Recovery of Antimony from Refinery Slag of Unified Mining Company (Emusa)

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Abstract

The process of obtaining antimony trioxide from Unified Mining Company S.A. (EMUSA) has two production lines. The refining slag from the second production line was stored since the plant started operations, registering high antimony contents which is the reason for this research project. To recover antimony from the slag, it was necessary to carry out a reducing fusion with slag using pyrometallurgical methods with ternary diagrams; FeO: Na$_2$O: SiO$_2$ and FeO: SiO$_2$: CaO the Sb recovery was done in two parts; the first part consisted of melting in a flame furnace and the second a melting in the IIMETMAT thermobalance. The flow of oxygen necessary for antimony recovery was 0.1 l/min higher flows oxidize antimony and lower recovery. The experiments showed that the reaction that controls the process is PbSb$_2$O$_6$ + 6C= 2Sb + Pb + 6CO. For the melting in the flame furnace, the best slag ratio used was 35:15:50 with the system and with the system, the best ratio was 35:15:50, with Sb recoveries of 98% in both cases.
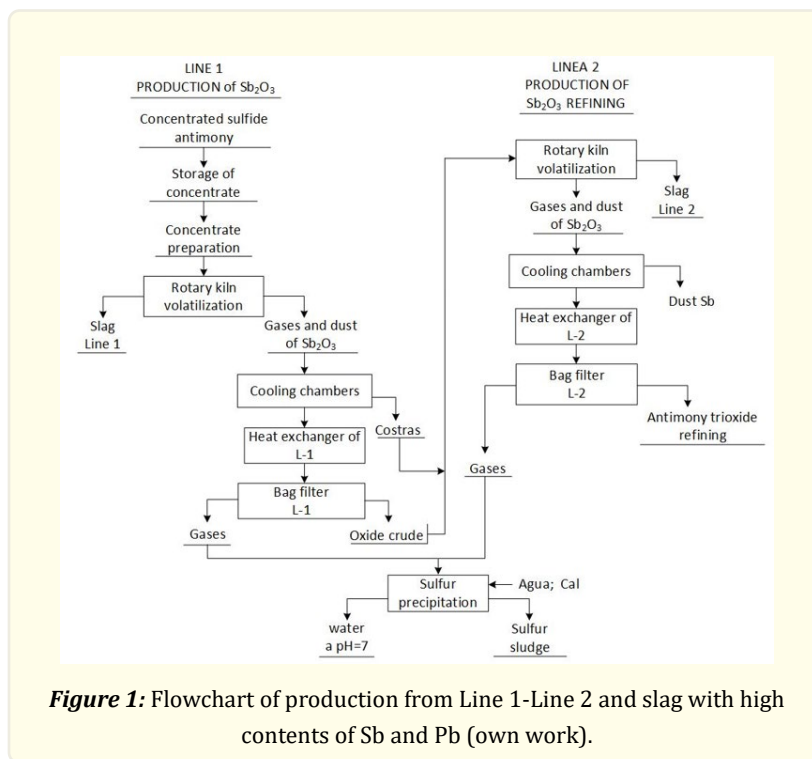
Keywords: Refining slag; Melting in the thermobalance; Antimony recovery

Introduction

Bolivia is one of the largest producers of antimony worldwide, in 2022 it ranked fifth with 2500 t according to es.statisca.com [1] and www.mineria.gob.bo [2], Bolivian production comes mainly from the mining centers of Caracota province Quijarro, Chilcobija province Sud Chichas in the Department of Potosí. Unified Mining Company S.A. (EMUSA) recovers antimony from an antimonite concentrate with antimony trioxide volatilization systems, the following flowchart in figure 1 shows the antimony production lines of EMUSA.

In line 1 of antimony oxide production shown in figure 1, the operating temperature is 1000℃ for the removal of sulfur as and obtaining the volatile "crude oxide" from a concentrate with an average grade of 55% Sb that avoids a higher frequency of slag bleeding. Line 2, is called the refining line, is intended for the production of high-quality antimony trioxide. In this line, approximately 3 t/day of "crude oxide" with an average grade of 80% Sb (Ref. EMUSA production data) is fed from the baghouse filter of line 1 production, the slag discharge is carried out every 2 months.

