

## **ANTIMONY PRODUCTION BY CARBOTHERMIC REDUCTION OF STIBNITE IN THE PRESENCE OF LIME**

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### **Abstract**

*Experimental work on the carbothermic reduction of  $Sb_2S_3$  in the presence of lime was carried out in the temperature range of 973 to 1123 K to produce antimony in an environmentally friendly manner. The results demonstrated the technical feasibility of producing antimony by this method without producing  $SO_2$  gas. Complete conversion of  $Sb_2S_3$  was obtained at 1023 K in about 1000 seconds and at 1123 K in less than 250 seconds using stibnite-carbon-lime mixtures with molar ratios  $Sb_2S_3:CaO:C = 1:3:3$ . It was found that the reduction proceeds through the formation of an intermediate oxide  $SbO_2$ , which is subsequently reduced by  $CO(g)$  to yield antimony metal and  $CaS$ . The kinetics of the  $Sb_2S_3$  reduction was analyzed by using the equation  $\ln(1-X) = -kt$ . The activation energy was  $233 \text{ kJ mol}^{-1}$  in the temperature range of 973 to 1123 K. This value would correspond to an antimony catalyzed carbon oxidation by  $CO_2$ .*

*Key words: Antimony sulfide; Stibnite; Carbothermic reduction; Direct reduction.*

### **1. Introduction**

Stibnite ( $Sb_2S_3$ ) is an abundant antimony bearing mineral and thus it is the main source for the production of pure antimony trioxide and/or metallic antimony. The conventional technology for the production of metallic antimony from stibnite concentrates is primarily by oxidizing roasting to convert the stibnite into volatile antimony oxide ( $Sb_2O_3$ ), which is subsequently reduced to antimony metal with carbon [1]. Although this conventional technology to produce  $Sb_2O_3$  is well established, the control of the temperature and the air draft in the roasting/smelting stages to produce  $Sb_2O_3$  without producing the non-volatile  $SbO_2$  is difficult [2]. In general, in the roasting/smelting of stibnite, the production of noxious antimony vapors and sulfur dioxide ( $SO_2$ ) is unavoidable; therefore, this process has serious problems of atmospheric contamination.

The direct reduction of metal sulfides in the presence of lime is a viable alternative method to produce metal values without emitting the contaminant sulfur dioxide. Several studies have been reported in the past which were concerned with the use of various reducing agents, namely hydrogen, carbon monoxide and carbon for the reduction of metal sulfide, using mainly  $CaO$  and  $CaCO_3$  for sulfur

capture. These studies included the direct reduction of copper, zinc, nickel, lead, and molybdenum sulfides [3-14].

The main experimental technique used by most researchers to determine the rate of reduction was thermogravimetric analysis, which was usually complemented with several analytical techniques. Concerning the use of gaseous reductants, Sohn and Won [3] studied the hydrogen reduction of cuprous sulfide in the presence of lime. In this case, the global reaction involved the hydrogen reduction of the sulfide to metal with the formation of  $H_2S$  and a subsequent reaction of the  $H_2S$  with  $CaO$ . These researchers modeled the successive gas-solid reactions in a porous pellet incorporating the intrinsic kinetics of the individual reactions, and compared the results with experimental values obtained using chalcocite and lime. Mankhand and Prasad [4] studied the hydrogen reduction of molybdenite in the presence of lime and found that lime enhanced tremendously the rate of reduction and reduced the  $H_2S$  concentration in the off gas to negligible values. Mohan et al. [5] reported the results of the lime enhanced carbon monoxide reduction of cuprous sulfide. The reduction results were analyzed by using diffusion through product layer control model, and determined an activation energy of  $169.6 \text{ kJ/mol}$  for

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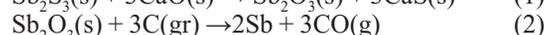
the range of 1123 to 1273 K.

On the other hand, the use of solid carbon as a reducing agent for metal sulfides has received considerable attention. Rao and El-Rahaiby [6] studied the reduction smelting of lead sulfide with C and CaO in the temperature range 1068 to 1255 K. The use of several catalysts on the rate of reduction was also studied. A 10-fold increase in the rate was observed for the catalyzed reduction in some cases using K, Na and Rb carbonates. Bronson and Sohn [7] studied the feasibility of reducing nickel sulfide with carbon and lime and found a rapid kinetics for the production of metallic nickel in the temperature range of 1273 to 1373 K. The carbothermic reduction of zinc sulfide has been studied using lime [8, 9] or calcium carbonate [10], as the sulfur scavenger. The results showed that the reduction reaction was rapid in the presence of catalyzers such as  $\text{Na}_2\text{SO}_4$  or NaF [8] and lithium carbonate [9]. The use of calcium carbonate as sulfur scavenger instead of lime was also effective; however, it prevented an accurate measurement of the rate of reduction by thermogravimetric analysis due to the decomposition of the carbonate in the reaction system. Wu et al. [10] studied also the carbothermic reduction of zinc sulfide using calcium carbonate and based only on relative intensity of diffraction peaks of XRD analysis of reduction products, proposed a complex reaction mechanism involving four stages and several sequential and parallel reactions. In 1997, the reduction of molybdenite with carbon in the presence of lime was studied by Padilla et al. [11], who reported that the reduction proceeded through the formation of intermediate  $\text{MoO}_2$  and calcium molybdate and using a first order kinetic model, they determined an activation energy of 218.8 kJ/mol for the molybdenite reduction with carbon in the temperature range of 1173 to 1473 K. Concerning copper sulfides, Jha et al. [12] and Padilla and Ruiz [13] studied the reduction of  $\text{Cu}_2\text{S}$  with carbon and lime. The later investigators determined the composition of the gas phase evolved during the carbothermic reduction of  $\text{Cu}_2\text{S}$ , which indicated that the controlling step was the Boudouard reaction. An activation energy of 363 kJ/mol was calculated for the reduction of  $\text{Cu}_2\text{S}$  with carbon and lime in the range of 1173 to 1323 K. Recently, Sundarmurti et al. [14] reported a study on a thermal analysis of lime added carbon reduction of chalcopyrite. These investigators claimed that chalcopyrite decomposes to copper and iron sulfides and each are reduced in distinct stages. The reabsorption of evolved sulfurous gases on lime was indicated as the reason for the observed weight gain of the sample.

