtained the best results in the preliminary tests. For that, the temperature, S and NaOH dosages, and S/L ratio were evaluated to study, in a deeper way, the leaching treatment of Pb-Ag concentrates (Table 3). Powdered sulfur (industrial grade > 95%) and NaOH (Merck, Rahway, NJ, USA) were directly added to the concentrate in a 1 L vessel (Figure 2) that contained 200 mL of water. The S/L ratio in the digestion stage was constant at 33.3% and lasted 20 min, and leaching time was kept in 60 min.

**Table 3.** Leaching variables studied.

Test	Levels			
Temperature (°C)	90	105	120	
S dosage (kg/t)	112	224	336	
NaOH dosage (kg/t)	114	228	342	456
S/L ratio (%)	10	15	20	

The temperature range for leaching was tested between 90 °C and 120 °C. Below 90 °C, the dissolution of S, the chosen leachant, was difficult. Similarly, values above 120 °C were discarded due to the complexity of managing the pressure generated in a closed leaching system. To ensure adequate reagent consumption and avoid the generation of insoluble complexes at higher concentrations due to reactions with other mineral species (such as iron), the ranges of S and OH tested were carefully considered. In terms of the S/L ratio, minimum values less than 10% were not tested because it may have wasted lixiviant, which is not economically feasible. On the other hand, higher S/L ratios cause a decrease in the quality of agitation due to an increase in suspended solids. The experiments considered a range between 10 and 20%, which was related to the standards for leaching that have a range of 5–50% [21].

After leaching, the solution was hot-filtered. The residue was immediately washed with distilled water and dried. The solution and residue were chemically analyzed by atomic absorption spectroscopy (AAS) to determine the As, Sb, Pb, and Ag content.

Knowing the most suitable conditions for temperature and sulfur and sodium hydroxide dosages, the effect of time in the leaching stage was initially studied at 30, 60, and 120 min, maintaining a digestion time of 20 min. In the other set, the digestion time was varied between 10 and 80 min, maintaining the leaching time of 60 min, with the purpose of evaluating the sensitivity of time in both processes.

### 2.2.3. Kinetic Leaching Study

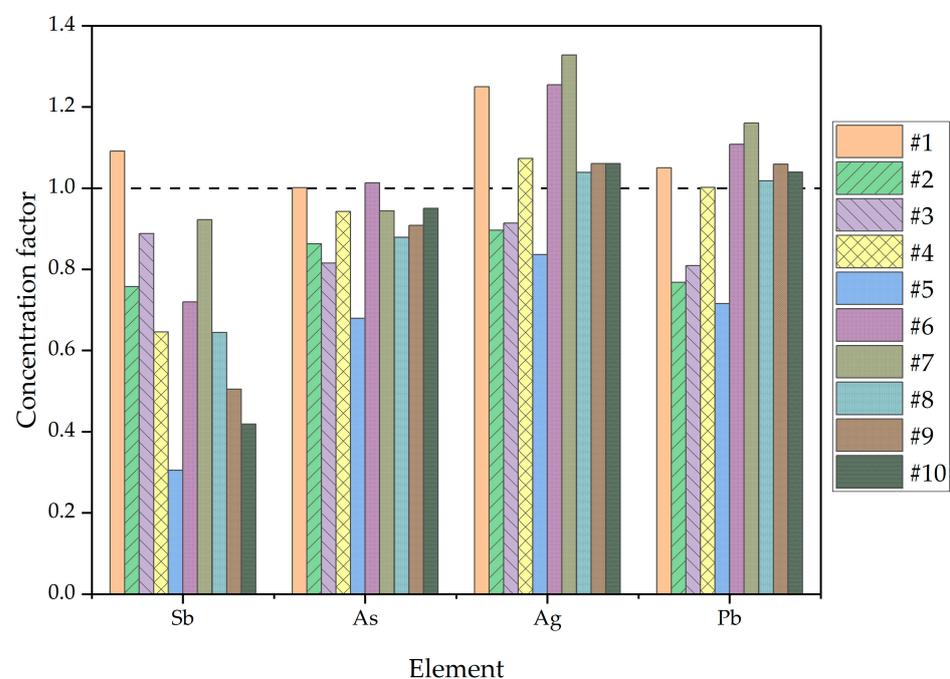
The third stage analyzed the kinetics of digestion at different temperatures, 90, 105, and 120 °C, to evaluate the effect of temperature and determine the activation energy. After each experiment, the mixture was filtered, and the residue and solution were analyzed chemically by AAS. The reacted fraction of As and Sb was correlated with chemical kinetic models to determine the controlling stage.

After identifying the most appropriate model, the activation energy ( $E_a$ ) was determined under the Arrhenius expression by correlating the experimental data. Knowing the  $E_a$  provides a better understanding of how temperature affects the removal of As and Sb and serves as a foundation for optimizing cleaning valuable concentrates.

## 3. Results and Discussion

### 3.1. Exploration of Alternatives for the Removal of As and Sb

Numerous studies have revealed encouraging results regarding As and Sb removal from different materials. However, it is important to note that not all these alternatives are suitable for a Pb-Ag concentrate. Figure 3 shows the screening results of the different options evaluated in this work with various leaching systems. The impact of these alternatives on As and Sb removal is specifically addressed while ensuring that they do not compromise Pb and silver Ag contents to preserve the economic value of the concentrate. The concentration factor was calculated as the ratio between grades in the resulting concentrate and the grades in the feed.



**Figure 3.** Behavior of As, Sb, Ag, and Pb leaching under different agents regarding concentration factor (grade in the remaining solid/grade in the feed). Number of runs are listed in Table 2, and grades are quantified by XRF.

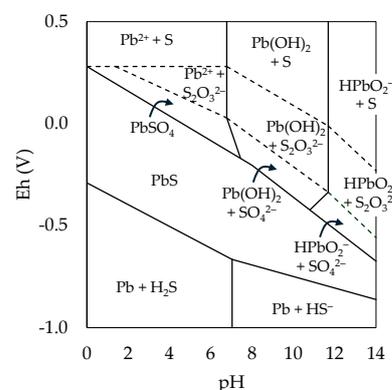
It was found that the use of sodium hypochlorite to eliminate As and Sb in either an alkaline or acidic environment did not result in the desired levels of less than 0.5%.