The excess oxygen insufflated in the metallurgical operation leads to increased production of non-volatile oxides. The non-volatile oxides that remain lodged in the slag of line 2; for this reason, the amount of antimony in the final slag is 20 to 30% antimony according to EMUSA production data. Likewise, a high lead content of 15 to 25% is recorded in the refining line slag, this component complicates Sb recovery as Sb$_2$O$_3$. For this reason, studying and suggesting an alternative for the treatment of the line 2 refining slag to recover antimony is the objective of this research work.

Figure 1: Flowchart of production from Line 1-Line 2 and slag with high contents of Sb and Pb (own work).

Bibliographic review

The major compound in the line 2 production slag is bindheimite, which is an alteration of antimony sulfides, oxides, and its crystal structure is of the pyrochlore type, (antimony associated with large cations) the stable structure is $[A^{3+}]_2 [B^{4+}]_2 [O]_7$ (Callister and Rethwisch,1995) [3]. In the case of the sample of the refining slag of line 2, the atom [A] is Sb^{3+} and [B] is Pb^{4+}. According to Mason & Vitaliano (1952) [4] its crystal structure would be found with defects in its networks (empty spaces) that lead to formulating bindheimite in more than one way with great variability in chemical composition and physical properties, assigning a chemical formula to bindheimite is not an easy task due to the above conditions and according to the same researchers, bindheimite can be formulated as $Pb_x Sb_{2-z} (O,OH,H_2O)_{6\,6\,7}$ where ''x'' varies up to 2 and ''z'' cannot be greater than 1 and the species (O,OH,H_2O) correspond to the results of X-ray diffraction analyses.

The following figure shows the free energies of Sb and Pb oxides that come from volatilization, as well as their interaction with carbon, monoxide, and carbon dioxide with their linearized Gibbs free energies, which were determined from Barin Knacke (1973 and 1977) [5] thermodynamic data, the diagram shows the stability of Pb and Sb oxides.

In figure 2, the reduction reactions of PbO, $Sb_2 O_4$, and $Sb_2 O_5$ with $CO_{(g)}$ and $CO_{2(g)}$ are shown, where it is observed that the reduction of these oxides to Sb and Pb with the formation of de $CO_{(g)}$, at 700°C their Gibbs free energies are more negative compared to when metallic are formed with $CO_{2(g)}$. The composition must also be controlled, for this reason, the composition vs. diagram is analyzed in figure 3.

Figure 3 shows the diagram composition % vs. n_{02}/n_{Sb2S3} (Velasco, 2002) [6] which says, the less oxygen there is in the medium, the more will be formed $SbS_{(g)}$ volatile from $Sb_2 S_{3(s)}$. This effect improves when the ratio of $n_{02}/n_{sb2} s_3$ is increased in a range of 3 to 4, more oxygen favors the formation of and will form SbO_2 a stable non-volatile solid phase that will remain in the antimony volatilization furnace.
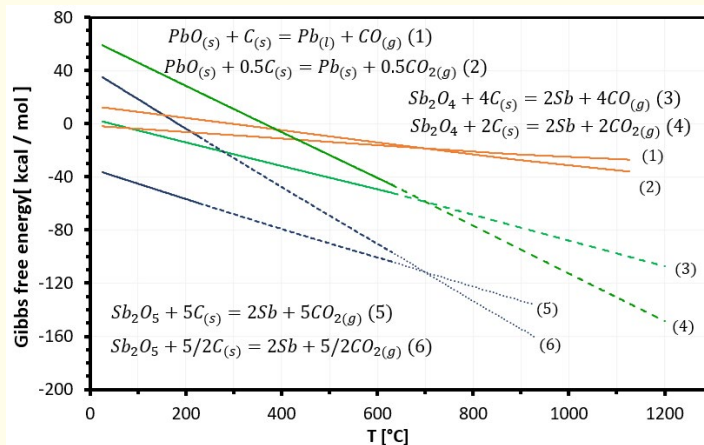
Figure 2: Ellingham diagram for reduction of antimony and lead oxides
(Barin, Knacke and Kubaschewski (1977) [5]).

