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Lead Recovery from a Lead Concentrate throughout Direct Smelting Reduction Process with Mixtures of Na_2CO_3 and SiC to 1000 °C

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Abstract: Lead was recovered through a direct smelting reduction route from a lead concentrate by using mixtures of Na_2CO_3 and SiC to 1000 °C. The lead concentrate was obtained from the mining State of Zacatecas, México by traditional mineral processing and froth flotation. The experimental trials showed that 86 wt.% of lead with a purity up to 97% can be recovered from the lead concentrate by a single step reduction process when 40 wt.% Na_2CO_3 and 0.4 g SiC were used in the initial charge. The process was modeled in the thermodynamic software FactSage 7.3 to evaluate the effect of adding different amounts of Na_2CO_3 on the lead recovery rates while holding constant the SiC amount and temperature. The stability phase diagram obtained showed that an addition of 34 wt.% Na_2CO_3 was enough to reach the highest lead recovery. It was observed that the interaction of Na_2CO_3 and SiC at a high temperature promotes the formation of C and Na_2O , and SiO_2 , respectively, where the Na_2O partially bonds with silica and sulfur forming Na_2S and sodium silicates which may decrease the SO_2 emissions and increase the weather degradation of the slag. The PbS was mainly reduced by the produced C and CO formed by the interaction between Na_2CO_3 and SiC at 1000 °C. The predicted results reasonably match with those obtained experimentally in the lead recovery rates and compounds formation.

Keywords: lead concentrate; direct reduction; Na_2CO_3 ; SiC ; slag

Citation: Gutiérrez Pérez, V.H.; Osorio Hernández, J.D.; Sánchez Alvarado, R.G.; Cruz Ramírez, A.; Olvera Vázquez, S.L.; Rivera Salinas, J.E. Lead Recovery from a Lead Concentrate throughout Direct Smelting Reduction Process with Mixtures of Na_2CO_3 and SiC to 1000 °C. *Metals* **2022**, *12*, 58. <https://doi.org/10.3390/met12010058>

Academic Editor: Felix A. Lopez

Received: 7 November 2021

Accepted: 22 December 2021

Published: 28 December 2021

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1. Introduction

As a result of its widespread use in metallurgy and the chemical industry, as well as in radiation protection, lead is an important non-ferrous metal with broad applications in batteries, machinery manufacturing, and medicine. Both primary lead ores galena-rich (PbS) and secondary resources—mainly waste lead-acid batteries—are used as raw materials for lead production [1]. In developed countries, lead resources mainly come from secondary lead in the recovery process. More than 80% of lead production in the United States is produced from secondary lead, and 90% of lead production in Europe is produced from secondary lead [2,3].

The production of primary lead is a process of extracting lead from lead sulfide concentrates by smelting. The smelting process includes the sinter plant–blast furnace route and direct smelting reduction, including oxidation, reduction, and refining. In the sinter plant–blast furnace route, PbS is oxidized in the solid state to remove sulfur, and PbO is produced at the same time. PbO is then reduced to metallic Pb, typically in a blast furnace charged with coke. Flux (lime, silica, and ironstone) is also added to decrease the melting temperature and form a molten slag in which the iron oxides are removed [4]. Nonetheless,

the traditional pyrometallurgical route still confronts many challenges to be tackled such as long process time, low efficiency in sintering step process, (return rate up to 70%), heat losses, and serious pollution problems due to Pb and SO₂ emissions [5]. Alternatives for lead production have been developed. The direct smelting reduction process means that oxidation and reduction steps take place in a single unit, including KIVCET, SKS, QSL, Kaldo, Isasmelt, and Ausmelt processes [6]. The above-mentioned processes mainly focus on the lead concentrate smelting and on the increasing fume concentration of SO₂ to produce H₂SO₄. For example, Ausmelt is a process, organized in cycles with a duration of around 9 h each. Every batch consists of two stages: smelting of around 7 h when the furnace is fed with raw materials and subsequent 1.5 h of slag reduction with lump coal. Both stages take place in a single vessel. At the end of the batch, the slag is tapped, granulated, and stockpiled for zinc recovery. All utilities, such as air, oxygen, and natural gas are injected through the lance submerged in the bath. The average direct lead recovery worldwide achieved in the first quarter of 2018 was 74.4% [7].

