Antimony recovery from recycled terminals of lead-acid batteries with Na$_2$CO$_3$ and SiC after firstly Sb$_2$O$_3$ formation

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(Received 16 June 2021; Accepted 04 November 2021)

Abstract: Terminals obtained from spent lead-acid batteries in Mexico contain around 2 wt% Sb. The terminals were melted in an electric furnace and then oxygen was injected to 750 °C and a gas flow rate of 2 L/min to produce high purity Sb$_2$O$_3$. The antimony trioxide obtained was treated with a mixture of Na$_2$CO$_3$-SiC to 1000°C to obtain metallic antimony. The antimony trioxide is reduced by the C present in reagents while silicon and sodium form a slag phase. The amounts of Sb$_2$O$_3$ and SiC were held constant while the Na$_2$CO$_3$ was evaluated in the range from 30 to 42 wt%. The antimony and slag produced were characterized by X-ray diffraction and SEM-EDS techniques. The addition of 34 wt% Na$_2$CO$_3$ leading the recovery of antimony up to 90.16 wt% (99.57 wt% purity) and the lowest antimony losses in the slag (2 wt%). In addition, the compounds Na$_2$SiO$_3$ and Na$_2$Si$_2$O$_5$ formed in the slag may indicate a more stable slag. Na$_2$CO$_3$ contents higher than 38 wt% decreased the antimony recovery since it promotes the Na$_2$Sb$_2$O$_7$ compound in the slag. The oxidation and reduction process was modeled in FactSage 7.3 software for a better understanding of the Na$_2$CO$_3$ and SiC additions on the antimony recovery rates and compounds formed in the slag.

Keywords: antimony, reduction, slag, batteries, thermodynamic

1. Introduction

Various unique properties of antimony determine its use in a diverse range of products and applications. Some of these properties include low melting point, enhancing workability at low temperatures, stability in the air at room temperature and in water to 250°C, resistance to most cold acids, dissolution in some hot acids and aqua regia, high density (6692 kg/m$^3$), low electrical and thermal conductivity, and expansion on freezing, like silicon bismuth gallium and germanium [1]. Antimony is a metal that has shown through decades different uses, most important applications of antimony are in the production of flame retardants, PET catalysis, ceramics, and glass [2,3]. Antimony is also widely used in metallic form in alloys and compounds, in lead alloys such as grids and terminals in lead-acid batteries to increase their hardness [4-7], and antimony bearing alloys (babbitts) which contain 4-5% of antimony for high anti-friction properties, low coefficient of friction in the bearings, and good conformability [8], as compounds with As, Ga and In, antimony is used for camouflage paints production [5]. Other uses of antimony as oxides or sulfides are in pigments and red rubber in vulcanizing applications [5,7]. After its use, once the end life cycle of those antimony-bearing products is completed, they are subject to disposing, recycling, or landfilling. Antimony content in products that reached their end life cycle is crucial to define if they can be considered as waste, reusable materials or if they can be treated in a recycling process for
its recovery. Some products such as lead grids and terminals in lead-acid batteries are considered as a secondary source of antimony since they contain between 1.6 and 7% antimony [9,10], the by-product from lead-smelting called antimonial dust also represents an important secondary resource. In the pyrometallurgical process for antimonial dust reduction, the reverberatory furnace is used to enrich its concentration in the intermediate product of crude lead-antimony alloy, then the resulting alloy should be converted and reduced several times until white antimony products quality is reached [11]. Z. Da-peng et al [12] recovered antimony from antimony-bearing dust through a reduction-roasting process. First, the dust was roasted and then a CO-CO₂ mixture was used as a reducing agent. The antimony recovery was in the range from 66 to 73.81 wt% when the temperature was increased from 650 to 800 °C, respectively. On the other hand, the main primary antimony production starts with the processing of mineral Stibnite (Sb₂S₃) which is an abundant antimony bearing mineral, and thus it is the main source to produce pure antimony trioxide and/or metallic antimony [13]. The conventional technology to produce metallic antimony from stibnite concentrates is primarily by oxidizing roasting to convert the stibnite into volatile antimony oxide (Sb₂O₃), which is subsequently reduced to antimony metal with carbon [14]. In pyrometallurgical antimony production, which is done in equipment such as the shaft furnace, rotary kiln, converter, or reverberatory furnace, a considerable amount of slag containing antimony and other impurities is formed. The amount of waste slag produced for each ton of antimony is about 5 tons. Slag waste is partially reused in the pyrometallurgical process to diminish antimony volatilization [3], nonetheless, in most cases, the desired recoveries and grades for antimony are not obtained in a single step process. The pyrometallurgical process for refining lead bullion includes the oxidation refining process and basic refining process, which both are based on the principle that antimony is oxidized more easily than lead therefore alloys containing lead and antimony can be separated pyrometallurgically, due to their vapor pressure difference [15]. J. Xu et al [16] determined the activities of the components of Pb-Sn-Sb ternary alloy by equilibrium test to 2 Pa and temperatures in the range from 1023 to 1223 K. The experimental vapor-liquid equilibria data of the ternary alloy was calculated with the Wilson equation and predicted values match reasonably with the experimental results. The proposed study is of great significance to the experimental design that involves vacuum distillation processes, specifically for the Pb-Sb-Sn recycling alloys. Z. T. Zhang et al [17] studied the antimony distribution of SiO₂ saturated Sb-Fe-O-SiO₂-CaO system by high-temperature experiments and quenching techniques. The ratios Fe/SiO₂ and CaO/SiO₂ on the Sb₂O₃ content were evaluated to 1200 °C for the proposed system. The phases contained in the slag were analyzed by X-ray diffraction and SEM-EDS techniques to 900 and 1200 °C. Higher antimony recoveries were obtained beyond 94 % which indicates the reduction of antimony content in the slag. Either from slags in primary antimony production or secondary antimony resources like by-products from lead-smelting, antimony is present or recovered mainly as antimony trioxide where metallic antimony can be reclaimed. Besides, some attractive alternatives have been proposed for antimony and lead recovery through the hydro/electro-metallurgy route. J.A. Barragan et al. [18] recovered Sb and Cu from electronic waste through hydro/electro-metallurgical techics, copper was recovered as the main component in a leaching solution, whereas the antimony (as Sb₂O₃ with commercial quality) recovery process was established as a purification step, achieving a rate of 81 wt.-%, while in [19] they calculated the values of potential (E vs NHE) and pH at which the leaching reactions occur spontaneously, as well as the deduction of a quadratic semiempirical model to predicts the copper, lead and silver
leaching efficiencies as a function of the stirring speed and the solid/liquid ratio, optimizing the leaching efficiency. Because of the growing recycling volume of lead-acid batteries in Mexico and the high lead and antimony content in the terminals of the battery, it is necessary to develop new routes for antimony recovery that allow maximum recovery and grade through a practical processing route. Taking these requirements into account, the pyrometallurgical route appears to be more suitable in the recovery of antimony from the recycling of lead acid battery terminals. Mixtures of Na$_2$CO$_3$ and SiC were used successfully for the lead paste reduction obtained from the recycling of lead-acid batteries by a pyrometallurgical route where a high lead recovery was obtained [20]. Thus, SiC was chosen as a reducing agent instead of traditionally used carbon for the antimony oxides reduction, with the advantage at the same time of both, the possibility of the formation of a stable slag based on silicates structures and to provide carbon as a reducing agent of antimony oxides. The aim of this work is focused on the antimony recovery from the terminals obtained from spent lead-acid batteries by an oxidation-reduction process. Oxygen was injected through a lance to the antimony volatilization and then the trioxide antimony was recovered which was reduced by a mixture of Na$_2$CO$_3$ and SiC to produce technical grade antimony. The obtained products (slag and antimony button) were analyzed by X-ray diffraction and SEM-EDS techniques. The pyrometallurgical process was thermodynamically modeled in FactSage 7.3 [21] and the predicted results match with the experimental phases obtained and the antimony recovery rates.