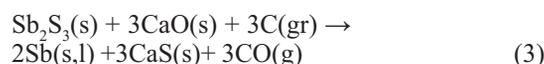
Generally, the main advantages of the reduction of metal sulfides in the presence of lime are that lime not only enhances tremendously the rate of reduction but

also reduces the sulfur dioxide concentration in the off gases to negligible values. Therefore, this alternative process seems appropriate for the treatment of stibnite concentrates especially for small to medium size plants frequently found in developing countries. Therefore, this paper is concerned with the carbothermic reduction of stibnite in the presence of lime.

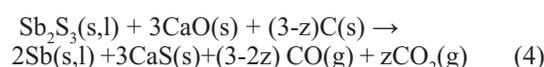
Little research has been done on this specific topic. The most relevant work was carried out by Igiehon et al. [15], who studied the reduction of antimony sulfide with coal and graphite and proposed the following sequence of reactions for the reduction of stibnite with coal and lime:



In reaction (1), called the exchange reaction, the  $\text{S}^{2-}$  ions of the stibnite are basically exchanged with  $\text{O}^{2-}$  from the calcium oxide to form antimony trioxide. The following step, reaction (2) is the reduction of the formed antimony trioxide with carbon. The overall reaction proposed by Igiehon et al. [15] for the  $\text{Sb}_2\text{S}_3$  reduction with carbon and CaO was as follows:

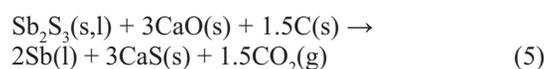


However, the formation of  $\text{Sb}_2\text{O}_3$  as an intermediate reaction product in the carbothermic reduction of stibnite has not been corroborated experimentally; consequently, the mechanism of the carbothermic reduction of stibnite still needs some clarification. Furthermore, the production of solely  $\text{CO}(\text{g})$  as the gaseous product under a variety of experimental conditions, as indicated by reaction (3), also needs corroboration. Therefore, a more general overall reaction that could represent better the direct reduction of stibnite using carbon as the reductant in the presence of lime can be written as:



with  $0 \leq z \leq 1.5$ .

This general reaction (4) allows for the possible emission of mixtures of  $\text{CO}(\text{g})$  and  $\text{CO}_2(\text{g})$  during the carbothermic reduction of stibnite in the presence of CaO, and it reduces to reaction (3) as a limiting case when  $z$  is equal to zero and to reaction (5) when  $z$  is equal to 1.5.



The actual relative amounts of the two carbon oxides evolved at a given experimental condition will depend on the thermodynamics and the relative kinetics of the intermediate reactions that occur in the reduction process.

Considering the above, in the present work, a

systematic study of the carbothermic reduction of  $\text{Sb}_2\text{S}_3$  in the presence of lime was carried out to determine the mechanism and kinetics of this process, and to assess the potential of this method as a more efficient and cleaner alternative for the production of metallic antimony than the current industrial practice.

## 2. Experimental

### 2.1 Materials

The reduction experiments were conducted using  $\text{Sb}_2\text{S}_3$  obtained from Aldrich Chemicals Co. which was a fine powder of 95.5%  $\text{Sb}_2\text{S}_3$ . The reducing agent used was activated carbon (charcoal activated GR, Merck). This carbon was 94% -75 micron and the determined fixed carbon was 90.7%. The calcium oxide for the experiments was produced by thermal decomposition of calcium carbonate powder (99.9 %  $\text{CaCO}_3$ , Merck). Various samples were prepared by mixing these materials thoroughly in a porcelain mortar in predetermined molar ratios of  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C}$ .

### 2.2 Reduction experiments

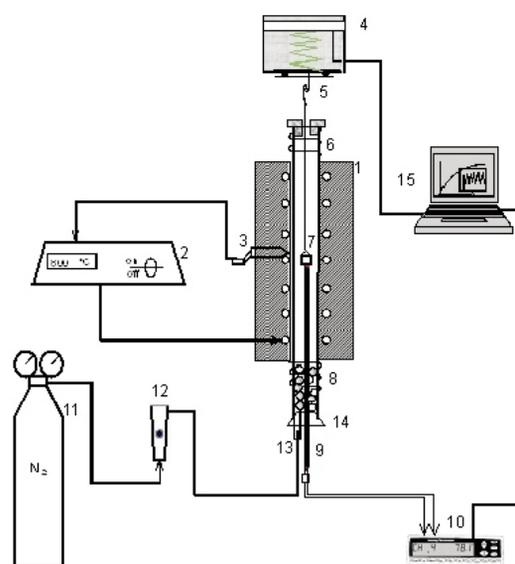
The reduction of  $\text{Sb}_2\text{S}_3$  (melting point 823K) was studied in a custom built thermogravimetric apparatus (TGA) where the instantaneous weight of the sample and the temperature were recorded as a function of time. In order to obtain quantitative information on the extent of reaction from the weight loss data of the reacting samples, it was necessary to exclude gaseous oxygen from the system, thus the experiments were carried out under an inert atmosphere using high grade nitrogen.