As per Tables S1–S3, the reactions between the hypochlorite ion and the sulfides of Pb and Ag are thermodynamically possible and hence inevitable. An increase in the As and Sb content was observed in alkaline environments. An increase in the content of Pb and Ag was attributable to various leaching and precipitation reactions between ions and the mineralogical phases of the concentrate. Some insoluble salts that could be formed include  $\text{NaSb(OH)}_6$ ,  $\text{FeAsO}_4$ , and  $\text{Ag}_3\text{AsO}_4$  (Table S2), where the As-Fe precipitate formation reactions are the ones that have the most negative Gibbs free energies, indicating that they are the ones that occur thermodynamically with the most spontaneity.

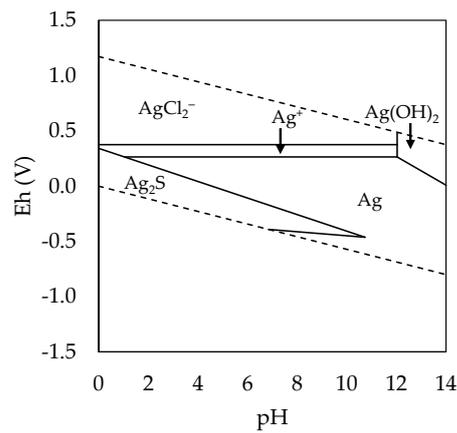
On the other hand, in an acidic environment, a reduction in the contents of As and Sb was achieved, but this also led to a decrease in the content of Pb, which was due to leaching reactions due to the oxidation of its minerals and the formation of different soluble complexes like  $\text{HPbO}_2^-$ ,  $\text{PbCl}_3^-$ ,  $\text{AgO}^-$ , and  $\text{AgCl}_2^-$  (Table S3). Consequently, the use of sodium hypochlorite for the selective removal of As and Sb from Pb-Ag concentrates was discarded for subsequent tests.

According to the data, the use of hydrogen peroxide resulted in a small reduction in the As and Sb content in the concentrate. However, the grades of Ag and Pb also decreased due to the oxidation of Pb and Ag sulfides, which led to the formation of soluble hydroxylated complexes,  $\text{HPbO}_2^-$  and  $\text{AgO}^-$ . Therefore, hydrogen peroxide is not recommended for the treatment of Pb-Ag concentrates with the aim of removing As and Sb. It was observed that the presence of pyrite is significant in the removal of As and Sb as it tends to form  $\text{FeAsO}_4$  thermodynamically. Moreover, the presence of silver can generate  $\text{Ag}_3\text{AsO}_4$  precipitates, which would limit the effective removal of As and Sb from a Pb-Ag sulfur concentrate, as shown in Table S4. The presence of sulfide ions prevents the formation of hydroxylated complexes of Pb and Ag that can form when oxidizing sulfides (Table S5). Additionally, the formation of soluble thiols of As and Sb can be favored, according to results found by other researchers.

Figure 3 shows that As and Sb are not removed from the concentrate when using sodium sulfide in the presence of sodium hydroxide in a direct leach. However, when the process is modified to digestion–leaching, the kinetics are favored, improving the removal of As and Sb, but the leaching of Pb and Ag is also favored, according to Figure 4. This could be because by decreasing the volume of the solution and maintaining the dosage of sodium hydroxide so that it is constant, the formation of hydroxylated complexes is favored and the amount of sulfide ions is preferentially consumed by As and Sb, leading to the leaching of Pb and Ag by the oxydryl ions. The high concentration of  $\text{OH}^-$  ions in the concentrated pulp and the sulfide consumption, preferably by As and Sb, leads to the formation of soluble Pb and Ag species, according to the Eh-pH diagrams (Figures 4 and 5).



**Figure 4.** Eh-pH diagram for the Pb-S-O-H system shows the regions of stability (solid lines) and metastability (dashed lines) for galena. The equilibrium lines correspond to the dissolved lead species where  $[\text{Pb}] = 10^{-3}$  M. Adapted from Marsden and House (2006) [22].

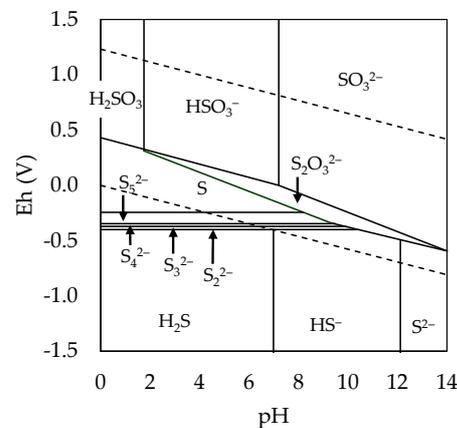


**Figure 5.** Eh-pH diagram for part of the Ag-Cl-S-O-H system at 25 °C and 1 bar. The activities assumed for the dissolved species are  $Ag = 10^{-8}$ ,  $S = 10^{-3}$ , and  $Cl = 10^{-3.5}$ . Dashed lines delimit the water stability region. Adapted from Brookins (1988) [23].

When sulfur is mixed with sodium hydroxide, various aqueous species can be formed. Table 4 illustrates the spontaneity of the formation of polysulfides ( $S_x^{2-}$ ), sulfates ( $SO_4^{2-}$ ), and thiosulfates ( $S_2O_3^{2-}$ ). Among them, the pentasulfide ( $S_5^{2-}$ ) is the most stable species thermodynamically. It has the most negative formation energy and a larger stability area in the Eh-pH diagram of Figure 6 compared to the other polysulfides. The presence of thiosulfate ( $S_2O_3^{2-}$ ) is also significant since it has ligand properties and can form complexes with metal ions and maintain them in the aqueous phase. However, the stability of polysulfides is quite low because they occupy a small area in the Eh-pH diagram. This indirectly indicates their high reactivity as they are unstable.