2. Experimental Procedures

2.1 Pb-Sb alloy

Terminals were obtained from spent lead-acid batteries and melted in an electric furnace to 400 °C. The lead-antimony alloy was poured into a pre-heated iron mold and sampled for chemical analysis.

2.2 Oxidation stage

The antimony volatilization from the Pb-Sb alloy was carried out with the scheme depicted in Figure 1.
Figure 1. Experimental array for the antimony volatilization

500 g of the Pb-Sb alloy were charged into an alumina crucible contained in an alumina chamber inside an electric furnace enabled with control of temperature to within ± 10 °C of the set values. The alumina chamber is tightly sealed by a stainless-steel lid, screws, and a high-temperature o-ring located on the inner side of the lid. The stainless-steel lid contains two inlets and one outlet. The inlets contain two stainless steel tube that allows the oxygen injection and the temperature measurement by a k-type thermocouple while the outlet allow the gas exhaust which was conducted to a water jacket-cooled glass vessel. The furnace temperature control was set up at 750 °C and when the inner temperature equals the programmed temperature, oxygen (99.5 wt% purity) was injected through a stainless-steel tube into the melted alloy at a rate of 2 liters per minute over 35 seconds (about 1.5 grams O₂). After oxygen injection, the furnace was switched off and it was left to be cooled. The collected powder was weighed and analyzed by X-ray powder diffraction and atomic absorption technics.