On the other hand, some proposals for the processing of smelting sulphidic materials in molten alkali with the generation of oxygen-containing gas have been done. These proposals allow the recovery of sulfides of lead, copper, nickel, and iron to metal at low temperatures from 340 °C up to 700 °C. The sulfides of these metals interact with molten alkali salts and form sodium and potassium sulfates in the presence of oxygen, which is necessary for reaction development. The given technologies produce a minor quantity, or even do not release sulfur containing-gases, leading to a minor contribution to SO₂ emissions. Combined sulphatization roasting of sulfide ores and carbonate or bicarbonate of alkali metals for extracting copper, nickel, cobalt, and zinc were presented in a Patent [8]. In addition to commercial direct smelting reduction processes, laboratory research and patents have been published using variants of the traditional direct smelting route. For instance, Baimbetov et al. [9] reviewed publications and patents related to interacting mechanisms of sodium and potassium carbonate-hydroxide with non-ferrous sulfides and investigated the system MeS-Na₂CO₃, where Me means a metal contained in a mineral concentrate such as Cu, Pb, Zn, or Fe. For reactions that take place in the process, free Gibbs energy was reported positive (sulfide metals mixed with Na₂CO₃ at 298 °C) to produce metal oxides and sodium sulfide, remarking the impossibility of spontaneous process occurrences. Reactions can be summarized as shown next (1):

Z. Szczygiel et al. [10] tested a direct smelting method on a pilot scale for the recovery of silver from sulfide minerals, adding iron as a reducing agent and soda as a fluxing agent or with soda ash as an oxidizer and carbon. The reactions suggested to 1400 K can be expressed as follows, where Me can be Pb, Zn, or Ag:

Additionally, soda ash slags and SiC have been tested successfully in the recovery of secondary lead [11], since reducing agent C and sodium silicate can be produced from Na₂CO₃ and SiC interaction as is shown in reaction (3). Nonetheless the input raw material in those cases, lead, is mainly presented as oxides and/or in sulfates form, with the advantage of fewer impurities and minerals species than those presented in a lead concentrate.

Global primary lead production is being increased by direct smelting route; however, alternatives must be investigated to improve recovery rates of lead from its concentrates, being environmentally friendly for both, less or not release sulfur-containing gases and lead in fumes, and at the same time to ensure as possible processing simplicity. Therefore, this work aims to produce crude lead with high recovery rates applying a single step pyrometallurgical process by using mixtures of Na₂CO₃ and SiC to 1000 °C. SiC was used

as a reducing agent for bullion lead production from a lead concentrate, 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 lead oxides. The effect of the interaction between the reducing agents (Na_2CO_3 and SiC) with the lead concentrate as PbS was analyzed with the thermodynamic software FactSage 7.3 through the obtention of a stability phase diagram to 1000°C .

2. Materials and Methods

In the present work, as raw material a lead concentrate from Zacatecas State located in the center area of Mexico was used. The concentrate was obtained in a processing polymetallic minerals plant through the traditional unit operations of crushing and milling and then concentrated by a direct froth flotation process. An amount of 500 g of Pb -concentrate was sampled and analyzed. Volumetric analysis was used to estimate the lead content in the used concentrate, where the reactants Xylenol-orange (Merck, Darmstadt, Germany) as indicator and Ethylenediaminetetraacetic acid disodium salt dihydrate EDTA (Merck, Darmstadt, Germany) for titration were used. Besides Atomic Absorption (AA), X-ray Diffraction (XRD), and Scanning Electronic Microscopy (JEOL, Peabody, CA, USA) with Energy Dispersive X-ray spectroscopy (SEM-EDS) technics were used. Reduction experiments for lead recovery were carried out by using a commercial reagent of Na_2CO_3 with $\geq 99.5\%$ of purity. Spent crucibles of SiC with high purity ($\geq 99\%$) were used with a mean particle size of 74–125 microns. Four trials were conducted to constant amounts of 4 g Pb -concentrate and 0.4 g of SiC , while the quantity of Na_2CO_3 was set to 1.50, 1.92, 2.38, and 2.88 g which correspond to 25, 30, 35, and 40 wt.%, respectively. The reagents for each trial were weighted in a Sartorius TE64 Talent Analytical Balance (Sartorius, Göttingen, Germany), $60\text{ g} \times 0.1\text{ mg}$ 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 Thermolyne Mod. 1200 (Thermo Fisher Scientific, Waltham, MA, USA) with control of temperature to within $\pm 10^\circ\text{C}$, and each experiment lasted 1 h to 1000°C . The temperature was measured with a type-K thermocouple. The experimental setup for lead recovery from a lead concentrate with Na_2CO_3 and SiC to 1000°C is shown in Figure 1.