A schematic drawing of the experimental apparatus is shown in Figure 1. The thermogravimetric apparatus consisted principally of a high temperature vertical tube furnace with a temperature controller, an electronic balance connected to a personal computer for recording continuously the weight of the sample, and a nitrogen delivery system to provide the inert atmosphere in the reaction tube. A quartz tube 45 mm inner diameter was used as a reactor to hold a 5 ml (20 mm high and 23 mm upper diameter) ceramic crucible containing the sample.

A typical experiment started by heating the tube reactor to the selected temperature under a slow flow of nitrogen. Once the set temperature was reached and stabilized, about 500 mg of a homogeneous mixture of  $\text{Sb}_2\text{S}_3\text{-CaO-C}$  contained in a loosely covered crucible was introduced in the quartz tube very rapidly (in 10 to 20 s approximately), and it was suspended from the balance by a gold chain. The use of a cover that did not fit tightly (there was a side slit between the cover and the crucible to allow flow of gas) was to eliminate back diffusion and dilution of

the gaseous products of the reaction. The sample temperature was constantly measured by a chromel/alumel thermocouple placed just below the crucible. To check the development of local temperature changes after insertion of the crucible in the reactor, few experiments were conducted with a thermocouple placed inside the crucible in direct contact with the reacting sample and with the thermocouple in empty crucible. The results indicated that the difference in the temperature profile for both cases was negligible for the small 500-mg sample used, and the sample heated rapidly to the set temperature in about 70 to 100 s, depending on the set temperature for the experiment. Thus, the weight loss of the sample was recorded and analyzed considering the indicated heating time.

The fraction of weight loss at any time was calculated from the instantaneous weight of the sample. The intermediate and final compounds formed during the reaction were determined by X-ray diffraction (XRD) analysis of partially and completely reacted samples using a Rigaku model Geiger Flex, copper anode spectrometer (Rigaku Corporation, The Woodlands, TX, USA). For this analysis, when the sample reacted for the predetermined time, the crucible with the sample was quickly lifted to the upper end of the reaction tube, where it was quenched with a cold flow of nitrogen, and then, the sample was



**Figure 1.** Schematic diagram of the TGA system. 1. Tubular furnace; 2. Furnace temperature controller; 3. Chromel/alumel thermocouple; 4. Sartorius precision balance; 5. Gold chain; 6. Quartz reaction tube; 7. Ceramic crucible; 8. Glass bead bed; 9. Chromel/Alumel thermocouple; 10. 12-channel scanning thermocouple thermometer; 11. Nitrogen gas cylinder; 12. Flow meter; 13. Gas inlet tube; 14. Rubber Stopcock; 15. Personal computer.

rapidly removed to a desiccator for final cooling. Most of the experiments were conducted at constant temperature under a constant flow of nitrogen until little weight change of the sample was observed. A few experiments were interrupted at short times in order to determine the intermediate compound formed by the reaction.

### 3. Results and Discussion

#### 3.1 Reaction products

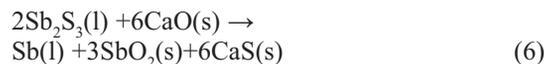
Preliminary experiments were run to check the adequacy of the custom TGA using carbon (coconut charcoal) of known composition under various gaseous atmospheres. The results of those experiments served also to define a flow rate of  $0.6 \text{ L min}^{-1}$  nitrogen into the reactor as sufficient to maintain the inert atmosphere. Thus using this nitrogen flow rate, several experiments were conducted in the temperature range of 973 K to 1123 K with homogeneous mixtures of  $\text{Sb}_2\text{S}_3$ -CaO and  $\text{Sb}_2\text{S}_3$ -CaO-C. The main purpose of these experiments was to determine the intermediate and final products that could be formed when heating mixtures of stibnite, carbon and lime with various compositions.

The results of the experiments obtained at 1073 K using mixtures with and without carbon, i.e., molar ratio of  $\text{Sb}_2\text{S}_3:\text{CaO} = 1:3$ , and  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$ , are shown in Figure 2. In this Figure, the weight loss fraction of the sample given by  $(W_0 - W)/W_0$  is shown as a function of time, where  $W_0$  is the initial weight and  $W$  is the weight at time  $t$ . In addition to the continuous line to represent the weight loss fraction of the sample, a symbol for intermittent data points are used mainly for clarity, especially when more than one curve corresponding to different conditions are shown in the figure.

As seen in Figure 2, the sample mixture with molar ratio of  $\text{Sb}_2\text{S}_3:\text{CaO} = 1:3$  loses weight at a very slow constant rate while the weight loss of the mixture  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  is very fast at this temperature.

Both reacted samples were analyzed by X-ray diffraction spectroscopy to determine the compounds formed during the experiments. The XRD spectrum of the  $\text{Sb}_2\text{S}_3$ -CaO sample reacted for 2400 s at 1073 K is shown in Figure 3, where it can be observed strong diffraction lines for  $\text{SbO}_2$  (cervantite), CaS, and metallic Sb.