2.3 Reduction stage

The reduction stage was carried out by using commercial reagents of Na₂CO₃ and Sb₂O₃ in powder form with ≥ 99.5 and 99.9 wt% of purity, respectively. High purity (≥ 99 wt%) spent SiC crucibles were used with a mean particle size of 74-125 microns. Four trials were carried out to attain constant amounts of Sb₂O₃ and SiC in 5 and 0.95 g, respectively, while the Na₂CO₃ was set to 2.5, 3.1, 3.7, and 4.3 g which correspond to 30, 34, 38, and 42 wt%, respectively. The reagents for each trial were weighted in a Sartorius TE64 Talent Analytical Balance, 60 g x 0.1 mg readability, and mixed thoroughly in an agate mortar. The mixtures were charged in alumina crucibles with a capacity of 20 mL, the crucibles were covered with alumina lids. The covered alumina crucibles with the corresponding mixed reagents for each trial were placed in an electrical resistance furnace with control of temperature to within ± 10 °C, each experiment lasted 1 hour to 1000 °C. The temperature was also measured with a type k thermocouple. The experimental setup for antimony oxide reduction with Na₂CO₃ and SiC is shown in Figure 2.
After the reaction time, the furnace was turned off. The products metal and slag were poured and cooled down in an iron mold. Metallic antimony and slag were separated, weighed, and analyzed by X-Ray Diffraction, Absorption Atomic Spectrometry, and Scanning Electron Microscope with Energy Dispersive Spectra (SEM-EDS) techniques.

2.4 Slag and antimony characterization

The slag and metallic antimony were analyzed in an X-Ray Bruker D8 Focus with monochromatic Cu Kα radiation working in θ/2θ configuration. The following parameters were set for data collection: angular range from 10 to 70°, step size of 0.02°, and counting time of 2° min⁻¹. The slags were crushed in an agate mortar and sampled, while the metallic antimony samples were analyzed on the center zone. The antimony contents of both slag and metallic antimony were determined from analytical methods for atomic absorption spectrometry. Qualitative chemical analysis, morphology, and size of resulting slags were determined in an SEM Jeol 6300 and with the energy dispersive spectra analysis. A film deposit of Au-Pd on the surface of the slags was necessary to make them conductive. Backscattering electrons technique with 15 kV and 10 A was used for image production.

3. Thermodynamic modeling

FactSage 7.3 [21] with the module Equilib was used to determine the concentration of the different chemical species once they reach the chemical equilibrium state. The user gives the initial amount of chemical species, the temperature, and the pressure of the system (usually 1 atm), then the program calculates the most stable species with the Gibbs free energy minimization method.

3.1 Oxidation stage

The Equilib module and the FactPS, FToxide, and FSlead databases were used to estimate the antimony oxidation from a Pb-Sb alloy. As input data, a Pb-Sb alloy containing 2.1 wt% Sb was considered (489.5 g Pb and 10.5 g Sb) which interacts with pure oxygen. The effect of the oxygen amount on the phase formation was determined for a temperature of 750°C and 1 atm. The oxidation reaction of antimony contained in the Pb-Sb melt is carried out according to reaction (1), where the Sb is volatilized to form the Sb₄O₆ (g) phase at high temperatures.

\[ \text{Sb}(l) + \frac{3}{4} \text{O}_2(g) \rightleftharpoons \frac{1}{4} \text{Sb}_4\text{O}_6(g) \]  

(1)

Afterward, the Sb₄O₆ (g) phase is deposited as the temperature is decreased to form the antimony trioxide as follows.

\[ \text{Sb}_4\text{O}_6(g) \rightleftharpoons 2\text{Sb}_2\text{O}_3(s) \]  

(2)
3.2 Reduction stage

The computer simulation was carried out using the FactPS, Fmisc, and the FToxid databases contained in the module Equilib. The effects of temperature and concentration of Na$_2$CO$_3$ and SiC in the recovery of antimony from antimony trioxide were theoretically estimated. The thermodynamic modeling considered the chemical composition of the antimony trioxide, sodium carbonate, and silicon carbide. The recovery process of antimony from Sb$_2$O$_3$ and Sb$_4$O$_6$ with Na$_2$CO$_3$ and SiC is established based on the following reactions:

\[
\begin{align*}
Sb_2O_3(s) + x Na_2CO_3(s) + y SiC(s) & \\
Sb_4O_6(g) + x Na_2CO_3(s) + y SiC(s)
\end{align*}
\]

Reaction (3) is carried out at lower temperatures while reaction (4) proceeds at higher temperatures, where according to G. Brooks et al [22] the stable antimony oxide is the Sb$_4$O$_6$ as a gas phase. The reduction trials were carried out at 1000 °C, thus reaction (4) is expected to occur for the antimony reduction. Stability phase diagrams were obtained considering the effect of increasing the amounts of Na$_2$CO$_3$ and SiC to reduce the Sb$_2$O$_3$. The initial data for simulating were 5 grams Sb$_2$O$_3$, 2.5, 3.1, 3.7, and 4.3 grams Na$_2$CO$_3$, which correspond to 30, 34, 38, and 42 wt.% Na$_2$CO$_3$, respectively. The addition of SiC was considered till 1.2 grams. The modeling was carried out considering a closed system to 1 atmosphere of pressure and the temperature was held constant to 1000 °C.