Figure 1. Experimental setup for lead recovery from a lead concentrate with Na_2CO_3 and SiC to 1000°C .

Each experiment lasted 1 h to 1000°C . Reaction time was started when the temperature measured by the thermocouple was equal to the temperature programmed in the electric resistance furnace. After the reaction time, the furnace was turned off. The products metal and slag were poured and cooled down in a pre-heated iron mold. Metallic lead and slag were separated, weighed, and analyzed by AA, XRD, and SEM-EDS techniques. In Figure 2 is the flow chart of the proposed process.

Figure 2. Flow chart for lead recovery from a lead concentrate with mixtures of Na₂CO₃ and SiC to 1000 °C.

2.1. Lead and Slag Characterization

The resulting products slag and metallic lead were analyzed in an X-ray Bruker D8 Focus with monochromatic Cu K α radiation working in $\theta/2\theta$ configuration. The following parameters were used for data generation: 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 lead button samples were analyzed on the center zone. The lead contents of both slags and metallic buttons were determined from analytical methods for atomic absorption spectrometry. An SEM Jeol 6300 (JEOL, Pleasanton, CA, USA) and with the energy dispersive spectra analysis (JEOL, Pleasanton, CA, USA) was used for qualitative chemical analysis, morphology, and size of resulting slags. An Au-Pd film was deposited on the surface of the slags to make them conductive. Backscattering electrons technique with 15 kV and 10 A were used for image production.

2.2. Thermodynamic Modeling

The Thermodynamic software—Facility for the Analysis of Chemical Thermodynamics (FactSage 7.3) [12] (Thermfact/CRCT, Montreal, QC, Canada) and GTT-Technologies Aachen, Germany—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 amounts 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.

The thermodynamic modeling considered only the main reduction reaction for PbS based on the chemical analysis of the lead concentrate where the impurities were neglected. The computer simulation was carried out using the FactPS, Ftmisc, and the FToxid databases contained in the module Equilib. The effects of temperature and concentration of Na₂CO₃ and SiC in the recovery of lead from the lead concentrate were theoretically estimated for a closed system. The chemical composition considered in the thermodynamic modeling was PbS (galena) as the main mineral species found in commercial lead concentrate, together with the commercial reducing agents sodium carbonate, and silicon carbide. The recovery process of lead from PbS with Na₂CO₃ and SiC to 1000 °C was expected to occur based on the following reaction:

Based on oxygen affinity for heavy metals ($\text{Cu} < \text{Pb} < \text{Fe} < \text{Zn}$) to $1000\text{ }^{\circ}\text{C}$ [6], oxidation of metallic sulfides including PbS occurs, since the process is open to the atmosphere and hence the reduction phenomena with SiC and Na_2CO_3 is carried out. Under experimental process conditions, it is expected from the lead concentrate that the lead and copper will be reduced and transferred into the metal phase (crude lead), whereas Zn and Fe may remain in the slag phase as sulfides or even as oxides. The reducing conditions could allow the reduction of ZnO, and the resulting Zn has a low boiling point of $908\text{ }^{\circ}\text{C}$, lower than process temperature, which could increase losses of Zn by volatilization.

3. Results and Discussion

3.1. Lead Concentrate Characterization

The chemical analysis of the lead concentrate is shown in Table 1.

Table 1. Chemical Analysis in wt.% of as received lead concentrate sample.

Element	Pb	Cu	* Ag	Fe	Zn	Si	S _{total}	Sb	As	Cd
Lead concentrate	53.69	7.43	105	7.35	3.31	5.82	19.21	0.18	0.14	0.19

* concentration in g/t.