This result suggests that at 1073 K in the absence of carbon stibnite is converted into cervantite and liquid antimony (Sb melting point 903.5 K) and CaO is transformed into CaS by the following reaction:



According to this reaction (6),  $\text{Sb}_2\text{S}_3$ -CaO mixtures should not lose weight as the reaction proceeds. Therefore, the constant weight loss of the sample shown in Figure 2 must be due to the partial volatilization of either initial  $\text{Sb}_2\text{S}_3$  or the product Sb since the  $\text{SbO}_2$  is non-volatile at 1073 K. Padilla et al. [16] in their study of volatilization of stibnite in nitrogen atmospheres found a constant volatilization rate of  $\text{Sb}_2\text{S}_3$  at 1073 K, which is consistent with the

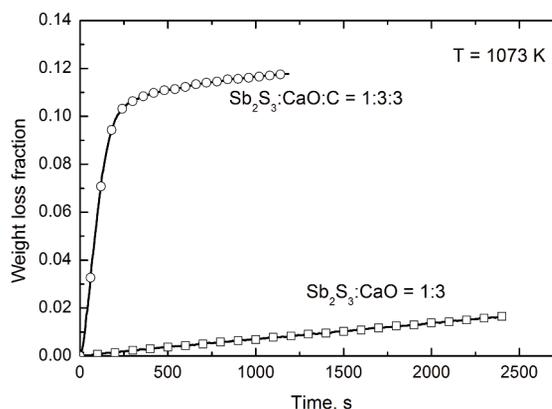


Figure 2. Comparison of weight loss fraction of samples with molar ratios of  $\text{Sb}_2\text{S}_3:\text{CaO} = 1:3$  and  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  reacted at 1073 K.

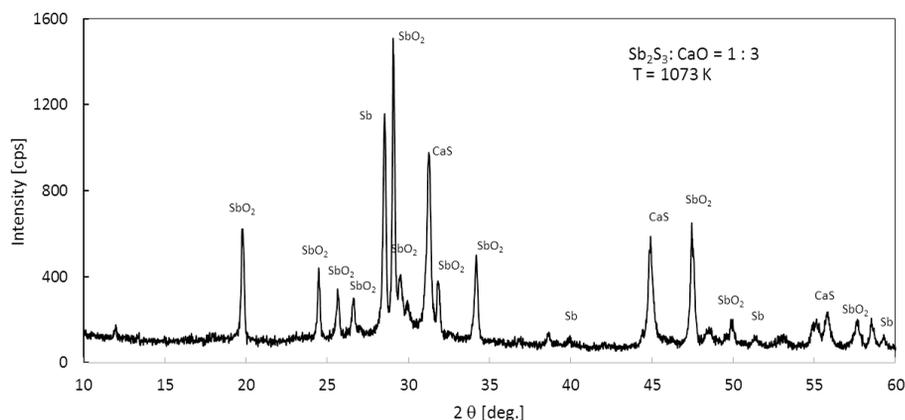


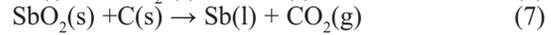
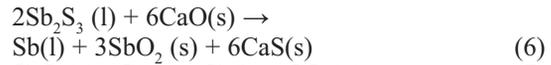
Figure 3. Spectrum of a reacted mixture of stibnite with CaO at 1073 K and 2400 second

results shown in Figure 2. Therefore, it is believed that the weight loss observed during the reaction of mixtures of  $\text{Sb}_2\text{S}_3$ -CaO in nitrogen atmosphere is mainly due to the volatilization of  $\text{Sb}_2\text{S}_3$ .

On the other hand, Figure 4 shows an XRD spectrum of a sample with molar ratios  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  which was reacted for 1250 s at the same temperature of 1073 K. It can be observed in this spectrum strong diffraction lines solely for Sb and CaS, indicating that at this temperature the  $\text{Sb}_2\text{S}_3$  reduction with carbon in the presence of lime yields only Sb and CaS as condensed products. An XRD spectrum of a partially reacted sample with the same molar ratios of  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  reacted at 948 K for 2400 s is presented in Figure 5. In this spectrum, strong diffraction peaks for  $\text{SbO}_2$  were also found in addition to Sb, and CaS peaks. The presence of  $\text{SbO}_2$  in this partially reacted sample demonstrates that the carbothermic reduction of stibnite in the presence of CaO proceeds through the intermediate compound  $\text{SbO}_2$ . The formation of  $\text{SbO}_2$  was also confirmed in samples that reacted for short times and large excess of CaO at 1023 K.

### 3.2 Reaction mechanism

Considering the XRD results discussed above, the following reaction scheme can be proposed for the reduction of stibnite with C in the presence of CaO for the temperature range of 973 to 1123 K:



Both reactions are thermodynamically favorable. However, despite the large value of the equilibrium constant for reaction (7) (see Table 1), it is unlikely to be the main reduction reaction of  $\text{SbO}_2$  in the system. The reason is that reaction (7) is a solid-solid reaction which requires direct contact between the antimony oxide and carbon particles. Therefore, once a small amount of Sb product is formed in the interface  $\text{SbO}_2$ -C, reaction (7) could only proceed further by the diffusion of the reactants through this product layer which generally is a slow process.