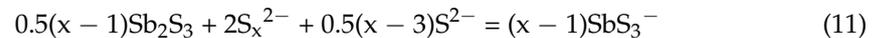
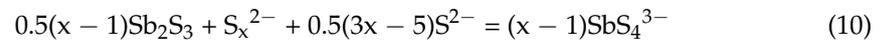
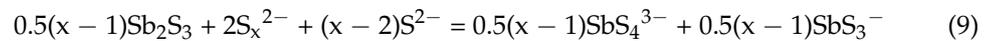
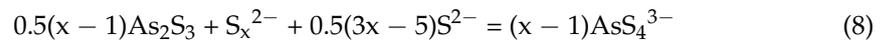
**Table 4.** Polysulfide standard Gibbs free energy of formation reactions.

Reaction	$\Delta G^0$ , kcal/mol			
	25 °C	90 °C	105 °C	120 °C
$8S + 14OH^- = 5S^{2-} + SO_4^{2-} + S_2O_3^{2-} + 7H_2O$	-69.582	-76.700	-78.462	-80.213
$13S + 14OH^- = 5S_2^{2-} + SO_4^{2-} + S_2O_3^{2-} + 7H_2O$	-77.045	-84.937	-86.071	-87.720
$18S + 14OH^- = 5S_3^{2-} + SO_4^{2-} + S_2O_3^{2-} + 7H_2O$	-84.036	-91.806	-93.615	-95.325
$23S + 14OH^- = 5S_4^{2-} + SO_4^{2-} + S_2O_3^{2-} + 7H_2O$	-89.377	-97.574	-99.469	-101.234
$28S + 14OH^- = 5S_5^{2-} + SO_4^{2-} + S_2O_3^{2-} + 7H_2O$	-93.218	-101.839	-103.820	-105.637
$33S + 14OH^- = 5S_6^{2-} + SO_4^{2-} + S_2O_3^{2-} + 7H_2O$	-93.186	-89.849	-88.795	-87.452

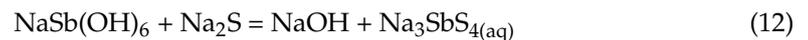


**Figure 6.** Eh-pH diagram for metastable sulfur. Dashed lines denote the thermodynamically stable region of water. Adapted from Anderson and Twidwell (2008) [24].

$\text{As}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_3$  are soluble in alkali polysulfides [25]. The dissolution reactions caused by the polysulfides formed from the dosed sulfur can be described by Equations (8)–(11).



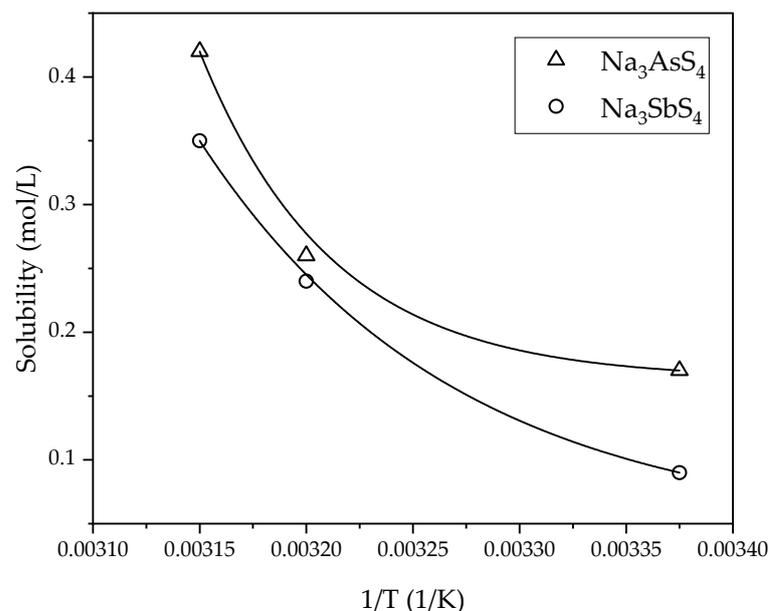
Sb in oxidizing and alkaline environments can form the insoluble salt  $\text{NaSb(OH)}_6$  [11]; however, it is soluble in solutions containing sulfide, according to Equation (12).



Experimentally, the use of elemental sulfur manages to remove mainly Sb from the Pb-Ag concentrate, while As cannot be removed to low values, and this is attributed to the fact that arsenic is capable of forming insoluble salts with iron and silver. Sulfur reacts with As and Sb to form the thiosalts  $\text{AsS}_4^{3-}$  and  $\text{SbS}_4^{3-}$ , which would cause the reduction in sulfur in the concentrate. Doubling the sulfur dosage did not improve the removal of As and Sb. However, it is better to dose it directly, and it would not be necessary to prepare the polysulfide solution previously; this mainly favors the removal of antimony.

### 3.2. Effect of Variables in the Sulfur Digestion–Leaching Technique for Eliminating As and Sb from a Pb-Ag Concentrate

The best alternative for the selective removal of As and Sb from Pb-Ag sulfide concentrates is the digestion process, followed by a leaching step with water, using powdered sulfur dosed directly to a concentrated pulp in an alkaline medium. This process must take place at high temperatures so that the sulfur melts and thermodynamically favors the formation of polysulfides (Table 4) and favors the solubility of the thiosalts formed, as seen in Figure 7.



**Figure 7.** Solubility of  $\text{Na}_3\text{SbS}_4$  and  $\text{Na}_3\text{AsS}_4$  in sulfide solutions. Adapted from Nadkarni and Kusik (1988) [26].