With the corresponding chemical analyses, XRD analysis results and thermodynamic aspects, the most suitable compound for the refining slag sample is $PbSb_2O_6$ o ($PbO \cdot Sb_2O_5$).
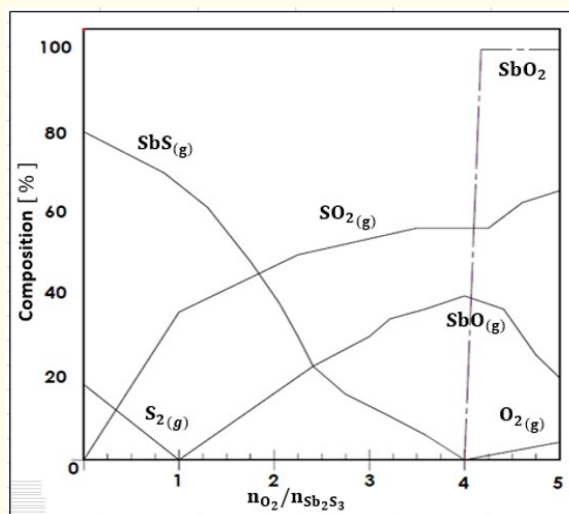

Figure 3: Diagram of the Sb-S-O system as a function of
oxygen at 900 (Velasco, 2002) [6].

Experimental work
Refining slag sample

The preparation consisted of crushing, grinding to a -65 mesh grain size of the Tyler series, homogenized, and quartered to obtain a representative sample. The chemical analysis report of the EMUSA line 2 refining slag sample is shown in table 1.

%Sb	%Pb	%Fe	%SiO2	%S	%Al	%Zn	%As	%Cu	%K	%Sn	%Mg	%Other
21.59	24.68	3.05	6.01	11.23	1.39	2.7	1.32	0.11	0.43	0.07	1.69	25.73

Table 1: Chemical composition, EMUSA refining slag (Lab. NOSTERTEC).

Fluxes and reducer

The fluxes and reducer used are shown in the following table, and their respective compositions were determined in the Nostertec and Conde Morales laboratories.

Flux	%Na_2O	%CaO	%SiO_2	%Fe	%S	%MgO
Caustic soda	30.51	0.518	6.84	0.08	11.03	
Sand		0.07	83.48	0.22	0.04	
Limestone		51.38	0.48			0.83

Table 2: Chemical composition of fluxes.

The vegetable coal has the composition C_f=85.94%, V=10.07%, H=3.07%, Cz=0.927% and the air flow insufflated in the tests was 0.1 l/min.

Experimental procedure

The project was developed in two parts; the first was worked on in a flame furnace where a reducing fusion was made with ternary diagrams FeO: Na_2O: SiO_2 and CaO; SiO_2: FeO. In the second part, in a thermobalance, the variables were established such as; reducer effect, flux effect, and temperature effect.

Results and discussion

Fusion tests in a flame furnace

Figure 4 shows one of the slag systems used. This figure shows the ternary FeO: Na_2O: SiO_2 diagram where a fusible slag can be obtained since 800°C. The system CaO; SiO_2: FeO was also analyzed. Based on the selected points, the fusion tests were carried out in a flame furnace with both slag systems considering the reduction reaction (7) of bindheimite with the formation of $CO_{(g)}$.

$$PbSb_2O_6 + 6C = 2Sb + Pb + 6CO \quad (7)$$
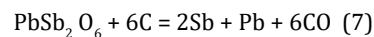
The results with the system FeO: Na_2O: SiO_2 are indicated in table 3 with the addition of sand, Caustic soda and vegetable coal, and the results with the system are in table 4 with sand, limestone, and vegetable coal as additives.

In tables 3 and 4, in addition to the slag ratios and their quantities, the metallic and slag phases are indicated, in these tests, the registered performance was from 96.22 to 98.32% for the system and for the system, the achieved performances vary from 96.45 to 98.42%, these performances are similar; however, the difference consists of the temperature from 800 to 1000°C in 30 minutes of melting for the first system and from 1100 to 1250°C in 50 minutes of melting for the second system.
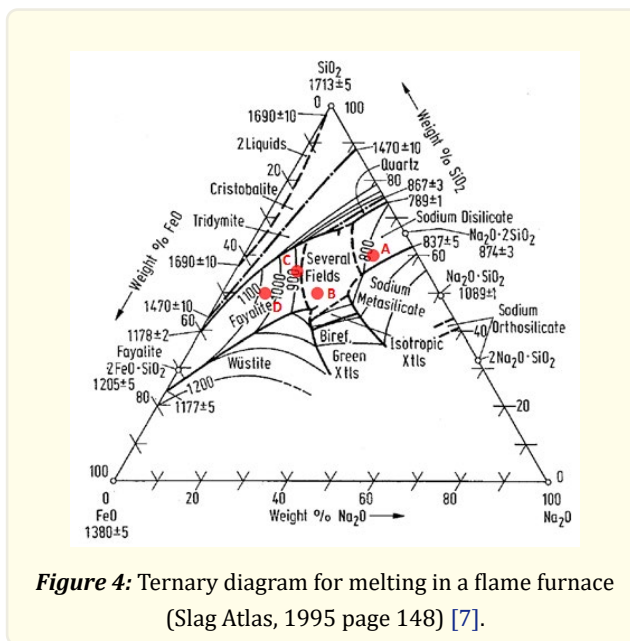
Figure 4: Ternary diagram for melting in a flame furnace (Slag Atlas, 1995 page 148) [7].

