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Research Article

The distribution of bismuth in the process of reductive smelting of lead agglomerate

Afrim Osmani [1], Bastri Zeka[2], Muharrem Zabeli[3*]

[1]University of Mitrovica, Faculty of Geosciences, Department of Materials and Metallurgy, 42000, Mitrovica, Kosovo
Email: afrim.osmani@umib.net - **ORCID:** 0009-0000-2566-8654

[2]University of Mitrovica, Faculty of Geosciences, Department of Materials and Metallurgy, 42000, Mitrovica, Kosovo
Email: Bastri.zeka@umib.net - **ORCID:** 0000-0001-9522-3263

[3]University of Mitrovica, Faculty of Geosciences, Department of Materials and Metallurgy, 42000, Mitrovica, Kosovo
***Corresponding Author Email:** Muharrem.zabeli@umib.net - **ORCID**: 0000-0001-6712-0005

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Abstract:

The world production of bismuth is largely supported by the pyro metallurgical processes of obtaining lead, where in this case bismuth is concentrated in gross lead around 94-98 %, from which elementary bismuth is exploited in the case of debismuthization. Bismuth production in the Trepça complex was based on its concentration in lead-zinc composite ores, with about 0.17 % Bi. While the concentration of bismuth in lead concentrates varies and ranges from 0.03-0.15 % Bi. Well, in addition to gross lead, bismuth is also concentrated in all other by-products of the process in which Pb is also concentrated. As a result of this, the recovery rate of bismuth in the case of bismuth enrichment is low and is around 65-78 % Bi. The rate of distribution of Bi in the products of the Pb refinery is as follows: 78 % of bismuth passes into refined bismuth; 6.62 % in Ca-Mg-Bi powder. Therefore, the purpose of this work is to intensify the debismuthization process by improving the recovery rate of Bi, where only the use of Ca as a reagent can reduce the content of Bi in Pb up to 0.04-0.005 %, while the use of only Mg as a reagent can to reduce the content of Bi in Pb up to 0.5 %. While the joint use of Ca and Mg, in a ratio of 1:2, can reduce the content of Bi in Pb to a value of 0.01 %. In cases where deep debismuthiation is required, then the amount of Sb in the molten lead is intervened and in this case the amount of bismuth in the lead is reduced to the values of 0.004 % Bi.

1. Introduction

The methods for processing natural raw materials of bismuth, with the aim of obtaining elemental bismuth, are both pyro metallurgical and hydrometallurgical methods.
Bismuth in the mass of lead ore is found mainly in the form of the isomorphs conductor, where in the case of processing we obtain the collective concentrates of lead-bismuth, where about 70 % of the bismuth in lead metallurgy is obtained. Bismuth in lead metallurgy is concentrated in lead-zinc composite ores, with about 0.17 % Bi, while the concentration of bismuth in lead concentrates varies and ranges from 0.03-0.15 % Bi. The amount of bismuth in gross lead is related to the composition of concentrates and lead and ranges from traces up to 0.4 % Bi [1]. The extraction of bismuth in lead metallurgy is reasonable both in terms of obtaining qualitative lead and in terms of its demand in the market, so it is also reasonable to obtain it in a content above 0.03 % Bi.
The bismuth in lead metallurgy is present in lead ores, then in lead concentrates, to continue in its agglomerate until the refining of lead, where we also obtain elementary bismuth. Bismuth in lead agglomerate is in the form of bismuth trioxide (Bi_2O_3), partially as bismuth oxide (BiO) and bismuth pentoxide (Bi_2O_5). From the table 1 it can be seen that the lead obtained by the smelting reduction process contain a significant amount of impurities, which is around 4-6 %. These impurities of raw lead make it impossible to use it for technical purposes. Therefore, lead refining is reasonable both from the aspect of obtaining pure lead which is used in industry, and from the commercial aspect, because lead impurities are of economic value and such sites have an impact on the general costs of the process.