The main metallic elements presented in the lead concentrate are Pb followed by Cu and Fe with almost the same concentration. Zinc was detected with a concentration of 3.31 wt.%. Other metals traditionally associated to lead concentrates such as Sb, As, and Cd were found in a lower concentration. Although silver is a key element to be considered in the feasibility of lead concentrate processing, for this case, silver concentration was found near the common inferior limit for commercial lead concentrates [6].

Figure 3 shows the X-ray pattern of lead concentrate used for lead recovery with Na_2CO_3 and SiC.

Figure 3. XRD pattern of used lead concentrate.

XRD-analysis results showed that used lead concentrate is constituted mainly by PbS (galena), Pb_2O_3 (lead oxide), PbO_2 (scrutynite), and PbSO_4 (anglesite). Copper was detected as CuFeS_2 (chalcopyrite) and CuS_2 (villamaninite). Mineralogical species considered as impurities such as ZnS (sphalerite), FeS (pyrrhotite), and SiO_2 (silicon oxide) were also detected.

Figure 4 shows the SEM-EDS mapping images for distribution of Pb, Zn, S, Cu, Fe, Si, and O in the lead concentrate, it also shows a qualitative chemical analysis of the lead concentrate.

Figure 4. SEM-EDS mapping and microanalysis images for distribution of Pb, Zn, S, Si, Fe, Cu, and O in the lead concentrate.

The images obtained through mapping elements in SEM-EDS for the lead concentrate show particles constituted with Pb and S, it is also observed that the Fe and Cu elements are also distributed within the Pb and S regions. The elemental distribution of Fe and Cu contained in the concentrate may occur as sulfide compounds. On the other hand, the elemental mapping signal obtained for Si and O are closely associated which may correspond to the SiO_2 compound (insoluble matter) and confirmed in the XRD pattern of Figure 3. The results in Figure 4 also show mineral particles that appear closely associated to lead and oxygen signals, and they may correspond to found mineral species such as anglesite (PbSO_4) and lead oxides (PbO_2 and Pb_2O_3) which were detected by XRD analysis. Zinc has a lower intensity signal, and it is distributed homogeneously throughout the analyzed concentrate surface. The microanalysis results reasonably match with both the chemical composition reported in Table 1 and the results of XRD-analysis of the lead concentrate.

3.2. Direct Smelting Reduction with Na_2CO_3 and SiC

Table 2 shows the chemical analysis for the metallic phase after the direct smelting reduction process. In all cases, 4 g of lead concentrate were put in contact with 0.4 g of SiC, and the Na_2CO_3 additions were 1.50, 1.92, 2.38, and 2.88 g which correspond to 25, 30, 35, and 40 wt.%, respectively, to 1000 °C. It is observed that the purity achieved in all cases was higher than 95%. The highest lead recovery and grade were obtained for the Na_2CO_3 addition of 40 wt.%, metallic luster for metallic button and easy phases separation after cooling was observed. When 30% Na_2CO_3 was used in the initial charge, a high recovery quota for the lead was also achieved; however, metal- and slag- phase separation was not easy, and the metallic phase did not show a metallic surface luster. For the case of fewer quantities of Na_2CO_3 , both the pouring of products and the phases separation were difficult, and hence the recovery of the metallic phase was lower. This could be due to the use of SiC, which could increase the melting point and the viscosity of the slag phase, this effect was minimized as the initial content of Na_2CO_3 was increased. Although silver is present

in a relatively low concentration in the lead concentrate (105 g/ton), its concentration in the metal phase increases steadily as increasing both, the addition of Na_2CO_3 and the rate recovery of lead.

Table 2. Chemical composition and weights of crude lead buttons for different amounts of Na_2CO_3 (25, 30, 35, and 40 wt.%), and 0.4 g of SiC to 1000 °C.

Na_2CO_3 (wt.%)	Pb-Button (g)	Chemical Composition (wt.%)						
		Pb balance	Cu	* Ag	Fe	As	Si	Zn
25	1.46	96.30	1.70	20	0.50	1.38	0.01	0.11
30	1.58	96.68	1.28	31	1.98	0.01	0.02	0.03
35	1.64	95.88	1.08	33	2.14	0.86	0.01	0.03
40	1.91	97.38	1.84	46	0.72	0.04	0.01	0.01

* concentration in ppm.