Test	FeO	Na2O	SiO2	Sand	Caustic soda	Coal	Metallic	Slag	Recovery
	%	%	%	[g]	[g]	[g]	[g]	[g]	%
CPT-01	30	15	55	0	5.60	11.45	56.44	20.45	98.03
CPT-02R	30	15	55	0	5.70	11.47	56.49	21.06	96.22
CPT-03	30	15	55	2.96	5.50	11.45	55.89	31.37	97.31
CPT-04	35	15	50	0.80	5.23	10.81	58.94	20.06	98.32
CPT-05	30	25	45	1.75	8.15	10.80	59.35	24.71	97.08
CPT-06	28	22	50	0.59	10.08	10.80	55.49	20.25	97.81
CPT-07	28	22	50	1.70	9.51	10.80	59.80	30.31	97.54

Table 3: Results of the melting tests with the system from 800 to 1000℃. Test FeO.

Test	FeO	SiO2	CaO	Sand	Limestone	Coal	Metallic	Slag	Recovery
	%	%	%	[g]	[g]	[g]	[g]	[g]	%
CP-01	47	38	15	0	2.86	11.50	60.60	46.86	98.16
CP-02	37	38	25	0	6.02	12.50	61.76	20.41	98.24
CP-03R	33	37	30	0	8.11	12.56	62.78	19.86	97.89
CP-04	32	37	31	0.60	8.68	10.80	58.41	8.73	98.17
CP-05R	40	45	15	0	3.18	10.78	58.01	17.95	98.33
CP-06	35	38	27	0	6.50	10.80	63.50	19.69	98.42
CP-07R	30	48	22	1.16	6.18	10.80	58.75	18.95	96.45

Table 4: Results of the melting tests with the system from 1100 to 1250℃.

Tests on the thermobalance
Determination of the reaction

These tests have the purpose of determining the type of reaction that governs the process, being necessary to propose the following reactions (8) and (9).

$$PbSb_2O_{6(s)} + 6C_{(s)} = 2Sb_{(M)} + Pb_{(M)} + 6CO_{(g)} \quad (8)$$

$$PbSb_2O_{6(s)} + 3C_{(s)} = 2Sb_{(M)} + Pb_{(M)} + 3CO_{2(g)} \quad (9)$$
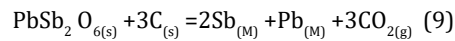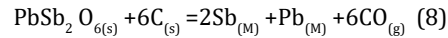
It is necessary to determine the following relationships.

$$R = (W_o - W_t) / W_{teo} = \Delta W/W_{teo} \quad (10)$$

The above equation (10) is not sufficient due to the high content of volatiles such as sulfur or other volatile materials. For this reason, equations (11) and (12) are proposed.

$$R = (\Delta W - W_{VT}) / W_{teo} \quad (11)$$

$$W_{VT} = W_S + W_{VC} \quad (12)$$

Reactants	%	Products	%
Sample slag refining	57.02	Metal (Sb, Pb)	26.39
Coal	4.83	Slag	58.17
Caustic soda	21.97	Cz	0.004
Exc Caustic soda 20%	4.4	C_{teo}	4.15
Sand	9.8	Volátil C	0.49
Exc Sand 20%	1.96	S	9.32
		H_2O	1.44
Total	100		100

Table 5: Distribution of reactants and products in the thermobalance.

Where: R: experimental weight loss fraction and theoretical weight.