4. Results and discussion

4.1 Pb-Sb alloy

Table 1 shows the chemical composition of the Pb-Sb alloy obtained from the molten terminals of lead-acid batteries.

Table 1. Chemical composition of the Pb-Sb alloy (wt.%)

| Alloy   | Sb  | Cu  | Fe  | Ag  | As  | Bi  | Pb       |
|--------|-----|-----|-----|-----|-----|-----|----------|
| Pb-Sb  | 2.099 | 0.013 | 0.098 | 0.005 | 0.070 | 0.002 | Balance  |

The concentration of antimony in lead-acid batteries has been declined in recent years due to advanced technology and the use of Ca, Al, and Sn alloys as a replacement [10]. As can be observed from Table 1 after lead, the major components in the alloys are antimony, followed by iron and arsenic with 0.098 and 0.070 wt.%, respectively. It is observed that arsenic and antimony existing in the terminals of lead-acid batteries like in other lead by-products. It is expected that arsenic and antimony will be volatilized during the oxygen injection as As$_2$O$_5$ and Sb$_2$O$_3$.

4.2 Oxidation stage

After selective oxidation, the formed oxide (white powder) was manually collected from the gas exhaust, however, a higher quantity of antimony trioxide was found on the inner side of
the lid. Figure 3a shows the stainless-steel lid during the oxygen injection and Figure 3b shows the antimony trioxide recovering from the inner side of the lid. The volatiles was cooled in colder regions of the inner chamber and deposited over them before were collected into a water-cooled condenser.

![Figure 3a](image1.jpg) ![Figure 3b](image2.jpg)

*Figure 3. Experimental array for the oxidation stage, a) stainless steel lid and b) antimony trioxide deposited on the inner side of the lid*

The residual lead-rich alloy and the antimony trioxide in powder form were picked up, weighed, and analyzed by atomic absorption. Table 2 shows the chemical composition, the mass of the alloy, and the volatilized antimony recovered.

| Product   | Mass (g) | Sb   | Cu  | Fe  | Ag  | As   | Bi  | Pb   |
|-----------|----------|------|-----|-----|-----|------|-----|------|
| Pb        | 484.72   | 0.23 | 0.005 | 0.085 | 0.001 | 0.048 | 0.002 | Balance |
| Sb oxide  | 9.49     | 80.14 | 0.002 | 0.002 | 0.001 | 0.089 | 0.001 | 0.27 |

The recovering of antimony as antimony trioxide was near to 78 wt.%. A Considerable amount of As and Fe remain in the lead-rich alloy. It has been reported that As is easy to volatilize as As$_2$O$_3$ reaching a volatilization rate of 93 wt.% in 120 min at 460 °C while the Sb$_2$O$_3$ also reaches 95 wt.% in 140 min at 600 °C [23, 24].

The antimony trioxide produced from the selective oxidation was analyzed by atomic absorption and X-ray powder diffraction. The results were compared with Sb$_2$O$_3$ commercial-grade reagent. Figure 4 shows the X-ray diffraction patterns for the Sb$_2$O$_3$ produced in the oxidation stage and the commercial chemical reagent.
Figure 4. X-ray diffraction patterns of the antimony trioxide for a) commercial reagent, and b) selective oxidation

The results of Figure 4 shows that the antimony trioxide produced in the selective oxidation contains as a major component the senarmontite phase (Sb$_2$O$_3$) with very lower amounts of bindeimita (Pb$_2$Sb$_2$O$_7$) and a Pb-Sb oxide (PbOSb$_2$O$_4$) while the commercial reagent shows only the senarmontite phase. The antimony trioxide produced reached 96 wt.% of purity. Taking as reference the purity of antimony trioxide from the selective oxidation from lead-antimony alloy and the few quantities of antimony trioxide produced, the experimental part concerning the reduction stage was conducted with analytical grade antimony trioxide.
4.3 Reduction stage

Tables 3 and 4 show the chemical composition by atomic absorption spectroscopy of the metallic antimony and the slags formed, respectively obtained by the trioxide antimony reduction process to different amounts of Na$_2$CO$_3$. Tables 3 and 4 also show the mass of the products formed.

**Table 3. Chemical composition of the antimony metallic to different Na$_2$CO$_3$ additions (wt.%)**

| Na$_2$CO$_3$ (wt.%) | Sb (g) | Chemical composition (wt.%) |
|---------------------|--------|-----------------------------|
| 30                  | 3.14   | Sb 98.62 Si 0.31 Na 1.05 Pb 0.0160 Bi 0.0006 Cu 0.0005 Fe 0.0002 |
| 34                  | 3.72   | Sb 99.69 Si 0.19 Na 0.12 Pb 0.0012 Bi 0.0006 Cu 0.0008 Fe 0.0003 |
| 38                  | 3.29   | Sb 98.62 Si 0.29 Na 1.08 Pb 0.0062 Bi 0.0012 Cu 0.0003 Fe 0.0005 |
| 42                  | 3.14   | Sb 98.71 Si 0.31 Na 0.98 Pb 0.0013 Bi 0.0009 Cu 0.0003 Fe 0.0005 |