On the other hand, once some initial  $\text{CO}_2$  is produced in the system by reaction (7), the carbon

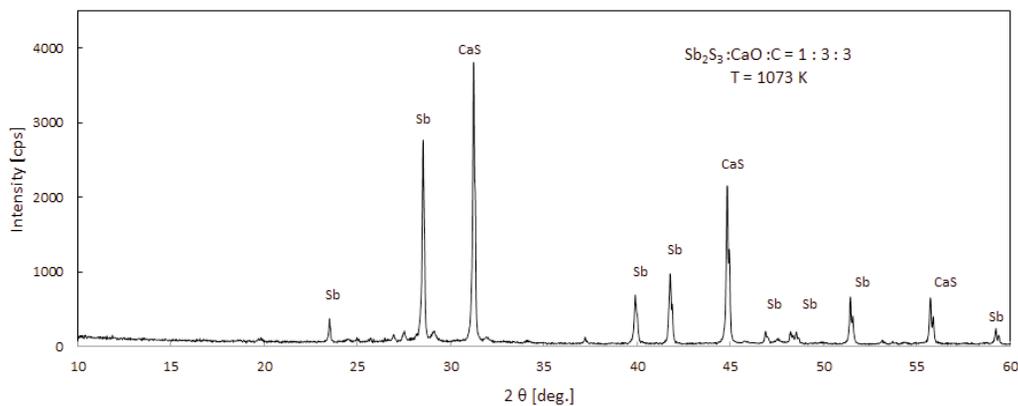


Figure 4. Spectrum of a reacted mixture of  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:1.5$  at 1073 K and 1250 seconds

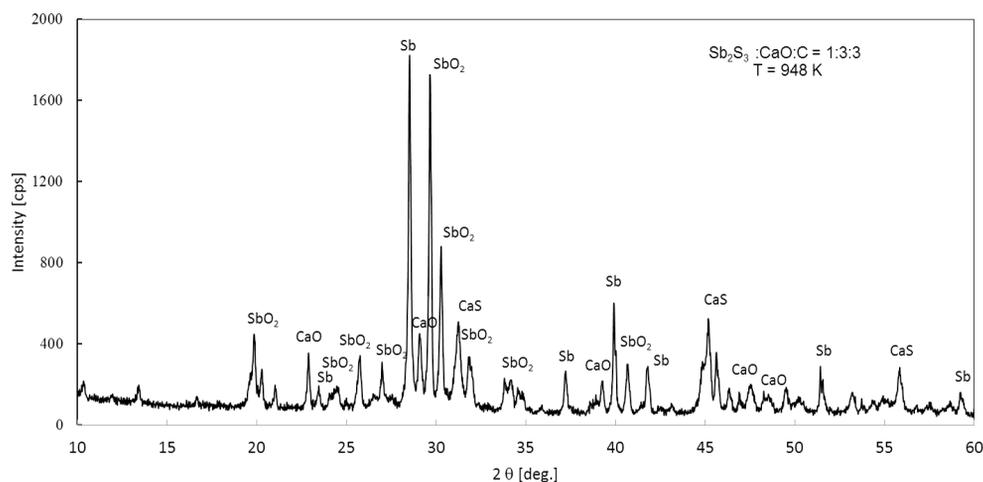
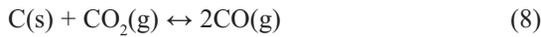
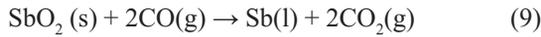


Figure 5. Spectrum of a reacted mixture of  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  at 948 K and 2400 seconds

oxidation reaction (8) (Boudouard reaction) must take place:



Thus, further reduction of the antimony oxide with CO(g) can easily occur through the gas phase according to the following reaction:



Reaction (9) is a gas-solid reaction and since diffusion in a gas phase is a rapid process (as compared to diffusion in a condensed state), reaction (9) should be the dominant reduction reaction of SbO<sub>2</sub> in the system, as indicated by the rapid kinetics observed in the experimental work. Therefore, the reduction of Sb<sub>2</sub>S<sub>3</sub> with C and CaO would occur by a first step of oxidation to Sb(l) and SbO<sub>2</sub>(s), according to reaction (6), followed by the reduction of SbO<sub>2</sub> with CO(g) as given by reaction (9). This SbO<sub>2</sub> reduction reaction would be coupled with the Boudouard reaction (8) for the regeneration of CO species. It is a well-documented fact in the literature that the reduction of sulphides or oxides with carbon occurs primarily through intermediate gaseous CO and CO<sub>2</sub> species, involving the Boudouard reaction [11, 13, 17, 18].

The equilibrium constants at 1000 K for the reactions considered in this study were calculated by using the HSC Chemistry data base [19] for all the chemical compounds except for the Sb<sub>2</sub>S<sub>3</sub>. The free energy values for Sb<sub>2</sub>S<sub>3</sub> given by HSC differ substantially from the values given by Barin [20] and Pankratz et al. [21] and since the latter references give comparable values, the free energy of formation for Sb<sub>2</sub>S<sub>3</sub> given by Barin [20] was used for calculating the equilibrium constants for reactions (5) and (6). The results are shown in Table 1, where it can be observed that all the reactions have large equilibrium constants at 1000 K with the exception of the Boudouard reaction (8), which is a reversible reaction. Thus thermodynamics predictions are in general agreement with the experimental results, particularly concerning reactions (5) and (6) of this study.

Therefore, according to the proposed mechanism for the reduction of Sb<sub>2</sub>S<sub>3</sub> with C and CaO, the actual composition of the evolved gas will depend on the relative rates of reactions (8) and (9) at a given temperature. If reaction (8) is significantly slower than reaction (9), the gaseous product of the overall reaction will be mostly CO<sub>2</sub>, and the overall reaction will be reaction (5). On the other hand, if the SbO<sub>2</sub> reduction reaction (9) is the slowest reaction, the composition of the gas produced will be close to the equilibrium composition of the Boudouard reaction (8) and a mixture of the two carbon oxides will be evolved with a predominance of the CO at higher temperatures, and the overall reaction will be reaction (4).