Table 3 shows the chemical composition and the amount of slag formed after the reduction trials. It is observed that by increasing the initial charge from 30 to 40 wt.% Na_2CO_3 , the content of Pb in the slag phase decreases, which agrees with the increase in lead recovery in the metallic phase. The lowest Pb content (2.82 wt.%) in the slag phase was obtained for an initial charge of 40 wt.% Na_2CO_3 . For this case, the most abundant components detected in the slag phase correspond to Na, S, and Fe. In smaller quantities, Si and Cu were found.

Table 3. Chemical composition and weight of the slags obtained after the reduction process with different amounts of Na_2CO_3 (25, 30, 35, and 40 wt.%), and 0.4 g of SiC to 1000 °C.

Na_2CO_3 (wt.%)	Slag (g)	Chemical Composition (wt.%)								
		Pb	Cu	* Ag	Fe	Zn	Si	As	S	Na
25	3.02	13.11	8.16	82	7.86	0.85	9.73	0.26	20.07	20.05
30	2.80	9.34	8.51	78	8.81	0.72	9.89	0.39	21.05	27.12
35	3.14	7.36	6.24	71	7.24	1.02	9.64	0.22	21.08	30.17
40	3.88	2.88	4.12	54	7.71	0.54	9.69	0.07	24.04	31.02

* concentration in ppm.

Figure 5 presents the contents of lead in the metal and slag phases after the reduction process when different amounts of Na_2CO_3 (25, 30, 35, and 40 wt.%) in the initial charge were used. It is shown that when the wt.% of Na_2CO_3 increases, the amount of lead in the metallic phase increases with the respective diminution of lead content in the slag phase. The tendencies show an important change from 25 to 35 wt.% Na_2CO_3 additions, nonetheless steeper slopes are observed in the tendencies from 35 to 40 wt.% Na_2CO_3 for metal and slag phases, respectively. When 25 wt.% Na_2CO_3 was used, the lead distribution lies at about 63% in the metallic phase and 19% in the slag phase, while about 87% lead was recovered in the metallic phase when 40 wt.% Na_2CO_3 was used in the initial charge, and 5% of the initial lead was reported in the final slag. From Table 2, it is observed that the purity of crude lead in all cases was higher than 93%.

Figure 5. Lead content in metal and slag phases with different amounts of Na₂CO₃ and 0.4 g SiC to 1000 °C.

In the primary process of lead production, the use of carbon promotes the reduction of lead oxides, but it also provides heat in the process (heat content of molten slag and lead bullion, exit gases, and even heat loss). An advantage that could offer the proposed processing route is concerning the amount of carbon required in the production of bullion lead. For instance, in the traditional sinter-smelting route, the demand of carbon per ton of lead bullion varies from 170 to 370 kg/ton [6], while in the proposed reaction (4) the carbon provided by reactants Na₂CO₃ and SiC to produce a mol (207.2 g) of lead from PbS is about 19.92 g of C, which would represent about 96.15 kg/ton. In the present work, laboratory-scale tests were done for the recovery of lead from a lead concentrate by mixtures of Na₂CO₃ and SiC to 1000 °C, and experimentally the consumption of carbon to produce 1 g of bullion lead was between 0.20 and 0.24 g, which would correspond to values between 200 and 240 kg/ton. Rigorous control of process parameters could result in a more efficient and simple operation process, it would be an attractive alternative route to produce lead by direct reduction with the advantage of probably less carbon consumption, decreasing the volume of produced greenhouse gases such as CO₂.

The metallic phase and slag obtained for the highest metallic lead recovery (40 wt.% Na₂CO₃) were characterized by X-ray diffraction and SEM-EDS techniques.

Figure 6 shows the X-ray diffraction pattern for crude lead obtained in the experiment using 4 g of lead concentrate, 2.88 g of Na₂CO₃ (40 wt.%), and 0.4 g of SiC at 1000 °C. It is observed that the main component in the metallic phase is lead, the presence of any other element was not detected, due to the relatively low concentration of elements such as Ag, Zn, Fe, Cu, Si, and As, which do not exceed 2.38 wt.%, as can be seen in Table 2.

Figure 6. X-ray pattern for crude lead obtained for an initial charge of 40 wt.% of Na_2CO_3 and 0.4 g of SiC to 1000 °C.