**Table 4. Chemical composition of the slags to different Na$_2$CO$_3$ additions (wt.%)**

| Na$_2$CO$_3$ (wt.%) | Slag (g) | Chemical composition (wt.%) |
|---------------------|----------|-----------------------------|
| 30                  | 2.85     | Sb 2.34 Si 15.58 Na 22.80 |
| 34                  | 2.78     | Sb 1.71 Si 20.22 Na 23.90 |
| 38                  | 3.46     | Sb 6.63 Si 15.25 Na 24.10 |
| 42                  | 3.96     | Sb 16.53 Si 15.55 Na 24.24 |

The chemical composition of the antimony metallic shows that the main impurities in the antimony metallic button are silicon and sodium. The highest recovery (90%) and grade (99.69 %) of the antimony metallic button were obtained in a single-step process for the addition of 34 wt.% Na$_2$CO$_3$. In all cases, reached grade for metallic antimony buttons was very close to the commercial antimony grade (99.65%). The slags obtained from the reduction process of trioxide antimony to different Na$_2$CO$_3$ amounts with SiC at 1000 °C show high Silicon and Sodium contents, above 15.25 and 22.80 wt.%, respectively. Antimony concentration in the slag reaches values between 1.71 and 16.53 wt.%. Its presence confirms the reaction between antimony oxide and the added reactants SiC and Na$_2$CO$_3$ to produce metallic antimony, where the carbon from the SiC and the Na$_2$CO$_3$ acts as reducing agents of trioxide antimony, while Silicon and Sodium are in the slag phase, which may form mainly sodium and antimony silicates. It has been reported [17] that the Sb$_2$O$_3$ content in SiO$_2$ shows a stable tendency within the temperature range of 900 to 1200 °C, therefore, the Sb-containing phase primarily changed from the solid solution phase to the Sb-silicate phase.

Figures 5 and 6 show the antimony recovery as a function of the different amounts of Na$_2$CO$_3$ added (30, 34, 38, and 40 wt.%), keeping the SiC constant in 0.95 g to 1000 °C for the antimony metallic button and the slag, respectively.
It is observed from Figure 5 that the recovery rates of the metallic antimony were in the range from 75.12 to 90.16 wt.%. These results are in the range reported in the traditional pyrometallurgical antimony route [3,10]. The antimony grade was between 98.62 wt% and 99.69 wt%. It is observed an increment of the metallic antimony recovery when the sodium carbonate increases from 30 to 34 wt%, reaching the highest antimony recovery value (90.16 wt%) for the \( \text{Na}_2\text{CO}_3 \) addition of 34 wt%. As expected, for the same \( \text{Na}_2\text{CO}_3 \) additions, the lowest antimony contents were obtained in the slag. However, as the sodium carbonate content increases from 34 to 42 wt.%, the recovery of metallic antimony decreases obtaining an increase of the slag mass and the antimony content, which reach a value up to 14.92 wt%. 

**Figure 5.** Antimony recovery from trioxide antimony reduction with SiC and different amounts of \( \text{Na}_2\text{CO}_3 \) to 1000 °C

**Figure 6.** Antimony content in the slag obtained from the trioxide antimony reduction with SiC and different amounts of \( \text{Na}_2\text{CO}_3 \) to 1000 °C
It was evident a difference in the brightness of the antimony metallic button obtained, low-grade antimony buttons showed an opaque luster while high-grade buttons showed a shining metallic. The luster differences on the antimony button are due to a residual slag film deposited on the metallic antimony formed after cooling and phase separation. The metallic antimony button obtained for the addition of 34 wt.% Na$_2$CO$_3$ was analyzed with the SEM-EDS technique and Figure 7 shows a micrograph of the metallic sample with its X-ray mapping images for Sb, Na, Si, and O. The micrograph shows the presence of particles with different morphology. It is observed type-whiskers particles constituted mainly by Na, Si, and O with the same distribution. On the other hand, antimony is concentrated in particles with rhombohedral and tetrahedral forms as well as columnar and elongated crystals. A low concentration of antimony small particles is distributed all over the analyzed surface.

*Figure 7. SEM micrograph and X-ray mapping images of metallic antimony obtained to 34 wt.% Na$_2$CO$_3$*

Figures 8a and 8b show the micrographs and their microanalysis of the whiskers and the elongated particles showed in Figure 7. Whiskers particles are mainly constituted by high contents of Na, Si, and O (Figure 8a) while the elongated morphologies particles correspond to the metallic antimony button (Figure 8b) which are notably bigger than whiskers particles of the residual slag film.