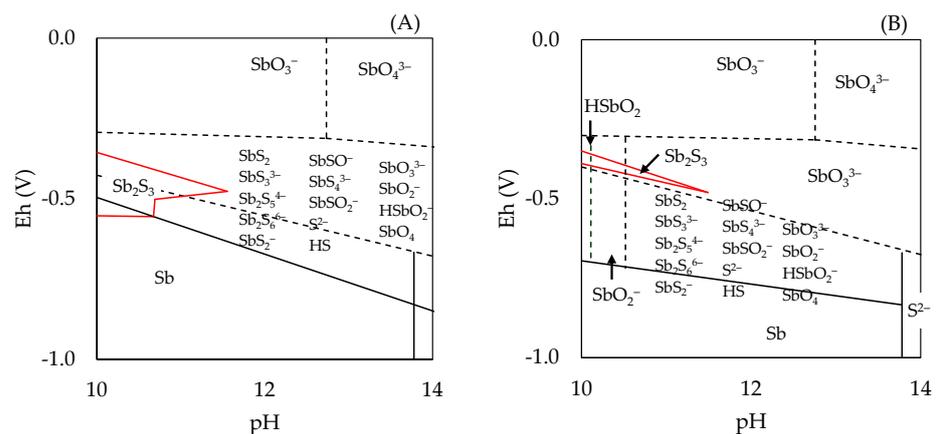
Below, the effect of the variation in temperature, the dosed amount of sulfur and sodium hydroxide, and the solid/liquid ratio on the removal of As and Sb from a Pb-Ag concentrate is shown.

The impact of sulfur addition on pulp has been carefully examined at a NaOH dosage of 228 kg/t and temperatures of 90 and 120 °C. The findings indicate that increasing the amount of sulfur added has a slight effect on the removal of As and Sb, with only 52.79% and 56.67%, respectively, being eliminated at 120 °C and 224 kg S/t. However, a higher quantity of sulfur addition results in a reduction in the grades of Pb and Ag. This could be attributed to the generation of sulfate and thiosulfate ions during the formation of polysulfides (as shown in Table 4). The thiosulfate ions may form highly soluble and stable complexes, as indicated in Table 5.

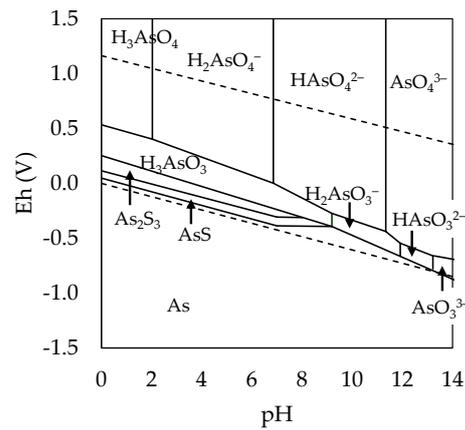
**Table 5.** Thermodynamic data of thiosulfate complex formation at 25 °C. Based on [25,27,28].

Reaction	log K	$\Delta G^0_{298^\circ K}$ , kcal/mol
$Ag^+ + S_2O_3^{2-} = Ag(S_2O_3)^-$	9.2	-12.550
$Ag^+ + 2S_2O_3^{2-} = Ag(S_2O_3)_2^{3-}$	12.5	-17.051
$Ag^+ + 3S_2O_3^{2-} = Ag(S_2O_3)_3^{5-}$	14.4	-19.643
$2Ag^+ + 3S_2O_3^{2-} = Ag_2(S_2O_3)_3^{4-}$	12.8	-17.461
$2Ag^+ + 4S_2O_3^{2-} = Ag_2(S_2O_3)_4^{6-}$	26.3	-35.876
$3Ag^+ + 5S_2O_3^{2-} = Ag_3(S_2O_3)_5^{7-}$	39.8	-54.291
$6Ag^+ + 8S_2O_3^{2-} = Ag_6(S_2O_3)_8^{10-}$	78.6	-107.219
$Pb^{2+} + S_2O_3^{2-} = PbS_2O_3(aq)$	2.42	-3.301
$Pb^{2+} + 2S_2O_3^{2-} = Pb(S_2O_3)_2^{2-}$	4.86	-6.630
$Pb^{2+} + 3S_2O_3^{2-} = Pb(S_2O_3)_3^{4-}$	6.2	-8.457
$Pb^{2+} + 4S_2O_3^{2-} = Pb(S_2O_3)_4^{6-}$	6.2	-8.457

The positive effect on removing antimony when dosing a greater amount of sulfur is notable. This can be attributed to the fact that an increase in the amount of sulfur in the system decreases the stability area of  $Sb_2S_3$  and favors the stability of the thiosals according to Figure 8. In the case of arsenic, although soluble thiosals are formed, arsenates are also formed, according to Figure 9, which can react with other metals and form precipitates such as  $FeAsO_4$  and  $Ag_3AsO_4$ .

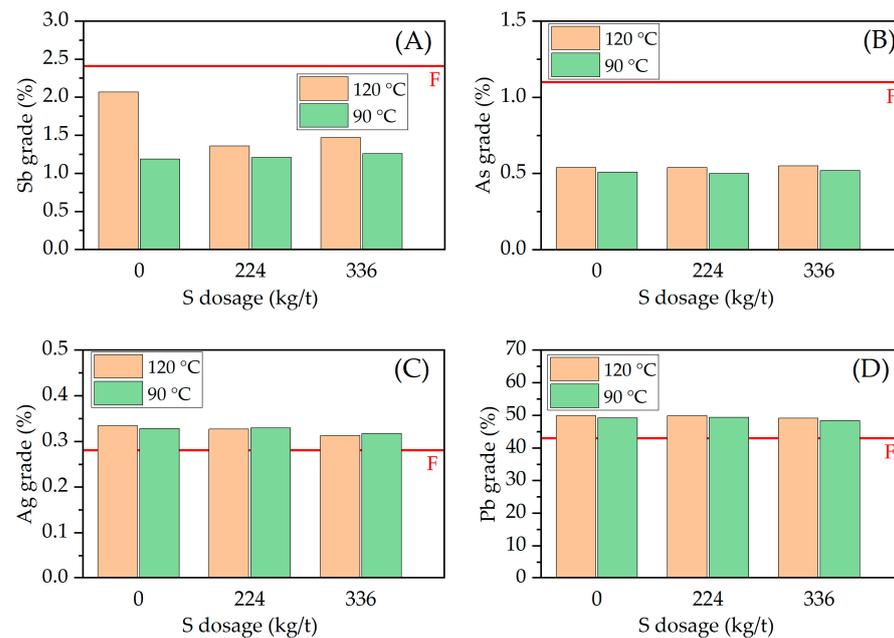


**Figure 8.** Eh-pH diagrams at 25 °C for the Sb-S-H<sub>2</sub>O system. (A)  $Sb_T = 1$  mol,  $S_T = 2$  mol. (B)  $Sb_T = 1$  mol,  $S_T = 3$  mol. Red lines denote the stability region of antimony trisulfide, which decreases as reducing S. Dashed lines denote stable regions of Sb species. Adapted and simplified from Tian-Cong (1988) [29].