***Table 1.** Distribution of bismuth in the shaft furnace-reductive smelting process*

Input	**t**	**% Bi**	**t**	**%**
Lead agglomerate	184073	0.092	170	99.3
Lead oxide	510	0.23	1.17	0.7
In total	-	-	171.17	100.00
output				
Gross lead	77840	0.196	152.56	89.1
Powder	11300	0.120	13.56	7.9
Granulate slag	87318	0.006	5.24	3.0
In total	-	-	171.38	100.00

***Table 2.** Distribution of bismuth from gross lead refining process*

Input	**t**	**% Bi**	**t Bi**	**%**
Gross Pb	68100	0.188	128	100.00
Output	t	% Bi	t Bi	%
Rafined bismuth	9995	99.98	9993	78.00
Powder of Ca-Mg-Bi	332	2.220	8.480	6.62
Rafined lead	65376	0.013	8.498	6.63
Lead oksid	693	0.250	1.732	1.35
Powder of Ca-Mg	1894	0.030	0.663	0.51
Bismuth slage „B"	925	0.070	0.694	0.54
Matte of Pb-Cu	2918	0..001	0.029	0.02
Shliker alkalic of dezincation	160	0.130	0.208	0.16
Speiss of flame furnace	582	0.008	0.046	0.03
Powder of likvational Ag	287	0.010	0.029	0.02
Slage of flame furnace	280	0.007	0.019	0.01
Slage of rotary furnace	297	0.006	0.017	0.01
Indefined losses	−	−	7.800	6.10

During the gross lead refining process, bismuth is always distributed in the intermediate products of the process, but most of it remains in the gross lead until the debismuthing stage. In this phase, the entire amount of bismuth passes into the rich bismuth foam, from which elementary bismuth is then obtained. From the table 2 it can be seen that the distribution of bismuth from the gross lead refining process is: 78 %Bi passes into elementary bismuth and 6.62 %Bi passes into the Ca-Mg-Bi powder and which is returned to the smelting process.

But except the Ca-Mg-Bi powder, these by-products can also be processed in the agglomeration process: Ca-Mg powder, Zn powder, liquational silver powder, so that the bismuth concentrated in them is returned to the process. Lead-copper matte, speissis and flame furnace slag, in a mixed state, were sold in copper metallurgy.

Bismuth ore B has no processing technology, therefor this also represents a significant loss of bismuth. Also, the significant amount of bismuth (6.10 % Bi) is lost in various ways that are not recorded [1,2]. The process of lead debismuth consists in the ability of bismuth to form compounds insoluble in lead and with high melting temperatures with alkaline and alkaline earth metals. These insoluble compounds float on the surface of the molten lead and form the so-called bismuth foam [3,4]. Bismuth with calcium forms two compounds: Ca_3Bi_2 with 22.3 % Ca and melting temperature 928 ºC and $CaBi_3$ with 6 % Ca and with a melting temperature of 570 ºC and two eutectics, one of which contains 0.5 % Ca and has a melting temperature of 270 ºC, while the other contains 58 %Ca and has a melting temperature of 786 ºC [5,6].

Bismuth with magnesium forms only one compound: Bi_2Mg_3 with melting temperature of 823 ºC and two eutectics. Figure 1 is phase diagrame of Bi-Ca and figure 2 is phase diagram of Bi-Mg.