The SEM and EDS patterns results of the slag obtained for antimony recovery from Pb-Sb alloy reduction trials with SiC are shown in Figures 9a and 9b for the Na$_2$CO$_3$ additions of 34 and 38 wt.%, respectively. The microanalysis showed that the amount of antimony in the slag increases when the amount of sodium carbonate was increased from 34 to 38 wt.%. The microanalysis shows in both cases the presence of silicon, sodium, and oxygen attributed to the raw materials used in the reduction trials. More defined morphologies like crystals normally presented in silicates are observed in the slag obtained to the addition of 34 wt.% Na$_2$CO$_3$, while the slag obtained to 38 wt.% Na$_2$CO$_3$ showed fewer crystalline particles, most
of them with undefined morphology. The detection of Gold and palladium is due to the Au-Pd film deposited on the slags to make them conductive.

**Figure 8.** SEM micrographs and microanalysis of the metallic antimony obtained for the Na$_2$CO$_3$ addition of 34 wt.% for a) whiskers particles and b) elongated crystals

**Figure 9.** SEM micrographs and microanalysis of the slags obtained to (a) 34 wt.% Na$_2$CO$_3$ and (b) 38 wt.% Na$_2$CO$_3$

The antimony metallic button and the slag obtained during the antimony trioxide reduction trials were characterized by X-ray diffraction and results are observed in Figures 10 and 11, respectively. Figure 10 shows that the metallic antimony obtained to 30 and 34 wt.% Na$_2$CO$_3$ is mainly constituted by metallic antimony, and few amounts of unreacted Na$_2$CO$_3$ and SiO$_2$ appear for the lowest Na$_2$CO$_3$ addition. When the Na$_2$CO$_3$ is increased, antimony remains as
the main phase, however, small amounts of the silicate Na$_2$Si$_2$O$_5$ and SiO$_2$ were detected to the Na$_2$CO$_3$ addition of 38 wt.%. For the highest Na$_2$CO$_3$ addition (42 wt.%), the antimony metallic contains the Na$_2$Si$_4$O$_9$ phase and unreacted Na$_2$CO$_3$. The highest recovery and grade of metallic antimony were obtained to the Na$_2$CO$_3$ addition of 34 wt.%, which agrees with its X-ray diffraction pattern, where only the presence of metallic antimony was detected.

**Figure 10.** X-ray diffraction patterns of the metallic antimony samples obtained after trioxide reduction with 0.95 g SiC and 1000 °C to different Na$_2$CO$_3$ contents

Figure 11 shows the X-ray diffraction patterns of the slags obtained for the antimony trioxide reduction trials. The X-ray pattern obtained for the addition of 30 wt.% Na$_2$CO$_3$ shows the presence of Sb$_2$O$_3$, Na$_2$CO$_3$, SiO$_2$, and C unreacted and the Na$_2$SiO$_3$ and hydrated Na$_2$CO$_3$ as compounds formed. It is evident for the Na$_2$CO$_3$ addition of 34 wt.% that the raw materials reacted to form mainly the Na$_2$SiO$_3$ and NaSb$_3$O$_7$ compounds. In addition, few amounts of Na$_2$CO$_3$ and C unreacted were also detected. For the higher Na$_2$CO$_3$ additions evaluated, it is evident an increase of the compounds formed such as sodium antimoniates NaSb$_3$O$_7$, Na$_2$Sb$_4$O$_7$, silicates such as Na$_2$SiO$_3$, Na$_2$Si$_2$O$_5$ with C and unreacted Na$_2$CO$_3$. Because of the
high volatility of trioxide antimony, it is observed in some slag samples their presence in few amounts. For the Na$_2$CO$_3$ addition of 38 wt%, the main compounds are Na$_2$CO$_3$ and hydrated Na$_2$CO$_3$, the amount of the Na$_2$SiO$_3$ compound is decreased while the Na$_2$Sb$_4$O$_7$ was formed. The slag obtained for the highest Na$_2$CO$_3$ addition shows an increase in the Na$_2$Sb$_4$O$_7$ compound and the appearance of the Na$_2$Si$_2$O$_5$ compound. Besides, the Na$_2$C$_2$O$_4$ compound was detected which corresponds to acetylene diolate. It is already known that alkali metals react with carbon monoxide [18, 25], in this case, Na$_2$CO$_3$ content allows the sodium acetylene diolate formation during the thermal decomposition of the carbonates in the charge. The carbonate-based slags (Na$_2$CO$_3$) also known as soda slags are easily leachable and hydrated as was observed in the results of Figure 11, however, the silica addition allows to obtain more stable slags [9]. It was observed for the addition of 34 wt.% Na$_2$CO$_3$, that the Na$_2$SiO$_3$ compound formed showed high stability to weather degradation. Experimentally, few and small hardly noticeable antimony droplets were found trapped in the slag phase, which was not taken into account in the antimony recovery rates and the slag characterization.

