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# High-Temperature Electrochemical Refining of Secondary Lead

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## Abstract

The present chapter is devoted to the analysis of the obtained data on the high-temperature electrolytic production of high-purity lead from secondary lead in chloride melts. Kinetic parameters of electrode reactions were calculated, and the sequences of the metal dissolution from the double lead-antimony (Pb-Sb), lead-bismuth (Pb-Bi), and antimony-bismuth (Sb-Bi) alloys were determined. A long-term electrolysis of the antimony (battery scrap), bismuth (lead-bismuth), and lead-containing raw materials in the electrolytic cell of original construction with a porous ceramic diaphragm impregnated with the eutectic KCl-PbCl<sub>2</sub> chloride electrolyte was performed. The anode lead alloy, containing 57.0 wt% of antimony and 36.0 wt% of bismuth, and cathode grade lead were obtained as a result of the electrolysis. The values of lead, antimony, and bismuth separation coefficients were calculated according to the values of the equilibrium potentials of the Pb-Sb, Pb-Bi, and Sb-Bi alloys. The values of separation coefficients were found to be  $6.5 \cdot 10^6$ – $1.5 \cdot 10^8$  for a single stage at the lead extraction from the Pb-Sb and Pb-Bi alloys, which proves the possibility of a highly effective lead extraction. The value of Sb-Bi alloy separation coefficient ranges from 5.5 to 6.5, which testifies the complexity and low effectiveness of the separation process. An electrolytic refining of lead-bismuth and secondary lead, obtained from the battery scrap, was performed.

**Keywords:** lead, antimony, bismuth, chloride melt, high-temperature electrolysis, liquid metals, separation coefficient

## 1. Introduction

Fusible metals play a key role in the development of technologies of separation and extraction of rare and dispersed elements using molten salts [1, 2]. There is published data on cerium extraction using a liquid zinc anode [3], holmium extraction using a liquid bismuth anode [4], and thulium extraction using a liquid zinc anode [5] in the LiCl-KCl electrolyte. Development of the technologies of the electrolytic separation of alloys in molten chloride systems requires understanding of the transformations, which take place at the surface of the liquid metal anode.

Lead is a renewable metal that may be used in materials production multiple times, because its production losses are negligible. A great number of lead-containing

devices withdrawn from operation form wastes that require recycling. Apart from that the lead, nonferrous and noble metal-containing cakes, dust, and sludge are formed as side products of nonferrous metallurgical processes. The concentration of the basic admixtures in such lead-containing rare products demonstrates that apart from lead it is possible to extract such products as antimony and bismuth. The technology of electrochemical lead refining in chloride melts is one of the most promising for selective extraction of nonferrous metals.

Electrodissolution of lead-bismuth (Pb-Bi) alloys is described in papers [6–8]. Nichkov studied polarization of the bismuth anode in the molten salt mixtures KCl-NaCl and KCl-LiCl, containing 0.1, 1.0, and 5.0 wt% of BiCl<sub>3</sub>. The bismuth ionization proceeds mostly with formation of Bi<sup>3+</sup>. The bismuth current efficiency, which is calculated for the three-electron reaction, is 109%, which denotes the formation of the lowest valence Bi<sup>+</sup> ions. The increase in the bismuth trichloride concentration in the melt leads to the polarization shift to the regions of more positive potentials, and at  $i > 1 \text{ A/cm}^2$ , it reaches the values of  $-0.76 \text{ V}$  relatively to the chloride reference electrode. The measurements of the lead electrode polarization denote that its dissolution takes place at the potentials 0.4 V more negative than those of bismuth dissolution under otherwise equal conditions [6]. Papers [7–8] illustrated that lead current efficiency is close to 100% if it is calculated for two-electron electrode reactions at the dissolution of Pb-Bi alloys containing up to 70 wt% of Bi. The peculiarities of bismuth and bismuth-containing alloys anode polarization are described in papers [9–13]. Pyatkov [10] measured anode polarization of Sb in the KCl-NaCl electrolyte at the temperatures of 680–780°C. The antimony polarization was found to proceed with formation of ions of various oxidation degree—Sb<sup>+</sup> and Sb<sup>3+</sup>. The temperature decrease and the antimony trichloride concentration growth in the melt were found to result in the antimony ionization according to the three-electron electrode reactions [9]. Papers [10, 11] reported on the studies of the possibility of the electrolytic separation of lead-antimony (Pb-Sb) alloys at the temperatures of 973–1073 K in the KCl-NaCl-PbCl<sub>2</sub> electrolyte. It is shown that the anode current efficiency is equal to 100% at the 10.0 wt% lead concentration in the anode. As the lead concentration decreases, the anode current efficiency drops to 30–40%. Wei et al. [13] studied the electrochemical behavior of antimony in the LiCl-KCl electrolyte. The square wave function was used to define the number of electrons, which participated in the electrode reaction ( $n = 3.02$ ). This fact denotes that during the experiment, the electrochemical reaction proceeds in a single stage with simultaneous transfer of three electrons. Hirofumi Ebe et al. [14] studied electrochemical transformations of antimony and bismuth in the AlCl<sub>3</sub>-KCl-NaCl melt with additions of antimony and bismuth trichlorides by voltammetry. The voltammograms of the melts, containing antimony ions, have one peak in the cathode direction and one peak in the anode direction of the potential sweep. The curves of the electrolyte with the bismuth trichloride addition have a more complex form. The authors suggest that under the electrolysis conditions, the oxidation-reduction reaction Bi<sup>3+</sup>/Bi<sup>+</sup> at the potentials of 1.1 V takes place (chlorine reference electrode) [13].