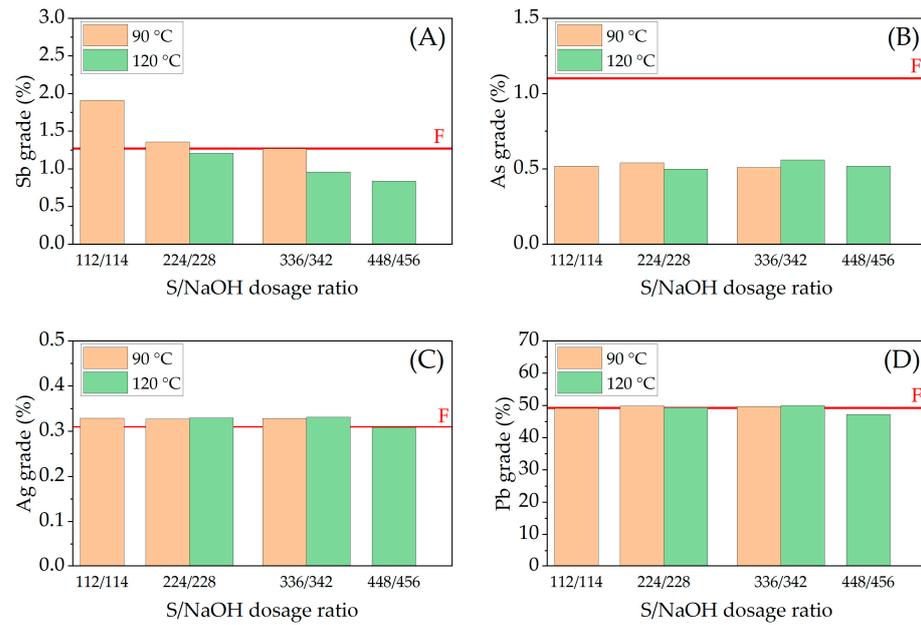
**Figure 9.** Eh-pH diagram at 25 °C for the As-S-O-H system. The concentration for the dissolved As species is  $10^{-4}$  M. Dashed lines correspond to water stability. Adapted from Marsden and House (2006) [22].

An increase in temperature favors the process mainly for two reasons: (1) temperature thermodynamically favors the formation of polysulfides, which form soluble species of As and Sb, and (2) the increase in temperature favors the solubility of the thiosals formed. Figure 10 also shows that an increase in the addition of sulfur does not positively affect the removal of As and Sb and does not favor the selectivity of the process.



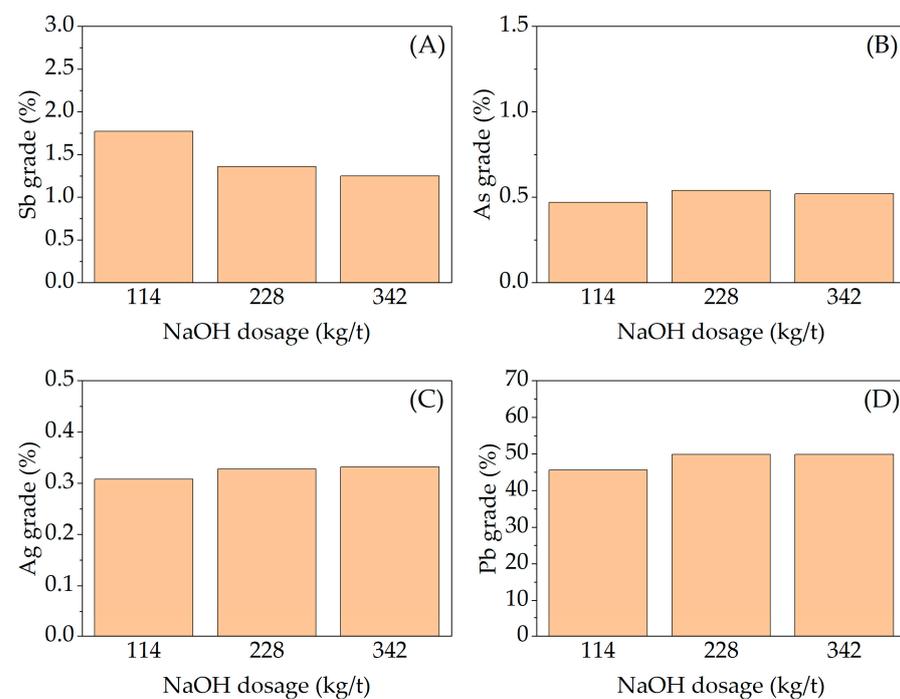
**Figure 10.** Effect of adding sulfur at 90 and 120 °C with 228 kg NaOH/t concentrate on metal grade. (A) Sb, (B) As, (C) Ag, and (D) Pb. F denotes the concentration on the feed.

The dosage ratio between sulfur and NaOH was approximately 1, which was determined considering stoichiometry criteria; however, the quantity of both reagents was studied because the proportion related to the concentrate was different. The most convenient dosage of both reagents was 224 kg of sulfur/t and 228 kg of NaOH/t (Figure 11). An excessive increase in both can generate the leaching of Pb and Ag, either due to excessive alkalinity or the excessive formation of thiosulfate that can dissolve them.