![Figure 11. X-ray diffraction patterns for slags obtained after trioxide reduction with 0.95 g SiC and 1000 °C to different Na$_2$CO$_3$ contents](image-url)
4.4 Thermodynamic modeling

4.4.1 Oxidation stage

Figure 12a, b shows a stability diagram that represents the oxidation stage of the antimony contained in a Pb-Sb alloy. Figure 12a shows the elements considered in the oxidation and the compounds formed at equilibrium when oxygen is reacted with 500 grams of a lead-antimony melted alloy at 750 °C. Formation of Sb₄O₆ (g) starts immediately with the presence of O₂, its amount increases steadily as the content of antimony in the lead-antimony alloy decreases, because antimony has a higher affinity with oxygen than lead, it reacts with oxygen to form Sb₄O₆ (g) easily. Lead oxide is formed until antimony is almost completely oxidized. As the lead oxide increases, the amount of melted lead decreases. Figure 12b shows a close-up image of selective oxidation of antimony According to the stability diagram, to separate almost all antimony as Sb₄O₆ (g) from 500 g lead-antimony (2.1% by weight antimony) alloy at 750°C are needed about 1.7 grams of oxygen, which represents at standard conditions of pressure and temperature 0.14 liters for each gram of antimony in the alloy. Under those conditions, the expected quantity that can be produced of Sb₄O₆ (g) is about 9.6 grams.

The Sb₄O₆ (g) formation occurs easily due to its high vapor pressure when oxidation reaction is carried out (Eq. 1), then, Sb₂O₃ (s) is deposited when the Sb₄O₆ (g) is cooled. Experimentally, 9.49 g were obtained which reasonably matches with the expected 9.7 g with the predicted results in FactSage 7.3.

4.4.2 Reduction stage

Figures 13a and 13b show the stability diagram calculated in FactSage 7.3 considering a mass and a molar charge for reaction (3), respectively. It is observed that as the reagent SiC is added up to 1.2 grams, the Sb₂O₆ (g) which is thermodynamically the stable antimony oxide to 1000 °C decreases, while Sb (l) phase increases. Because of its volatility, a quantity of reduced antimony in the gas phase is formed. Antimony volatilization also happens in the
traditional antimony production mainly from sulfides concentrated ores by pyrometallurgical route, where antimony losses by volatilization can reach values up to 20 wt.% or even higher [26, 27]. To 1000 °C, the Na₂CO₃ thermally dissociates to form Na₂O (s) and CO₂ (g), the Na₂O reacts with Si from the SiC to form slag with two different types of silicates Na₆Si₂O₇ and Na₂SiO₃, both in a liquid phase, while the CO₂ (g) is later reduced with higher amounts of SiC added to form CO (g). It is expected that during the reduction stage, the CO (g) formed, and the C from the SiC aids in the antimony reduction. The stability of each silicate depends on the concentration of SiC, even Na₆Si₂O₇, and Na₂SiO₃ partially coexist in the range from 0.1 to 0.2 and from 0.6 to 1.2 g SiC, respectively. According to FactSage 7.3 equilibrium results, the highest amount of antimony is produced when 0.6 g of SiC are added to 5 g Sb₂O₃ reaching up to 3.9 g of liquid antimony and 0.2 g of volatilized antimony. For the experimental conditions evaluated, the reduction results reasonably match with the predicted results. If SiC content increases from 0.6 to 1.2 grams, the content of formed silicates Na₆Si₂O₇ and Na₂SiO₃ increases, while melted Na₂CO₃ reacts totally. Over this content interval of SiC, the volatilized antimony quantity increases slightly with the corresponding diminution of the liquid antimony.

The silicate phases Na₆Si₂O₇ and Na₂SiO₃ experimentally formed were successfully predicted by the FactSage software, however, the phases formed containing antimony (NaSb₃O₇ and Na₂Sb₄O₇) were not predicted because the databases used did not contain them. However, the thermodynamic modeling allows understanding more precisely the experimental results of the pyrometallurgical process involved in this study.

The conventional reduction-smelting of lead-acid batteries is conducted in reverberatory or rotary furnaces. A crude lead-antimony alloy and an antimony-rich slag are obtained from the melt of the secondary materials. Antimony oxide in the slag is subsequently reduced with carbon contained in coke to produce antimony metal [1]. In this work, mixtures of Na₂CO₃-SiC were used to reduce the antimony trioxide in laboratory-level tests obtaining good antimony recovery and grade. However, it must be noted that SiO₂ and C have been successfully used instead of SiC in the recovery of antimony from antimonial dust [11] which may represent the cheapest option if the temperature and viscosity of the melt are controlled.
5. Conclusions

Antimony was recovered from recycled terminals from spent lead acid-batteries by a pyrometallurgical process which comprises an oxidation stage to produce Sb$_2$O$_6$ (g) that is cooled and recovered as Sb$_2$O$_3$ (s) and further reduced with a mixture of SiC and Na$_2$CO$_3$ to 1000 °C. The results are summarized as follows:

1. The recycled terminals from spent lead-acid batteries allow to obtain a Pb-2 wt% Sb alloy with arsenic and iron as main impurities.

2. High purity Sb$_2$O$_3$ (96 wt%) was obtained during the oxidation stage by the oxygen injection to 2 L min$^{-1}$ O$_2$, for 0.5 min to 750 °C. The recovery obtained was 78 wt%.