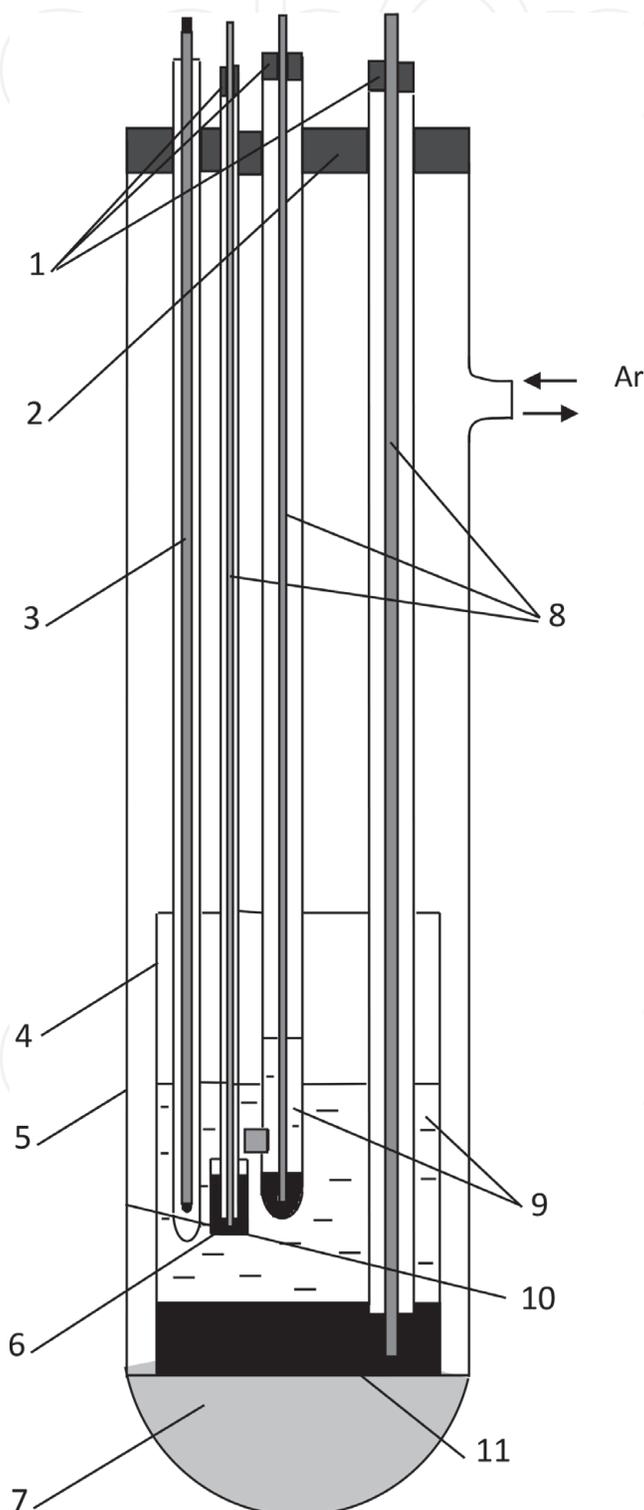
The analysis of the literature data on the binary Pb-Sb and Pb-Bi alloys separation elucidates that the process temperature growth leads to the increase in the Sb<sup>+</sup> and Bi<sup>+</sup> ion concentrations and therefore to the decrease in the Sb<sup>3+</sup> and Bi<sup>3+</sup> ion concentration. The presence of two metal ion types of different valence decreases the process performance, because part of the current will be spent on the recharge of the ions of the lowest and highest valences. That is why the preferable temperature of the electrochemical separation of double lead alloys should not exceed the melt liquidus temperature by more than 30–100°C.

The present chapter illustrates the results of the studies of the anode dissolution of Pb-Sb, Pb-Bi, and Sb-Bi double alloys.

## 2. Methodology

Electrodissolution of lead and antimony and lead and bismuth alloys was studied by the galvanostatic method. The polarization was measured in the moment of polarization current switch off [14–17].