Figure 7 shows the elemental mappings analysis obtained for the metallic phase for the experiment carried out with 40% by weight Na_2CO_3 and 0.4 g of SiC to 1000 °C. The microanalysis shows mainly Pb and Cu. It is possible to observe that both Pb and Cu are uniformly distributed throughout the analyzed surface. Copper is normally found in crude lead produced by the pyrometallurgical route and then it is separated in the refining process for its further recovery, which is done either by air injection and mechanical removing or even by S addition for the case of low copper concentrations [13]. The copper removing operation is done to temperatures just above the melting point of lead.

Figure 7. SEM-EDS results for the metallic phase obtained for 40 wt.% Na_2CO_3 and 0.4 g of SiC to 1000 °C.

Figure 8 shows the X-ray diffraction pattern of the slag obtained for the addition of 40 wt.% of Na_2CO_3 and 0.4 g of SiC to 1000 °C. Different sodium silicates were mainly found (Na_2SiO_3 and Na_4SiO_4) because of interaction between sodium oxide and silicon oxide (SiO_2), which were in the first instance formed to a high temperature in the slag phase since Na_2CO_3 and SiC were added as mixtures in the initial charge for direct smelting reduction trials. Sodium was also detected as disodium sulfide (Na_2S) which contributes to

diminishing the formation and consequently emissions of SO_2 in the gas phase. Sodium reacts because of its high affinity to sulfur. Copper and Iron partially react with sulfur to form FeS_2 (Marcasite) and CuS (Covellite), respectively. In the pyrometallurgical route for lead production, it is known that iron oxide or shredded scrap iron can be added to promote the reduction of lead compounds; this practice has been done in different regions worldwide [6]. The interaction between iron and lead sulfide produces lead and iron matte, which can limit the formation of SO_2 , as can be seen in equation (5) and it can represent the cheapest option if the process parameters, and the consumption of additives and reducing agents such as iron are controlled to produce a slag with low lead content.

Figure 8. X-ray pattern for the slag obtained for an initial charge of 40 wt.% of Na_2CO_3 and 0.4 g of SiC to 1000 °C.

In this work, a lead concentrate was treated with Na_2CO_3 and SiC mixtures to 1000 °C. A high lead recovery and grade were obtained in a single-step process while the Na_2CO_3 addition allows obtaining sodium silicate structures and the Na_2S compound which is thermodynamically more stable than lead and iron-sulfides, thus higher slag stability is expected.

Challenges must be overcome in technologies used to produce either primary or secondary lead by pyrometallurgical processing such as the flexible Kaldor process (TBRC—Top Blow Rotary Converter) or the short rotary furnace. Some issues that must be addressed in these processes are the infrastructure, since a high level of mechanical equipment is necessary with attendant maintenance issues, and the fluctuant SO_2 rich gas production. The laboratory-level tests carried out in this work were focused to contribute to environmental protection through the avoidance of hazardous emissions as SO_2 and the recovery of a more stable slag than those obtained in the conventional processes.

In addition, iron reacts also with oxygen to form FeO_2 (Goethite). Lead and zinc compounds were difficult to be distinguished by XRD-technic in the slag phase after the direct smelting reduction process, which can be attributed to their low concentration (2.88 and 0.58 wt.%, respectively) according to chemical analysis results shown in Table 3. During the reduction trials, a yellowish film was observed in the slag surfaces which corresponds

to $\text{Na}_2\text{C}_2\text{O}_4$ (sodium oxalate also known as Natroxalate) as a result of Na_2CO_3 and formed CO interaction according to reaction (6). In addition, unreacted Na_2CO_3 was also detected.

Figure 9 shows the SEM-EDS results of the slag obtained for the trial carried out for an addition of 40 wt.% Na_2CO_3 . The resulting slag phase is composed of agglomerated particles that contain mainly Na, C, O, Si, S, and Fe. Pd was detected since a film Au-Pd was necessary on the slag surface to make it conductive. The SEM image shows particles with crystalline morphology and the intensity of Na, C, O, and S are notably high which, according to Figure 9, could be associated with a high concentration of compounds such as silicates, sulfides, and oxides.

Figure 9. SEM-EDS results for the slag phase obtained for 40 wt.% Na_2CO_3 and 0.4 g of SiC to 1000 °C.