3. It was possible to carry out the antimony reduction from Sb$_2$O$_3$ by using SiC-Na$_2$CO$_3$ mixtures to 1000 °C.

4. The highest metallic antimony recovering (90 wt%) and grade (99.69 wt%) together with the lowest slag amount containing the lowest Sb content was obtained for the Na$_2$CO$_3$ addition of 34 wt%.

5. During the Sb reduction, the addition of 34 wt% Na$_2$CO$_3$ promoted mainly the Na$_2$SiO$_3$ compound formation with small amounts of NaSb$_3$O$_7$, however, when the sodium carbonate was increased, the Na$_2$Sb$_3$O$_7$ compound was formed, increasing the Sb content in the slag.

6. The thermodynamic modeling reasonably matches with the experimental results for the oxidation and reduction stages involved as well in the compounds predictions.

Acknowledgments

The authors wish to thank the Institutions CONACyT, SNI, COFAA, and SIP-Instituto Politécnico Nacional for their permanent assistance to the Process Metallurgy Group at ESIQIE-Metallurgy and Materials Department.

References

[1] G. Gunn, Critical Metals Handbook, Chapter 4 Antimony, First Ed., John Wiley & Sons, 2014.

[2] C. Zhang, C.R.A. Catlow, J. Catal., 259 (1) (2008) 17-25.

[3] C.G. Anderson, Chemie der Erde, 72 (S4) (2012) 3-8.

[4] T. Liu, K. Qiu, J. of Hazardous Mater., 347 (2018), 334-340.

[5] S. Ravinder, T. Feldmann, G.P. Demopoulos, Hydrometallurgy, 164 (2016) 141–153.
[6] D. Lin, K. Qiu, Environ Sci. Technol., 45 (2011) 3361-3366.
[7] C.G. Anderson, JOM, 53 (2001) 18-20.
[8] V.A. Krenev, N.P. Dergacheva, S.V. Fomichev, Theor. Found Chem. Eng., 49 (2015) 769-772.
[9] T.W. Ellis, A.H. Mirza, J. Power Sources, 195 (2010) 4525-4529.
[10] D. Dupont, S. Arnout, P.T. Jones, K. Binnemans, J. Sustain. Metall., 2 (2016) 79-103.
[11] W. Liu, T. Yang, D. Zhang, L. Chen, Y. Liu, JOM 66 (2014) 1694-1700.
[12] Z. Da-Peng, L. Lei, T. Cheng, J. Cent. South Univ. 25 (2018) 1904-1913.
[13] R. Padilla, L.C. Chambi, M.C. Ruiz, J. Min. Metall. Sect. B-Metall., 50 (1) (2014) 5-13.
[14] J.G. Yang, C.B. Tang, Y.M. Chen, M.T. Tang, Metall. Mater. Trans. B, 42B (2011) 30-36.
[15] A. Arnold, B. Friederich, Proceedings of EMC, (2011) 1-13.
[16] J. Xu, J. Gao, L. Kong, B. Xu, B. Yang, D. Liu, J. Min. Metall. Sect. B-Metall., 56 (3) (2020) 327-335.
[17] Z.-T. Zhang, H.-P. Nie, K. Yan, J. Min. Metall. Sect. B-Metall., 57 (1) (2021) 13-19.
[18] J. A. Barragan, C. Ponce de León, J. R. Alemán, A. Peregrina, F. Gómez, and E. R. Larios. ACS Omega, 5 (2020) 12355–12363.
[19] J. A. Barragan, J. R. Alemán, A. Peregrina, M. Sánchez, E. P. Rivero and E.R. Larios. ACS Omega, 6 (2021)12063-12071.
[20] A. Sánchez, V.H. Gutiérrez, A. Cruz, R.G. Sánchez, Russ. J. Non-Ferrous Metals, 57 (2016) 316-324.
[21] C.W. Bale, A.D. Pelton, W.T. Thompson. Facility for the Analysis of Chemical Thermodynamics (FactSage, v. 7.3), User’s Manual, 2018.
[22] G.A. Brooks, W.J. Rankin, N.B. Gray, Metall. Mater. Trans. B, 25B (1994) 873-884.
[23] G.A. Brooks, Ph. D. Thesis, University of Melbourne, Melbourne, Australia, 1993.
[24] A. Aracena, O. Jerez, C. Antonucci, Trans. Nonferrous Met. Soc. China, 26 (2016) 294-300.
[25] M. Reddy, Ph. D. Thesis, University of Hyderabad, India, 1995.
[26] Y. Hua, Y. Yang, F.L. Zhu, J. Mater. Sci. Technol. Sehenyang, 19 (2003) 619-622.
[27] Q. Wen-qing, L. Hong-lin, L. Wei, Z. Yong-xing, Y. Kang, H. Jun-wei. J. Cent. South Univ. 22 (2015) 868-873.
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