The current amplitude was changed from 1 mA to 1A using an IPC-Pro potentiostat (Russian Federation). The polarization value was determined using the IPC-Pro software. The experiments were performed in a quartz cell (**Figure 1**),



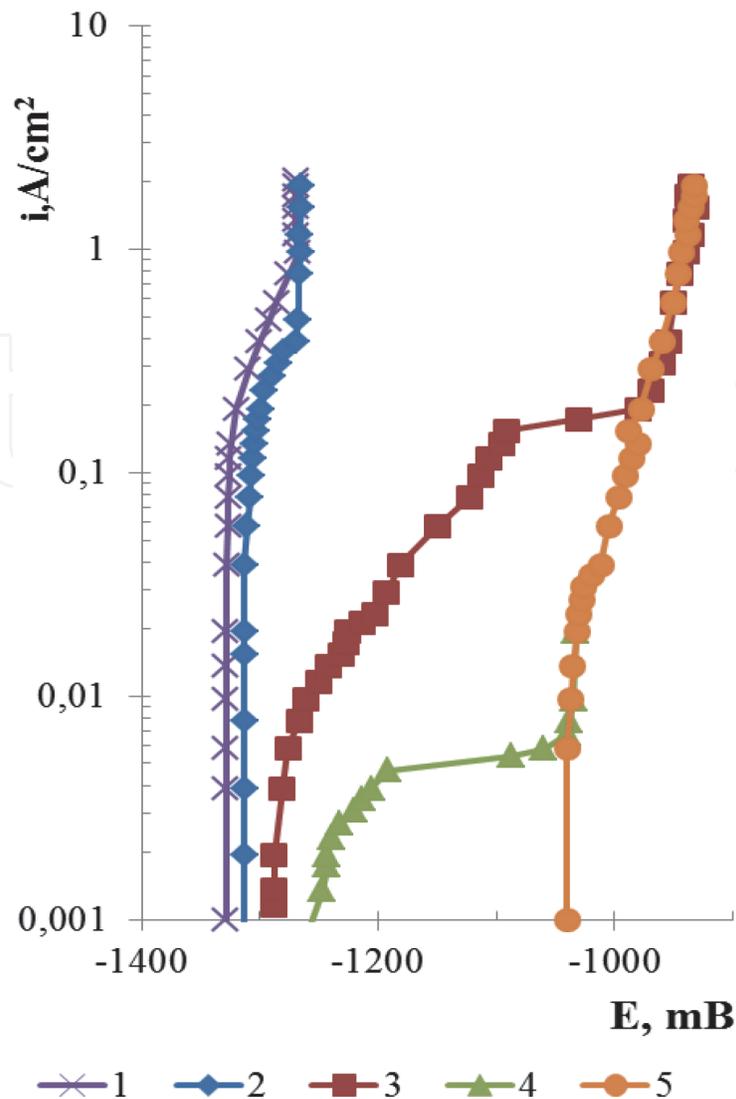
**Figure 1.** Schematic of the electrochemical cell. (1) rubber plugs, (2) fluoroplastic lid, (3) thermocouple, (4) alumina crucible, (5) quartz cell, (6) working electrode, (7) platform, (8) current leads to electrodes, (9) electrolyte, (10) reference electrode, (11) auxiliary lead electrode.

which was hermetically closed with a fluoroplastic lid (2), in argon atmosphere. An alundum container (4) was mounted onto a platform made of the fired refractory material (7). A counter electrode (11) and the mixture of potassium and lead chlorides (9) were put into the container. A reference electrode (10), a working electrode, (6) and a thermocouple (3) were lowered into the cell from the gas phase after the electrolyte melting. The alloys of the following compositions were used as working electrodes: lead-antimony, Pb-Sb (70–30), Pb-Sb (50–50), and Pb-Sb (30–70); lead-bismuth, Pb-Bi (59.3–40.7), Pb-Bi (32.5–67.5), Pb-Bi (17.1–82.9), and Pb-Bi (3–97); and antimony-bismuth, Sb-Bi (25–75), Sb-Bi (94–04), and Sb-Bi (99–01). The alloy of the same composition as the working alloy was used as a counter electrode. Capsulated lead served as a reference electrode. Current leads to liquid alloys and to lead were made of molybdenum (8). In the electrolyte area, molybdenum was screened from the melt by alundum. The cell was maintained hermetically sealed with rubber plugs (1). The temperature was controlled using a Varta 207 thermoregulator (Russian Federation). In the electrolyte, the temperature was controlled by a chromel-alumel thermocouple. The electrolyte was prepared from potassium chloride of the chemically pure grade and lead chloride of the analytically pure grade. The prepared electrolyte was electrolytically purified. The compositions of the working electrodes were prepared from lead of the C-1 grade, antimony of the Su-0 grade (antimony concentration 99.9 mol%) and bismuth of the Bi-00 grade (bismuth concentration 99.99 mol%).