**Table 1.** Equilibrium constants for the reactions involved in the reduction of stibnite with carbon in the presence of lime [19, 20, 21]

Chemical Reaction	Equilibrium constant, K T = 1000 K
$\text{Sb}_2\text{S}_3 + 3\text{CaO} + 1.5\text{C} \rightarrow 2\text{Sb} + 3\text{CaS} + 1.5\text{CO}_2(\text{g})$ (5)	4.19x10 <sup>11</sup>
$2\text{Sb}_2\text{S}_3 + 6\text{CaO} \rightarrow \text{Sb} + 3\text{SbO}_2 + 6\text{CaS}$ (6)	1.19x10 <sup>3</sup>
$\text{SbO}_2 + \text{C} \rightarrow \text{Sb} + \text{CO}_2(\text{g})$ (7)	4.87x10 <sup>6</sup>
$\text{C} + \text{CO}_2(\text{g}) \leftrightarrow 2\text{CO}(\text{g})$ (8)	1.76
$\text{SbO}_2 + 2\text{CO}(\text{g}) \rightarrow \text{Sb} + 2\text{CO}_2(\text{g})$ (9)	2.76x10 <sup>6</sup>

For the range of temperatures studied here, the weight losses by evaporation of the condensed reagents or products are negligible. Thus, the CO and/or CO<sub>2</sub> evolution during the reduction can be resolved from the total weight loss of the sample for complete conversion. This can be accomplished by comparing the experimental weight loss data to the theoretical values calculated from the stoichiometry of the overall reaction (5) for CO<sub>2</sub> evolution, and reaction (4) for the evolution of a mixture of CO and CO<sub>2</sub> gases at a given temperature considering the Boudouard reaction equilibrium. Such a comparison is presented in Figure 6, which shows the fractional weight loss data for two experiments carried out with molar ratios Sb<sub>2</sub>S<sub>3</sub>:CaO:C = 1:3:3 one at 998 K and the other at 1023 K. The theoretical weight loss of the sample considering the formation of only CO<sub>2</sub> according to reaction (5) is shown as a horizontal line, and the formation of a mixture of CO and CO<sub>2</sub> according to the reaction (4) at 998 K and 1023 K with z = 0.68, and z = 0.54, respectively, are also shown in the figure. The values of z for both temperatures were determined considering the equilibrium constant for the Boudouard reaction and a total pressure of 1 atmosphere (P<sub>CO</sub> + P<sub>CO2</sub> = 1) which was the case for our experimental conditions with the sample reacting in a slackerly covered crucible as described above.

As can be seen in this Figure 6, at both temperatures, the experimental weight loss approached asymptotically to the theoretical weight loss value for the CO<sub>2</sub> formation only. Therefore, the carbothermic reduction of stibnite in the presence of lime can be represented accurately by the overall reaction (5). These results also indicate that the Boudouard reaction is the slowest step in the reduction of stibnite with carbon in the presence of CaO. The Boudouard reaction has been previously reported as the controlling reaction in the carbothermic reduction of various metals oxides and

sulfides [11, 13, 17, 18]; therefore, it is not unexpected this is also the case in the stibnite reduction with carbon in the presence of lime.

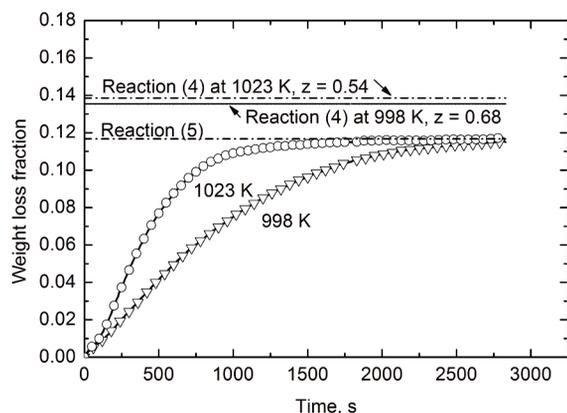


Figure 6. Experimental weight loss fraction compared to the theoretical weight loss fraction according to the reactions (4) and (5).

### 3.3 Effect of temperature

At temperatures lower than 973 K the rate of reaction was very slow to be of practical interest. On the other hand, at temperatures higher than 1123 K the vaporization of the antimony product became noticeable and the reacting samples continued to lose weight at a slow rate with time. The results of reduction experiments for samples with molar ratios  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  (100 % excess of carbon) are shown in Figure 7, where the data are presented as the conversion of stibnite,  $X$ , versus reaction time. Since the reduction of  $\text{Sb}_2\text{S}_3$  proceeds with the evolution of  $\text{CO}_2$  as discussed above, the conversion was calculated as  $X = \Delta W/W_{\text{th}}$ , where  $W_{\text{th}}$  is the theoretical weight loss for the complete conversion of stibnite with the formation of  $\text{CO}_2$  according to the overall reaction (5).

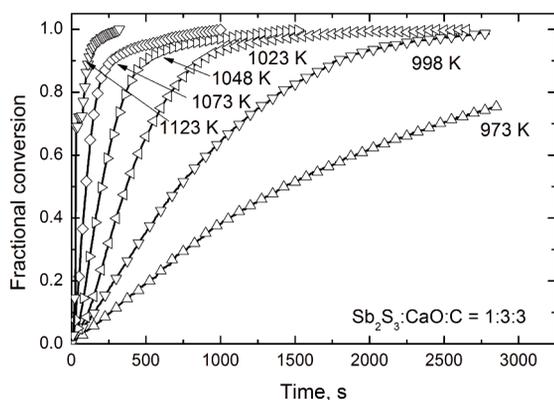


Figure 7. Effect of temperature on the carbothermic reduction rate of  $\text{Sb}_2\text{S}_3$  in the presence of lime. Sample used  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$ .