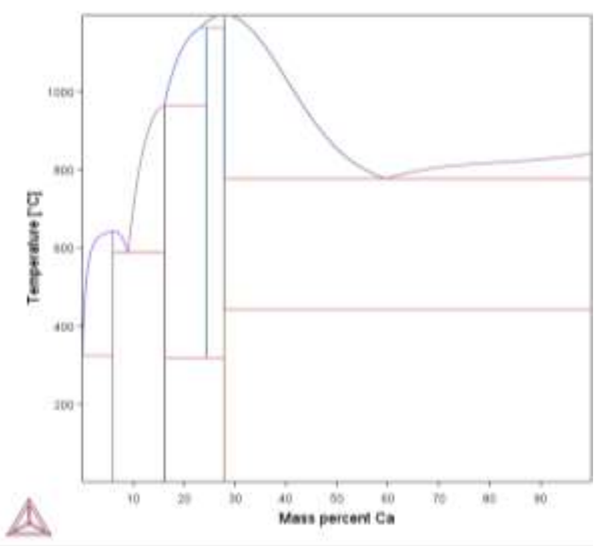

***Figure 1.**Phase diagrame of Bi-Ca*

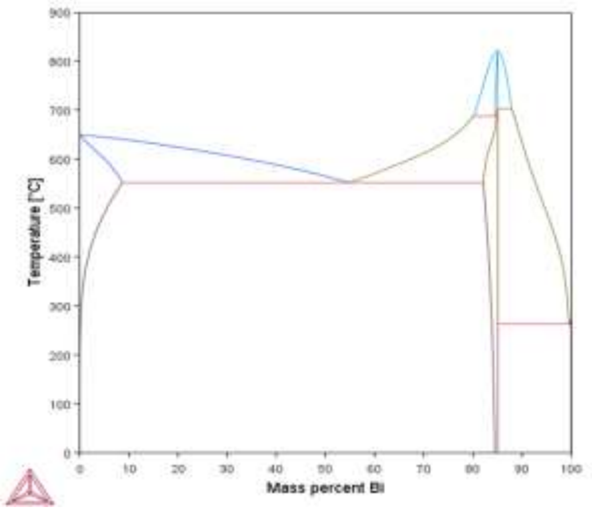

Figure 2. *Phase diagram of Bi-Mg*

In the same way, calcium and magnesium also form compounds with lead Pb_3Ca, PbCa, Pb_2Mg, Ca_3Pb_4Mg etc. However, if in the denzication lead are present: Zn, Cu, As, Sb, Ag, etc. Then these elements would also react with calcium and magnesium, forming different chemical compounds that would pass into the bismuth foam. contaminating it, while the presence of As and Sb affects negatively the formation of bismuth foam [7,8]. The temperature of the decommissioning process is 360-380 ^oC, in which case Ca and Mg form the compounds: Ca_3Bi_2, Bi_2Mg_3, Ca_3Bi_2, Bi_2Mg_3, which, due to their limited solubility and higher melting temperature, float on the surface of lead and then leave in the form of bismuth foam [9,10]. Similar works also reported in the literature [11-14].

2. Material and Methods

2.1 The practice of the debismuthing process

The lead which has been refined before must not contain more than 0.01 % of impurities and then it is subjected to the process of desmuthisation in the kettle, which is special for this process. After the dezincation process, the surface of the lead is cleaned from mechanical impurities and when the temperature of 380-400 ^0C is added the blocks of poor foam with bismuth in the kettle, from the previous operations and then we start with the addition of reagents. The measured amount of magnesium is placed in the cylinder, which is then placed in the kettle by the elevator and dipped (immersed) in the mass of molten lead. After that, the mixer which is in the cylinder is locked, which helps dissolve the magnesium in the mass of molten lead. After that, it continues with the addition the amount of calcium, which is added near the mixer. Due to the high reactivity between the reagents, a considerable amount of energy is released, which means that we have to do with the development of exothermic reactions.

$Ca+0.5O_2 = CaO - Q$
$Mg+0.5O_2 = MgO- Q_2$
$Ca+PbO=CaO+Pb-Q_3$
$Mg+PbO=MgO+Pb-Q_4$
$Bi_3Ca_2+2PbO=2CaO+2Pb+3Bi-Q$

After 20 min. by throwing Ca, the mixer is switched off and remove from the kettle together with the elevator, and then starts with the removal of the bismuth-rich foam. Then it continues with the cooling of the kettle up to the temperature 370-360 ^0C, at which temperature the poor bismuth foam will be removed, which goes for further processing. The poor bismuth foam removes in the temperature of 360-350 ^oC, which is subjected to the first stage of the debismuth process. (according to variant I). The process is considered complete when the content of bismuth in the lead reaches 0.01 % Bi. After removing the poor foam with bismuth, if it is necessary to obtain lead with high purity, then deep refining with antimony is done.

2.2 Processing of rich bismuth foam

The rich bismuth foam which is obtained during the process of lead, is removed from the surface of the kettle with hole shovels and transferred to the kettle of 30t in which its further processing is done with the aim of obtaining bismuth.
The processing of bismuth-rich foam is subject to these processes:
1. Melting and liquation, foam rich in bismuth
2. Decomposition of bismuthures
3. Chlorination of Pb-Bi alloy and
4. Final refining of bismuth.

3. Results and Discussions

3.1Melting and liquation of foam rich in bismuth

The process of liquation of foam rich in bismuth is done with the aim of separating the lead found in the rich foam, mechanically included, from this material.
The process developed at temp. 550-600 ^0C, and lasted 10 hours, after that the cooling process continues, where at the beginning of cooling a metal cone is sinks in the material, with the extraction of which a hole is opened in the crust that forms during cooling to place the pump for pumping the lead decanted. After the end of cooling, which lasted 16 hours, liquid lead falls to the bottom of the bathroom on the surface, due to the high melting temperature, the material in which bismuth is found in quantity.

In the hole formed by pulling the metal cone, the pump head is placed for pumping the decanted lead, which is sent to the debismuthing process.