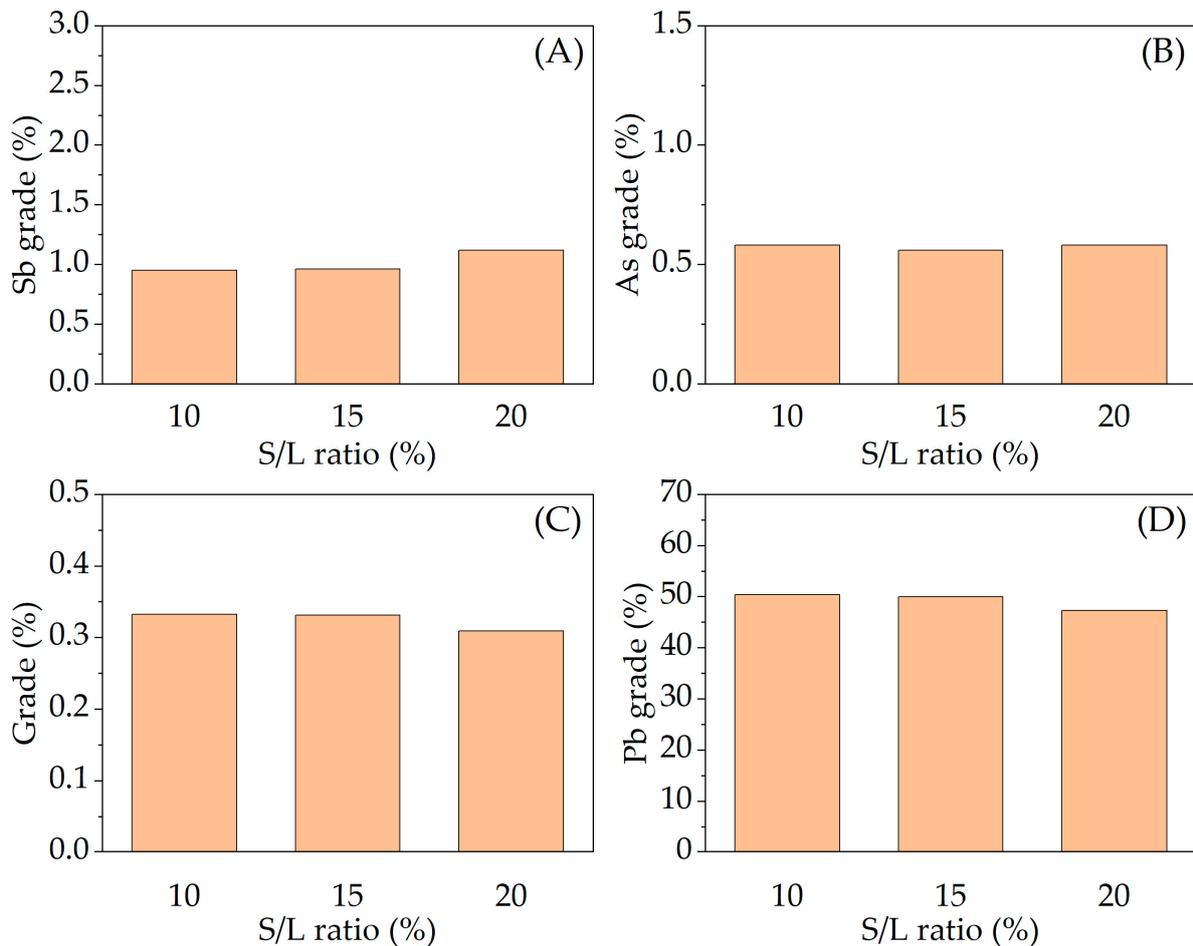
**Figure 11.** Effect of the increase in the addition of sulfur and NaOH at 90 and 120 °C on the grade. (A) Sb, (B) As, (C) Ag, and (D) Pb. F denotes the concentration on the feed.

Figure 12 illustrates the effect of the amount of NaOH dosed at 90 °C on a sulfur dosage of 224 kg/t. The results show that 55.4% of As and 50.9% of Sb can be removed. However, when a lower amount of NaOH is dosed, the content of Pb and Ag in the resulting concentrate decreases. On the other hand, if the amount of NaOH dosed is increased to 228 kg/t, the concentrate can be enriched after the process. This is because not all the added sulfur reacts to efficiently form the polysulfides. Instead, the NaOH is mainly consumed by the Pb and Ag sulfides. Therefore, maintaining an adequate dosage relationship between sulfur and sodium hydroxide improves the presence of polysulfide ions.



**Figure 12.** Effect of NaOH dosage at 90 °C with 224 kg/t S on the concentrate grade. (A) Sb, (B) As, (C) Ag, and (D) Pb.

After digestion, the solid/liquid ratio, expressed in % solids, was studied for the leaching stage at 120 °C, with a sulfur addition of 336 kg/t and a NaOH addition of 342 kg/t. The results indicate that an increase in the amount of water in the leaching stage favors the selectivity of the process, that is, although no strong effect is observed on the removal of As and Sb, it is observed that the Pb and Ag grades increase. This is due to the decrease in the concentration of ions that dissolve Pb and Ag in a more concentrated pulp (Figure 13).



**Figure 13.** Effect of the S/L ratio on the solid grades at 120 °C with 224 kg/t S on the concentrate grade. (A) Sb, (B) As, (C) Ag, and (D) Pb.