3.3. Thermodynamic Modeling

The first approach in thermodynamic modeling was performed considering that the lead contained in the lead concentrate correspond to PbS, since it would represent the most difficult lead compound (compared either with lead oxides or lead sulfate) to be reduced by the proposed mixtures of Na_2CO_3 and SiC. The thermodynamic trials of the direct smelting reduction process were carried out to 2.45 g PbS which are contained in 4 g of lead concentrate and 0.4 g of SiC, both amounts were held constant while the amount of Na_2CO_3 was evaluated in the range from 1.5 to 2.88 g. Figure 10 show the equilibrium diagrams obtained in grams and mole, respectively, when the initial compounds reach the thermodynamic equilibrium at 1000 °C.

(a)

(b)

Figure 10. Thermodynamic analysis for products metal and slag, (a) in grams and (b) in mole, when 2.45 g PbS, 40% of Na_2CO_3 by weight (2.88 g), related to 4 g of lead concentrate and 0.4 g of SiC are used in the initial charge to 1000 °C.

It is observed that the interaction of Na_2CO_3 with SiC produces C, Na_2O , and SiO_2 in the slag phase. As the Na_2CO_3 is increased the Na_2O and SiO_2 react to form sodium silicate structures, while the C starts to reduce the lead sulfide contained in the galena.

The PbS reacts in the slag phase with C and CO from Na_2CO_3 and SiC to produce metallic lead, while S from PbS reacts with Na to produce Na_2S , the reaction occurs until the whole PbS is consumed at 1.9 g Na_2CO_3 . CO and CO_2 in the gas phase increases as the

addition of Na_2CO_3 increases. When the amount of Na_2CO_3 increases from 1.9 to 2.9 g, the silicate $\text{Na}_2\text{Si}_2\text{O}_7$ is formed, coexisting with Na_2SiO_3 in the range from 1.92 to 2.75 g Na_2CO_3 , and the formation and evolution of CO_2 in the gas phase take place. Theoretically, it was expected the formation of Na_2SiO_3 for the Na_2CO_3 additions in the range from 1.5 to 2.75 g, for higher additions of Na_2CO_3 the formation of $\text{Na}_2\text{Si}_2\text{O}_7$ was predictable. However, when 2.8 g Na_2CO_3 (40 wt.%) was used in the initial charge to 1000 °C and based on the X-ray diffraction results (Figure 8), two different silicates structures are mainly formed: Na_4SiO_4 and Na_2SiO_3 . The compounds Na_2CO_3 , Na_2SiO_3 , and SiO_2 were predicted by the thermodynamic analysis, and they were also observed experimentally in the slag phase by the X-ray diffraction measurements. It is also observed from Figure 10 that additions higher to 2.4 g Na_2CO_3 theoretically allow the recovering of almost all lead from the PbS , which fits with the experimental results obtained, where the highest recovery and purity of lead were obtained with the corresponding lowest lead content in the slag phase to 2.8 g Na_2CO_3 (40 wt.%). Another compound found experimentally in the slag phase corresponds to sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), which is formed because of interaction between sodium carbonate and formed carbon monoxide. Soda slags are well known for their easy hydration and leachability; nevertheless, the silica formed in the slag phase as a result of SiC addition allows the formation of silicates compounds, which would be more stable to weather degradation. The environmental stability of lead slags depends on different factors: the mineral phase in the slag phase, the influence of the atmosphere, and the interaction time between slag and water or medium [14], which could act as a leaching agent. Besides silicates, other compounds were found in the slag phase, such as FeS_2 (Marcasite), and Na_2S . The Na_2S was also expected by thermodynamic calculations and it could be leached to recover valuable sodium compounds, for example as sodium thiosulfate.