ΔW: Difference of the initial weight and the final weight recorded on the thermobalance.

W_{VT}: weight of total volatiles.

W_S: weight of sulfur in the sample.

W_{VC}: weight of the charcoal volatiles.

From table 5, the W_{Cteo} = 4.15%, W_S = 9.32% and W_{VC} = 0.49% and with the masses recorded in the thermobalance in real time ΔW every 5 seconds the conversion factor R calculates the recovery of the metal, a diagram for the P-50 test is shown in figure 5 where $W_{Esc\,Ref}$ = 2.8906 g, W_{Met} = 5.096 g and the limits of the reactions (8) and (9) are W_{teo} = 0.476 g $CO_{(g)}$ and W_{teo} = 0.374 g $CO_{2(g)}$.

Figure 5, indicates the limits determined by the W_{teo} where 0.4757 g corresponds to the formation of CO and 0.3737 g corresponds to the formation of CO_2, the experimental values of the test approach the limit of 0.4757 g of CO determined according to the reaction (8) and the relationship between the experimental weight and the theoretical weight is of 95.56% and according to the reaction (9) with formation CO_2 goes far away from the established limit of 0.3737 g. For this reason, the reaction that controls the reduction process to metallic Sb-Pb is the reaction (8) with CO formation, these results agree with the thermodynamic information analyzed in figure 2 shown above.

Figure 5: Experimental weight loss fraction compared to the theoretical weights according to reactions (8) and (9).
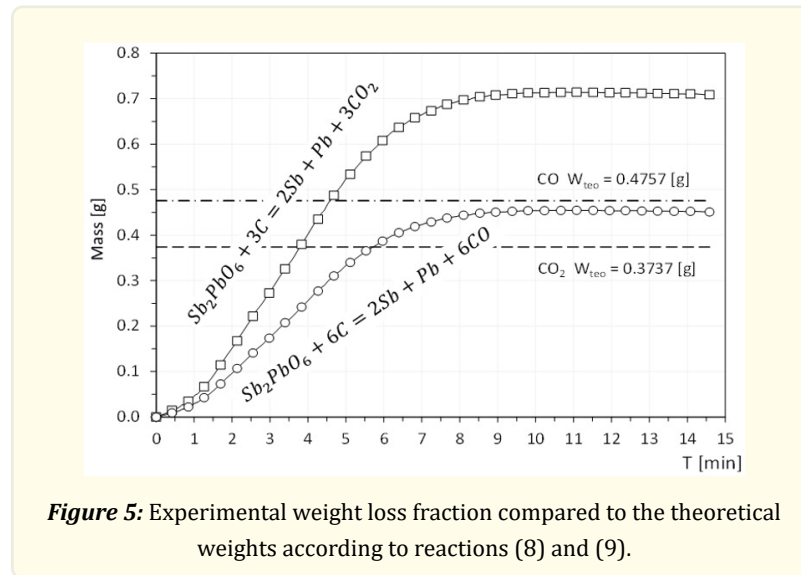
Effect of the amount of reducer

For the effect of the reducer on the refining slag sample, the $FeO:Na_2O:SiO_2$ system was used with the slag ratio 30:15:55 based on reaction (8) where $PbSb_2O_6:C=1:6$ is the stoichiometry ratio, it was considered to vary the amount of carbon in the following percentages: 20%, (r=1:7.2), 30%, (r=1:7.8), 50%, (r=1:9) and 80 %,(r=1:10.8) The results of this series of tests are shown in figure 6 for 900℃.

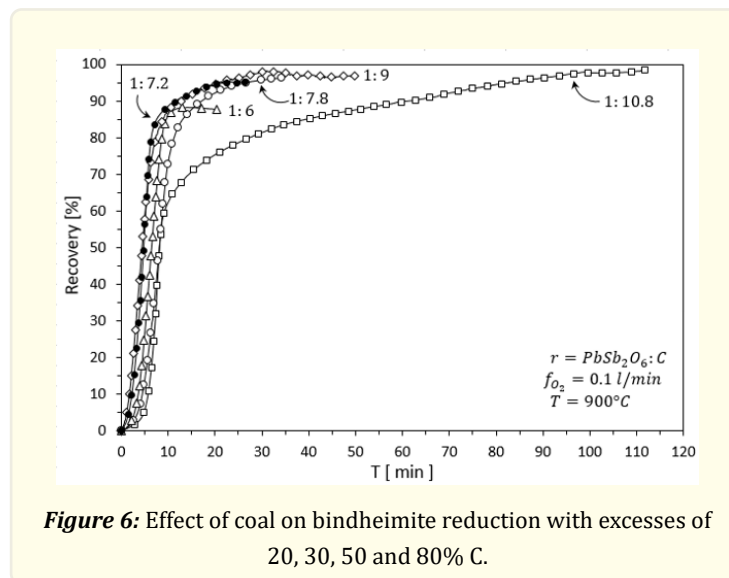*Figure 6:* Effect of coal on bindheimite reduction with excesses of 20, 30, 50 and 80% C.