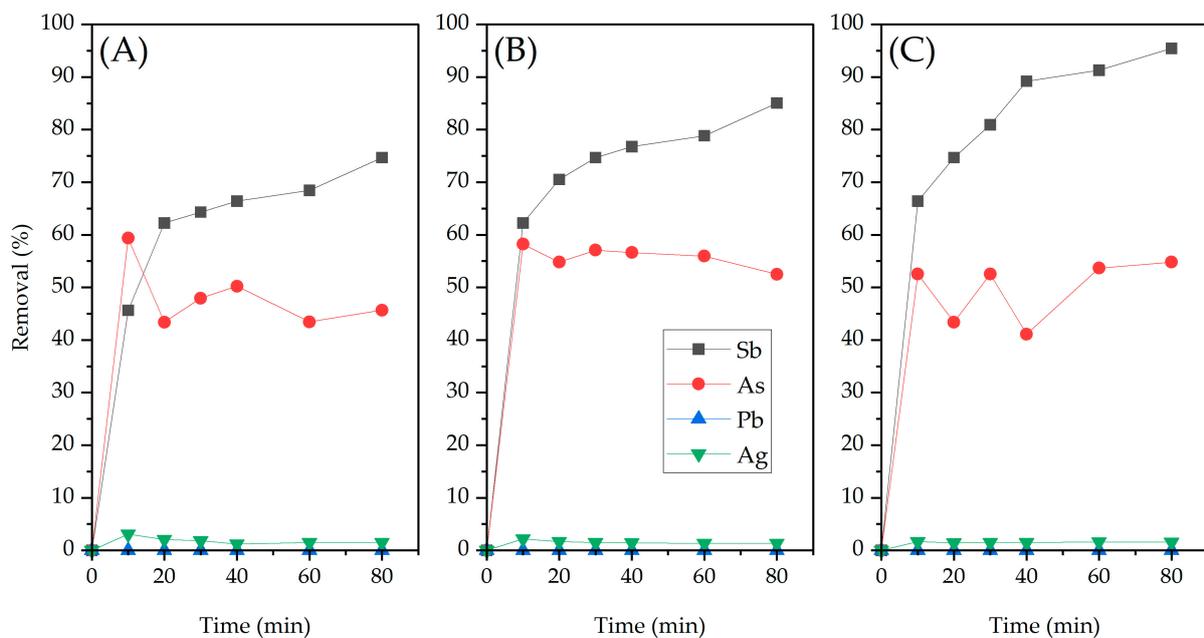
Under the most favorable conditions for removing As and Sb, which are at a temperature of 120 °C, using 336 kg of S/t, 342 kg of NaOH/t, and an S/L ratio of 33% during digestion and 15% during leaching, with a digestion time of 20 min and a leaching time of 60 min, a better quality concentrate can be achieved, as shown in Table 6. The weight loss during this process is 4.56%, with lower As and Sb content and a minor increase in Pb and Ag grades.

**Table 6.** Metal composition of concentrate before and after the digestion–leaching procedure at the best conditions.

Element	Grade before (%)	Grade after (%)
Sb	2.72	0.96
As	0.96	0.56
Pb	47.70	49.97
Ag	0.32	0.33

### 3.3. Kinetic Study of the Digestion–Leaching Technique for the Removal of As and Sb from a Pb–Ag Concentrate

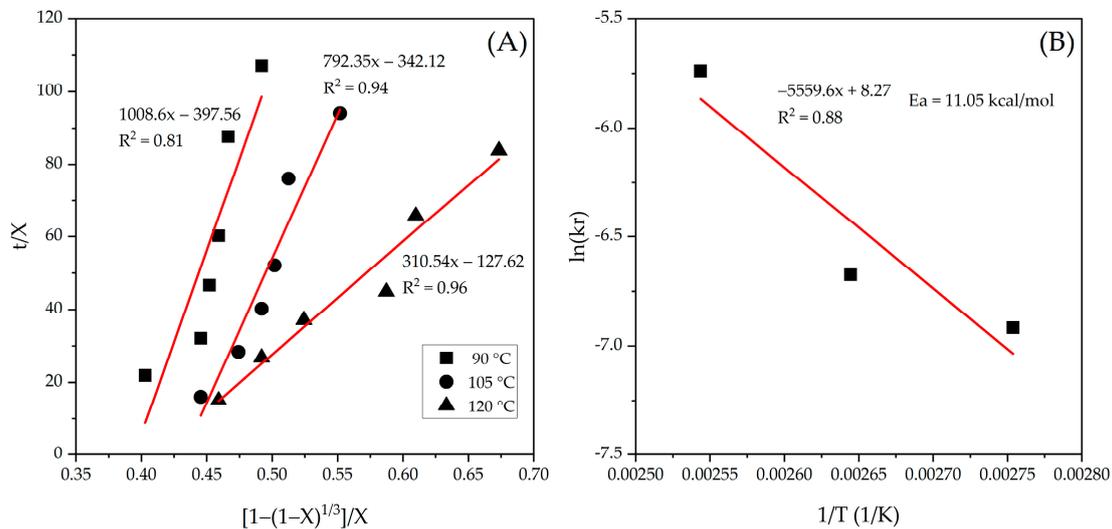
Tests were conducted to observe the effect of time on digestion, with and without the leaching stage, regarding the removal of As and Sb and the selectivity with Pb and Ag, under the most favorable conditions found previously. The activation energy was determined from the slopes of the model by a mixed control by diffusion through the layer, and the data and results are presented in Figure 14. Previous tests studying the parameters and thermodynamics of different reactions had already foreseen that there were various reactions in the process, mainly for Pb, Ag, Fe, and As, which involved leaching and precipitation reactions. Figure 14 shows that different reactions occur, allowing the leaching of Pb, Ag, and As, reaching an equilibrium approximately after 40 min. It is possible that Ag leaching is due to the presence of thiosulfate ions formed from sulfur, and initially, the concentration of thiosulfate is higher than that of the leached silver, giving rise to the formation of complexes such as  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  and others. The precipitation of Ag may be due to deprotonation reactions of thiosulfate, which is caused by the presence of other metal ions. The leaching of lead is attributed to the presence of oxydryl and thio-sulfate ions. At the same time, precipitation reactions could occur due to the formation of sulfides caused by the presence of sulfide ions and the consumption of oxydryl ions during the reactions.



**Figure 14.** Removal of metals in the digestion stage as a function of time and temperature. (A) 90, (B) 105, and (C) 120 °C. Removal of Pb (blue triangles) was negligible over time.