The chlorination method consists of summary reactions

$Bi_2Mg_3+3PbCl_2 =2Bi+3Pb+3MgCl_2$

$Bi_2Ca_3+3PbCl_2 =2Bi+3Pb+3CaCl_2$

The temperature of the process is 550-600 °C and during this calcium and magnesium are combined with chlorine forming the solid scale which appears on the surface of the metal, while the Pb-Bi alloy remains in the kettle. In addition to chlorination, the process of oxidation of calcium and magnesium with the oxygen of the air also takes place.

Alkaline oxidation method

Developed at a temperature of 400-420 °C in the presence of caustic soda, where salt is added after a time. Oxidation in the presence of caustic soda developed according to the reactions:

$Bi_2Mg_3+6NaOH=2Bi+3MgOxNa_2O+3H_2$

$Bi_2Ca_3+6NaOH=2Bi+3CaOxNa_2O+3H_2$

These oxides are processed in the furnace, while the material that remains in the kettle represents the so-called bismuthed lead with 6-8 % Bi, which is processed by the chlorination process or by the electrochemical process.

3.2 Chlorination process

The Pb-Bi alloy, which is obtained by decomposing calcium and magnesium bismuths, contains 8-12 % Bi. The processing of the Pb-Bi alloy in the Trepça complex is done by means of the chlorination process, which after the reconstruction of the refinery is expected to be realized electrolytically.

The chlorination process is realized in a kettle with a capacity of 5 tons, where the kettle covered with a cast-iron lid and with holes for the installation of steel pipes, through which chlorine gas is blown into the mass of the molten alloy, with which the chlorination process is realized.

The process starts with melting the Pb-Bi alloy and heating it up to temperatures of 450-500 ºC, after which the process developed without heating, based on the exothermic heat of the lead chlorination process. The process is based on the higher affinity of lead to chlorine and develops according to the reaction.

$Pb\text{-}Bi+Cl_2=PbCl_2+Bi$

The lead chloride which does not dissolve in the Pb-Bi alloy is separated on the surface of the molten metal, from where it is poured into a special container through a special channel and solidifies.

As a result of the chlorination process, we have the gradual increase of bismuth in the kettle and the removal of lead in the form of lead chloride. The process is considered complete when the lead content in the kettle is reduced to 0.012 % Pb, after which the final refining process of bismuth begins. Based on the results obtained, the following conclusions can be drawn:

- The largest amount of bismuth is found in crude lead, with a concentration of 89.1% Bi.
- The bismuth content in lead powder is approximately 7.9%, and it is recoverable.
- The amount of bismuth lost during the reduction smelting process is around 3% Bi. This represents an irreversible loss; however, research is underway to process the slag from shaft furnaces in the future, which may enable the recovery of this bismuth.
- During the lead refining process, approximately 78% of the bismuth is transferred into refined bismuth.
- In the Ca-Mg-Bi powder, the bismuth content is 6.62% Bi. This does not represent a loss because it is returned to the processing cycle.
- Refined lead contains 6.63% Bi, and this amount could potentially be reduced through future improvements in processing techniques.
- The bismuth concentrations in Ca-Mg powder (0.5% Bi), Zn powder (0.16% Bi), and liquation Ag powder (0.02% Bi) are recoverable through processing, ensuring that the bismuth in these intermediate products is returned to the production process.
- Pb-Cu matte, slag from the flame furnace, and speiss from the flame furnace are sold.
- Bismuth ore B currently lacks a processing technology, resulting in process losses. Research is ongoing to address this issue.
- Unrecorded losses account for approximately 6.10 % Bi.

4. Conclusions

Given that bismuth concentrates are bismuth-poor raw materials and the recovery rate of bismuth during enrichment is low (65–80%), processing them in lead metallurgy is not economical. This highlights the need for more advanced methods for enriching bismuth ores, improving recovery rates, and processing these ores more efficiently.

Special attention must be given to the distribution of bismuth across products and by-products in the lead production process. It is essential to minimize bismuth losses at all stages of lead processing, including reduction smelting and refining. The bismuth losses occurring during lead extraction in shaft furnaces are expected to decrease with the commissioning of the new refinery at the Trepça complex. An alternative for reducing bismuth losses in lead metallurgy could be the electrochemical extraction of bismuth.

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

- **Acknowledgement:** The authors declare that they have nobody or no-company to acknowledge.

- **Author contributions:** The authors declare that they have equal right on this paper.

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- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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