Figure 6 shows time performance with excesses of 20, 30, 50 and 80% coal. 0.1 l/min and 900℃ oxygen flow. The performance of the stoichiometric test (r 1:6) gave a value of 88.24% in 15 minutes, this result is due to the impurities of the bindheimite that affected its performance. When performed with carbon excesses of 20, 30 and 50% performance improves to 93.80% in 20 minutes of process time. However, when excess coal is 80% yield is 75.43% in 20 minutes, this low result is probably due to insufficient oxygen flow which does not allow the refining slag sample particle to react completely. To corroborate the result of 80% excess carbon, a test was carried

out with oxygen flows of 0.3 l/min, 900°C and the same slag ratio used in the previous tests. The result is shown in figure 7 below.

Figure 7: Effect of excess carbon 80% r = 1: 10.8, reduction of bindheimite to 0.3 l/min.
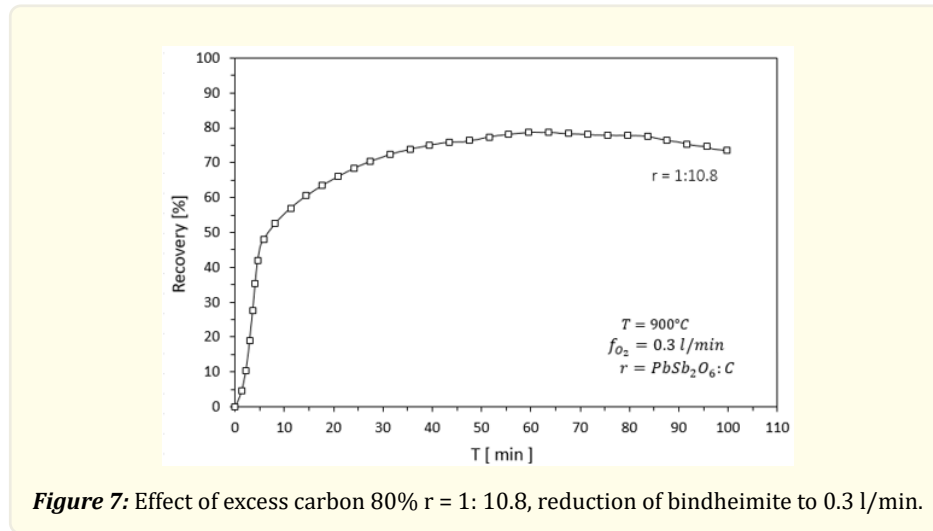
Figure 7 shows that the yield is 77.5% in time of 50 minutes, at higher processing times it is observed that the yield decreases with the recording of an increase in weight due to the formation of volatile antimony oxides or compounds with higher degree of oxidation.

Effect of the composition of the slag

The temperature and composition of the slag are related, according to the system FeO: Na_2O: SiO_2 for obtaining a molten and fluid slag, in the diagram in figure 4 several types of slag were analyzed and with the addition of Na_2O decreases the fusing temperature of slag to 800°C. The results of these tests to 800°C and FeO: Na_2O: SiO_2 = 10:30:60 show themselves in the figure 8.

Figure 8 shows the effect on the reduction of bindheimite without excess fluxes R 0:0, the yield achieved is 85.62% in a time of 10 minutes, when working at R 10:10 the yield increases up to 89.16% in a time of 10 minutes, when the R 20:20 ratio was used, the maximum performance of 93.65% was reached in a time of 15 minutes and when working with the R 50:50 ratios, the test ended in 12 minutes. With a yield of 71.43%, this effect is due to the fact that in the ternary diagram the position in the type A slag moves towards the vertex of Na_2O with the initial phase of sodium disilicate and 800°C of melting temperature to the phase of sodium metasilicate approaching the 874°C melting point isotherm. The combination of several tests to observe the effect of the type of slag is shown in figure 9.