Figure 7 shows that a change in temperature from 973 to 1123 K produces a large increase in the rate of reduction. At 1048 K and above, the reduction occurs rapidly, reaching complete reduction in less than 500 seconds. The same great effect of temperature was found when using the stoichiometric amount of carbon i.e. molar ratios of  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:1.5$ , except that the reduction rate at each temperature was somewhat slower in this case, as shown in Figure 8.

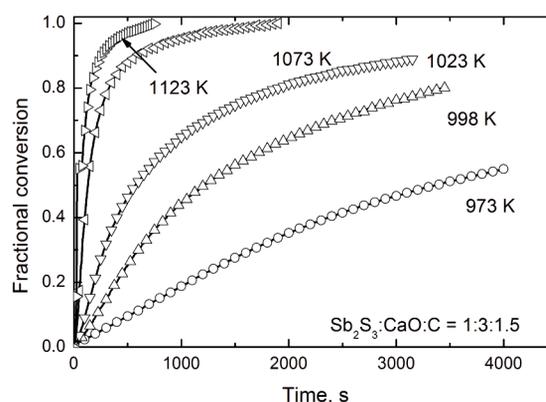


Figure 8. Effect of temperature on the reduction rate for the stoichiometric mixture  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:1.5$ .

### 3.4 Effect of the amount of CaO

To study the effect of the amount of CaO on the overall rate of reaction, experiments were performed at 998 K with different molar ratios of  $\text{Sb}_2\text{S}_3:\text{CaO}$  while maintaining the amount of carbon in the mixture at 3 moles of C per mole of  $\text{Sb}_2\text{S}_3$ . It should be pointed out that the amount of CaO in the reacting sample should affect directly the rate of formation of  $\text{SbO}_2$ , i.e. reaction (6) and indirectly the rate of reduction of this oxide. The experimental results are presented in Figure 9, where it can be observed that an increment in the amount of CaO above the stoichiometric ratio increased somewhat the overall

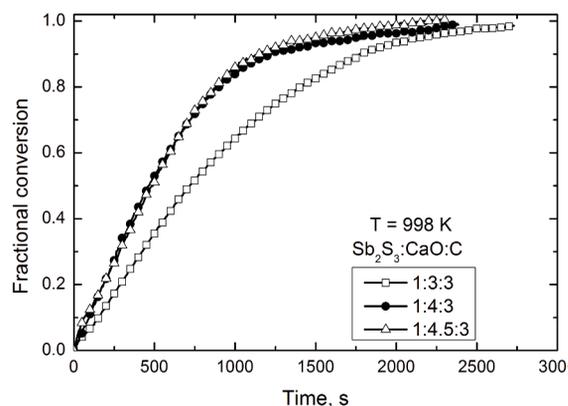


Figure 9. Effect of the amount of CaO on the rate of reduction of  $\text{Sb}_2\text{S}_3$  with carbon.

rate of stibnite reduction. It can also be observed that higher than 4 moles of CaO per mole of  $\text{Sb}_2\text{S}_3$  is not needed since the effect is negligible.

### 3.5 Effect of the amount of carbon

Figure 10 shows an important effect of varying the amount of carbon on the rate of reduction of stibnite at 998 K using a stoichiometric amount of CaO in the mixture. A similar effect of the amount carbon on the rate of reduction was also seen at other temperatures.

An increment in the amount of carbon in the sample increases the available surface area for the Boudouard reaction to take place. Therefore, if the Boudouard reaction were the controlling step, the carbon increment definitely should increase the rate of the overall reaction. Thus the observed effect of the amount of carbon on the rate of reaction further supports the assumption that the Boudouard reaction is the controlling step of the overall reaction of stibnite reduction.

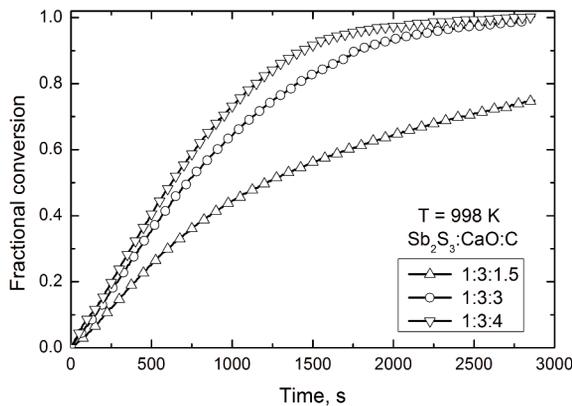


Figure 10. Effect of the amount of carbon on the reduction rate of stibnite in the presence of lime.

### 3.6 Reduction kinetics

The rate of the overall stibnite reduction can be described by a simple model assuming a chemical control. The following first order rate expression with respect to the fractional conversion has been found to fit the experimental data well.

$$\ln(1-X) = -kt \quad (10)$$

In this equation, X is the fraction of stibnite reacted at time t and k is the apparent rate constant. This kinetic expression has also been used in the carbothermic reduction of other metal sulfides and oxides [10, 11, 17], where the overall reduction process was controlled by the oxidation of carbon by  $\text{CO}_2$  (Boudouard reaction). According to the proposed model, the rate constants can be determined from the experimental data shown in Figure 7 and Figure 8 by plotting  $\ln(1-X)$  versus t. Thus the data obtained for

experiments with molar ratios of  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$  are depicted in Figure 11. As seen in this figure, the experimental data fit the kinetic model well up to a fractional conversion of approximately 0.95. The deviation observed for higher conversions was attributed to slow diffusional processes arising at the end of the reaction.