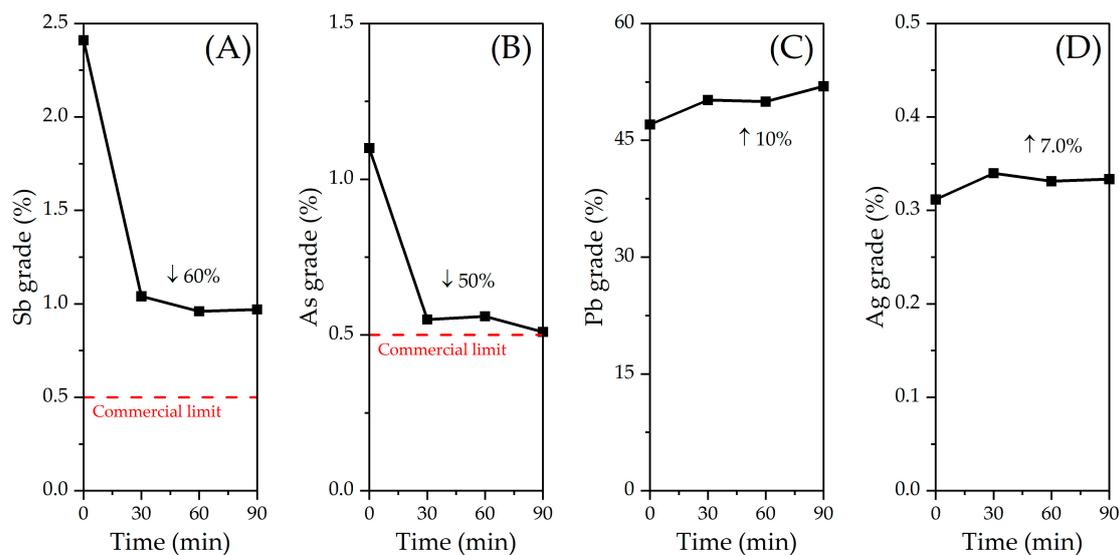
Modeling experimental data to identify the control of the digestion process was possible for As, Pb, and Ag due to the fluctuations in their leaching curves as a function of time. The Sb leaching curves were adjusted for a mixed control by diffusion through the boundary layer and chemical reaction, as shown in Figure 15. A high concentration of the solution due to the high amount of dissolved sulfur and other salts in the aqueous phase caused an increase in the viscosity of the solution; this made it difficult for the leaching agent molecules to diffuse through the boundary layer. On the other hand, a higher concentration of reactants increased the activation energy, leading to control by a chemical reaction. The activation energy for this process resulted in 11.05 kcal/mol, which was in a range that suggested it was controlled by chemical reactions. However, in the literature, in the work of Limpo (1997) [30], the experimental data adjusted to a mixed control with an activation energy of approximately 16 kcal/mol with a very good

fit, although Levenspiel (2004) [31] states that processes with activation energies greater than 10 kcal/mol are dominated by chemical reactions. However, the experimental value found and that of Limpo (1997) [30] are not very far from 10 kcal/mol. Activation energies greater than 50 kcal are definitely controlled by chemical reactions. The fitting of a mixed control for Sb leaching is shown in Figure 15.



**Figure 15.** Kinetic study of Sb in the digestion stage. (A) Fitting experimental data for mixed control by diffusion through the boundary layer and chemical reaction and (B) empirical determination of the activation energy. Trend lines are shown in red.

In Figure 16, the effect of increasing the leaching time is observed; there is no substantial influence on the removal of As and Sb. The increase in digestion time, in a process that does not include the leaching stage, favors Sb removal but not As, and also the Pb and Ag grades remain almost constant. If the digestion time continues to increase, the Pb and Ag grades increase again. The most convenient digestion time is 20 min, and the leaching stage allows the precipitation of dissolved Pb and Ag.



**Figure 16.** Effect of time in the leaching stage at 120 °C, 336 kg sulfur/t, 342 kg NaOH/t, S/L ratio of 33% in digestion and 15% in leaching, 20 min of digestion. (A) Sb, (B) As, (C) Pb, and (D) Ag.

#### 4. Conclusions

Different leachants were tested for As and Sb removal from concentrates. Sodium hypochlorite and hydrogen peroxide were ineffective due to low selectivity and precipitation reactions. Elemental sulfur was a better alternative than  $\text{Na}_2\text{S}$ , which was dosed in powder to the pulp. A mass ratio of about 1 of sulfur and NaOH, with an increase in temperature, favored the selective removal of impurities.

The alkaline digestion–leaching process with elemental sulfur reduced considerably the As and Sb content (50–60% decrease) while increasing the grade of Pb (10% increase) and Ag (7% increase). The best conditions were at 120 °C, 336 kg of S/t, 342 kg of NaOH/t, and an S/L ratio of 33% in digestion and 15% in leaching, with a digestion and leaching time of 20 and 60 min, respectively. Arsenic cannot be removed below 0.5% (the commercial limit), which may be due to the presence of iron in the concentrate, which would cause the precipitation of  $\text{FeAsO}_3$  or other insoluble Fe-As salts.

The reactions that may explain the As and Sb alkaline removal from the concentrate with elemental sulfur to produce  $\text{Na}_3\text{AsS}_4$ ,  $\text{Na}_3\text{SbS}_4$ , and thiosulfate are thermodynamically and kinetically complex due to the leaching and precipitation reactions occurring in the system with other species in the concentrate such as Pb, Ag, and Fe. The digestion stage is a very important step of the process, which is controlled in a combined way by the diffusion through the boundary layer and by the chemical reaction.

This study contributes significantly to the existing knowledge on low-environmental-footprint hydrometallurgical treatment for the elimination of metallic impurities. Although the levels of arsenic (As) and antimony (Sb) achieved in this study are not yet in compliance with the commercialization standards, it provides a foundation to suggest methodologies that can approach these standards and potentially exceed them under optimized conditions.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/mining4020017/s1>. Table S1. Reactions of PbS and  $\text{Ag}_2\text{S}$  with sodium hypochlorite. Data obtained from HSC database. Table S2. Reactions of PbS,  $\text{Ag}_2\text{S}$ ,  $\text{FeS}_2$ ,  $\text{As}_2\text{S}_3$ , and  $\text{Sb}_2\text{S}_3$  with sodium hypochlorite in an alkaline medium. Data obtained from HSC database. Table S3. Reactions of PbS,  $\text{Ag}_2\text{S}$ ,  $\text{FeS}_2$ ,  $\text{As}_2\text{S}_3$ , and  $\text{Sb}_2\text{S}_3$  with sodium hypochlorite in acid medium. Data obtained from HSC database. Table S4. Reactions of PbS,  $\text{Ag}_2\text{S}$ ,  $\text{FeS}_2$ ,  $\text{As}_2\text{S}_3$ , and  $\text{Sb}_2\text{S}_3$  with hydrogen peroxide in an alkaline medium. Data obtained from HSC database. Table S5. Reactions of Pb and Ag species with sulfide or hydroxide ions. Data obtained from HSC database.

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