Figure 9 shows the effect of the type of slag where the excesses of sand and caustic soda are R = 20:20 do not have a significant effect because in all these experiments a yield of approximately 91.06% is achieved in a time of 10 minutes; however, the excess of any of the overdubs adversely affects the yield of obtaining Sb-Pb metal as indicated in figure 8 with the ratio R = 50:50. A clear advantage of using slag FeO: Na_2O: SiO_2 of 10:30:60 is the low temperature of fusibility of 800°C, however, the balance of mass was made based on the amount of Fe of 3.05% of the refining slag for which more sand and dosing caustic soda are required.
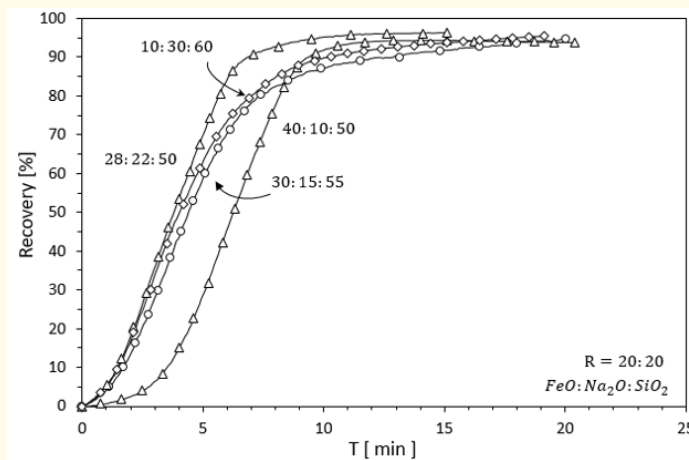
Effect of Temperature

The following figure shows the effect of temperature on the bindheimite reduction of the refining slag sample where the system slag FeO: Na_2O: SiO_2 has been considered from 10:30:60 to an oxygen flow of 0.1 l/min and excess melt ratio R = 0:0 (no excess).
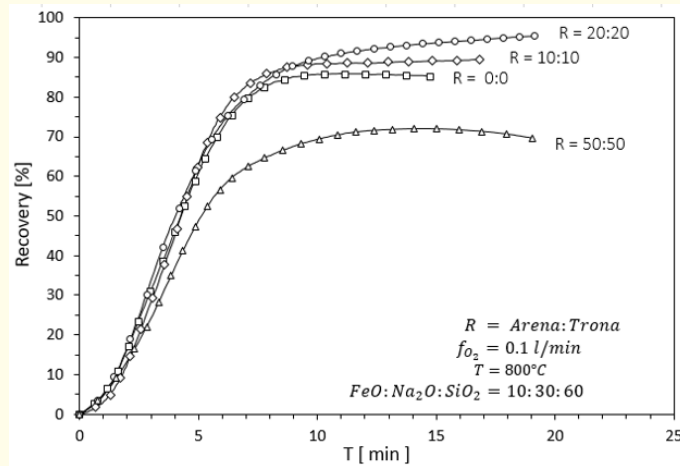
Figure 8: Effect of slag ratio FeO: Na$_2$O: SiO$_2$ = 10:30:60 at 800℃ and 0.1 l/min on bindheimite reduction.

Figure 9: Effect of slag type FeO: Na$_2$O: SiO$_2$ with excess R = Sand: Caustic soda = 20% in bindheimite reduction.

As shown in figure 10 to 800℃ with type A slag (10:30:60) a yield of 79.96% is achieved in a time of 20 minutes, 850℃ the performance achieved is 80.53% in a time of 20 minutes, 900℃ performance is 82.63% in a time of 20 minutes and when working to 1000℃ the performance increases up to 87.50% in a time of 17 minutes. The effect of temperature is evident when the same is raised whereas the melting temperature of the slag of the ratio FeO: Na$_2$O: SiO$_2$=10:30:60 is 800℃; also, at higher temperatures the yield curve moves to the left with faster melting times.