Interaction for stoichiometric amounts between Na_2CO_3 and SiC is addressed in reaction (3). Nevertheless, the experimental parameters used in this research were explored to 1000 °C and for non-stoichiometric amounts of Na_2CO_3 and SiC that lead to the formation of C , CO , SiO_2 , Na_2O , and sodium silicates. Thermodynamic calculation in FactSage 7.3 was done to explore the theoretical products that could be formed for the reaction of 0.4 g of SiC to different additions of Na_2CO_3 at 1000 °C, as is shown in Figure 11. The initial 0.4 g of SiC are totally reacted with 0.6 g of Na_2CO_3 to form C , SiO_2 , and Na_2O . With this addition of Na_2CO_3 , the formation of CO starts. To 1.7 g of Na_2CO_3 , the amount of SiO_2 and Na_2O decreases almost totally and the sodium silicate structure Na_2SiO_3 together with CO are the main compounds formed, in this point the generation of CO_2 takes place. Amounts between 1.6 and 2.4 g of Na_2CO_3 allows the presence of a second sodium silicate structure $\text{Na}_6\text{Si}_2\text{O}_7$, which between 2.2 and 2.4 g of Na_2CO_3 decomposes to form again SiO_2 , Na_2O , and unreacted Na_2CO_3 also appears. The amount of SiO_2 , Na_2O , and unreacted Na_2CO_3 increases as the addition of Na_2CO_3 increases. The Na_2SiO_3 decreases from 1.8 to 2.8 g of Na_2CO_3 , which is attributed to the partial formation of the second silicate structure and to the increase of SiO_2 and Na_2O .

It must be observed that the non-considered external oxygen could affect the final products obtained in theoretical calculation. External oxygen measurement and control could give important and more precise information about the process mechanism. In the present work FactSage 7.3 calculation was used as a tool to obtain a first approximation to the expected products after PbS direct reduction with mixtures of Na_2CO_3 and SiC to 1000 °C.

Figure 11. Amount of sodium silicate compounds formed by the interaction between 0.4 g of SiC and different amounts (from 1.5 to 2.8 g) of Na_2CO_3 at 1000 °C, calculated in FactSage 7.3.

4. Conclusions

In this work, lead was recovered through a direct smelting reduction route from a lead concentrate by using mixtures of Na_2CO_3 and SiC to 1000 °C. The results obtained are summarized as follows:

1. A high recovery of crude lead (86 wt.%) with a purity up to 97% was obtained in a single-step process by using a mixture of 40 wt.% Na_2CO_3 and 0.4 g SiC to 1000 °C;
2. The C consumption to produce 1g bullion lead was between 0.20 and 0.24 g (200–240 kg C/ton) which represents a lower C consumption than the traditional sinter-smelting route for primary lead production and hence a lesser amount of CO_2 would be produced;
3. The slag obtained was composed mainly of sodium silicates Na_4SiO_4 and Na_2SiO_3 , sulfides as FeS_2 , and Na_2S , and fewer amounts than 2 wt.% of ZnS , CuS , and PbS . The sodium silicates could be more stable to the slag weather degradation while the sulfides contribute to decreasing the SO_2 emissions;
4. The thermodynamic modeling showed that the higher lead recovery was obtained for an addition of 34 wt.% Na_2CO_3 which matches reasonably well with the experimental addition required;
5. The thermal decomposition and oxidation of Na_2CO_3 and SiC promote the formation of Na_2O , SiO_2 , CO, and CO_2 . The Na_2O bonds partially with silica to form stabilized sodium silicates, the PbS is reduced with C and CO to produce metallic lead, while the S from PbS reacts with Na_2O to produce Na_2S , partially decreasing the formation of SO_2 ;
6. FactSage calculation was used as a tool for a first approximation to the estimation of products after PbS direct reduction with Na_2CO_3 and SiC to 1000 °C and good agreement was found in the compounds predictions with those obtained experimentally.

Author Contributions: Conceptualization, V.H.G.P. and R.G.S.A.; Data curation, S.L.O.V.; Funding acquisition, V.H.G.P.; Investigation, J.D.O.H., A.C.R. and S.L.O.V.; Methodology, V.H.G.P., R.G.S.A. and A.C.R.; Supervision, R.G.S.A.; Visualization, J.D.O.H. and J.E.R.S.; Writing—original draft, R.G.S.A.; Writing—review & editing, V.H.G.P. and A.C.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: The authors wish to thank the Institutions CONACyT—Research project 287521, SNI, COFAA, and SIP-Instituto Politécnico Nacional for their permanent assistance to the Process

Metallurgy Group at ESQIE-Metallurgy and Materials Department, as well as C. Gallardo-Vega for technical support.

Conflicts of Interest: The authors declare no conflict of interest.

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