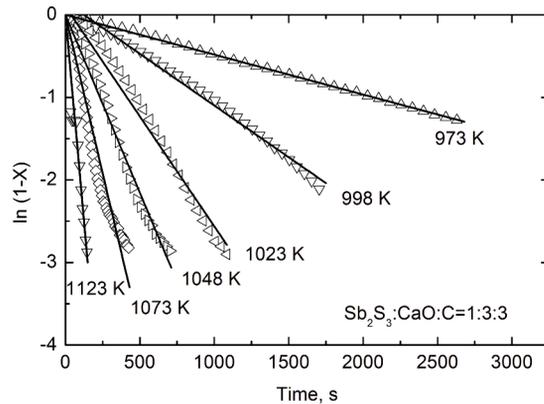


Figure 11. Kinetics of the stibnite reduction with carbon in the presence of lime for samples with molar ratios  $\text{Sb}_2\text{S}_3:\text{CaO}:\text{C} = 1:3:3$ .

The apparent rate constants obtained from the slopes of the straight lines in Figure 10, and similar figure for the ratio 1:3:1.5, were used to draw an Arrhenius plot, which is shown in Figure 12. In this figure, it can be observed that for the two mixtures the rate constant dependence on the temperature fits a straight line well. In addition, the slopes for both set of data are nearly identical; indicating that the controlling step of the overall reaction is the same regardless of the amount of carbon in the mixture. The calculated activation energy was 233 kJ/mol, for the temperature range of 973-1023 K. Activation energy values reported for the uncatalyzed oxidation of carbon by  $\text{CO}_2$  vary from 251 to 359.8 kJ/mol [22-24], which are higher than the value determined in this

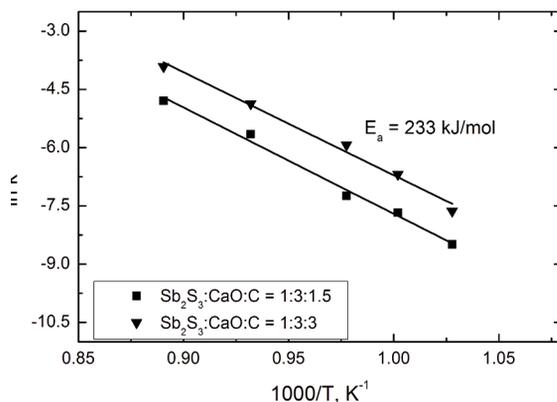


Figure 12. Arrhenius plot for the carbothermic reduction of stibnite in the presence of lime.

study. On the other hand, the reported values for the catalyzed carbon oxidation in the reduction of molybdenum sulfide [11] and lead sulfide [6] were 218.8 and 236.8 kJ mol<sup>-1</sup>, respectively, which are close to the value of 233 kJ mol<sup>-1</sup> obtained in the present research. Therefore, this suggests that the activation energy value determined in this work would correspond to the oxidation of carbon catalyzed by antimony metal.

In overall, the results of this study have demonstrated the feasibility of producing antimony metal from stibnite by direct reduction of the sulfide with carbon in the presence of lime. A major advantage of this method is that the stibnite concentrate can be reduced to antimony at moderate temperatures of 973 to 1123 K, which are significantly lower than the temperature range of the conventional technology practiced by industry (1423 to 1623 K) [1, 2]. Therefore, the carbothermic reduction of stibnite decreases the energy requirements and lowers the losses of antimony by volatilization. Furthermore, it will require also less gas handling and cleaning facilities than the conventional process due to the low volume of gas produced, which will contain little or none SO<sub>2</sub>. Consequently, this method will also minimize the ambient contamination with SO<sub>2</sub> due to the strong desulfurizing power of lime. Finally and most importantly, since this method comprises fewer chemical steps, it is suitable for the small scale production of antimony. The post reduction treatment to recover the antimony from the waste CaS and unreacted compounds present in the solids was not studied in this research. However, unit operations such as grinding and gravimetric methods could accomplish the metal separation from the other components.

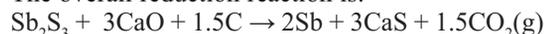
#### 4. Conclusions

From the results of this study, the following can be concluded.

The production of antimony by directly reducing the stibnite with carbon in the presence of lime is technically feasible.

The reduction of Sb<sub>2</sub>S<sub>3</sub> with carbon in the presence of CaO occurs through the formation of SbO<sub>2</sub> as intermediate compound, which is reduced subsequently by CO(g) to yield antimony metal.

The overall reduction reaction is:



Temperature has a large influence on the reduction rate. Complete conversion of Sb<sub>2</sub>S<sub>3</sub> was obtained at 1123 K in less than 250 s using sample mixtures with molar ratio of Sb<sub>2</sub>S<sub>3</sub>:CaO:C equal to 1:3:3.

At temperatures higher than 1123 K, the vaporization of the antimony product becomes

noticeable.

The kinetics of the Sb<sub>2</sub>S<sub>3</sub> reduction can be analyzed by the equation  $\ln(1-X) = -kt$ . The activation energy was determined to be equal to 233 kJ mol<sup>-1</sup> for the temperature range of 973 to 1123 K.

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