Figure 10: Effect of temperature on system FeO: Na_2O: SiO_2 = 10:30:60 and f_{o2} = 0.1 l/min without excess R = 0:0.
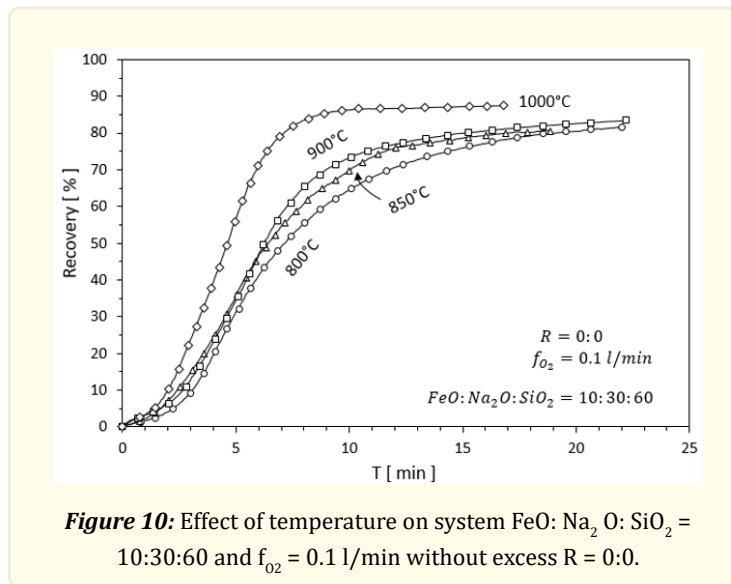
Conclusions

Based on the obtained results and the set objectives, antimony was successfully recovered from refining slag with values of 98%. The most suitable compound for line 2 slag is $PbSb_2O_6$ ($PbO·Sb_2O_5$). Experimental tests on a thermobalance identified the controlling reaction in the process ($PbSb_2O6 + 6C = Pb + 2Sb + 6CO$), which is supported by thermodynamic information. In the thermobalance tests, it was determined that an excess of 20% charcoal as the reducing agent achieved yields greater than 96%, and an excessive amount of this reagent is unnecessary. When the oxygen flow is increased above 0.1 l/min, antimony begins to volatilize, leading to a decrease in its recovery.

With a slag composition of FeO: Na_2O: SiO_2 at 10:30:60, a recovery of metallic antimony of 85.62% was achieved. This recovery increased to 93.65% when the amount of fluxes (sand and Na_2CO_3) was increased to 20%. However, the recovery decreased to 71.43% when the amount of fluxes was increased to 50%. Varying the slag composition while simultaneously adjusting the amount of added fluxes resulted in similar recoveries of around 93%, indicating that this result depends more on the slag's fusibility temperature than its composition. Experimental tests on the effect of temperature showed that working at temperatures higher than the slag's fusibility temperature slightly increased yields and accelerated the test kinetics. With a slag composition of FeO: Na_2O: SiO_2 at 10:30:60, a recovery of 81% was achieved at 800°C, which increased to 87.50% when the temperature was raised to 1000°C.

References

1. es.statista.com. Ranking de los principales países productores de antimonio a nivel mundial en 2020 (2021).
2. Ministerio de Minería y Metalurgia. Anuario Estadístico (2019).
3. William D Callister and David G Rethwisch. Ciencia e ingeniería de los materiales (2da ed.) Department of Materials Science and Engineering The university of Utah, USA (1995).
4. Mason B and Vitaliano ChJ. "The mineralogy of the antimony oxides and antimonates". Indiana University. Bloomington, Indiana. U.S.A (1952).
5. Barin I, Knacke O and Kubaschewski O. "Thermochemical properties of inorganic substances". Supplement 1977. Verlag Stahleinsen m.b.H. Düsseldorf (1977).
6. Velasco HC. Equilibrio en el sistema Sb-S-O a temperatura elevadas. Universidad Técnica de Oruro Facultad de tecnología. Oruro, Bolivia (2002).

7. Springorum D. Slag Atlas Editet by Verein Deutscher Eisenhuttenleute (2da Ed.) (1995).

8. Zeballos VM and Velasco HC. Obtención de antimonio por reducción de trióxido de antimonio gaseoso. Universidad Técnica de Oruro. Bolivia (2013).

9. Anderson CG. Antimony production and Commodities (2018).

10. Webmineral.com Bindheimite.

Volume 6 Issue 3 March 2024