### 3. Measurement results

The polarization of lead-antimony working electrodes Pb-Sb (70–30), Pb-Sb (50–50), and Pb-Sb (30–70) was measured at the temperature of 873 K in the current density region of 0.001–2 A/cm<sup>2</sup>. **Figure 2** illustrates in a graphic form the obtained results. The potentials of lead-antimony alloys are appropriately located between the potentials of individual lead and antimony. Lead is the most electro-negative element in the system. According to the measurement results, it is seen that ionization proceeds with the insignificant shift of the polarization values to the positive potential region in the samples with the lowest antimony concentration (**Figure 2**, curve 2) at the polarization current amplitude from 0.001 to 0.09 A/cm<sup>2</sup>. This is explained by the fact that under experimental conditions, the compositions of salt and metallic phases in the area near the anode layer do not change. As the values of the polarization current exceed 0.1 A/cm<sup>2</sup>, the anode potential changes more intensively, but the potentials of pure antimony dissolution are still not reached in the whole interval of current impulses. The increase in the antimony concentration in the anode causes changes in the form of the polarization curves (**Figure 2**, curves 3, 4). The measurement results of the polarization of Pb-Sb alloys containing from 50.0 to 70.0 mol% of antimony demonstrate that the form of the curves does not change. The curve may be conditionally divided into two regions: the changes in polarization of the first region are analogous to the form of polarization curve for alloys with small antimony concentration. As the definite value of  $i_a$  is reached, the electrode potential shifts abruptly to the positive polarization region until the corresponding values of antimony ionization are reached. The numerical value of the limiting diffusion current density decreases as the concentration of the more electropositive component of the melt increases.

The polarization of lead-bismuth working electrodes Pb-Bi (59.3–40.7), Pb-Bi (32.5–67.5), Pb-Bi (17.1–82.9), and Pb-Bi (3–97) was measured at the temperature



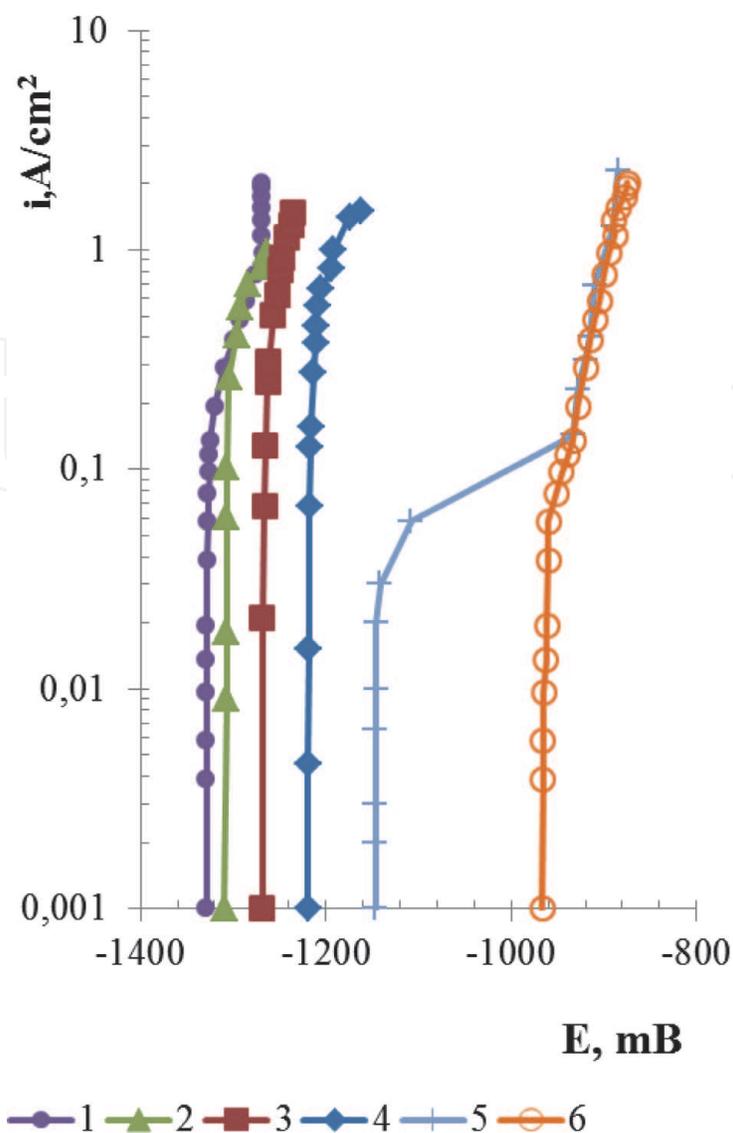
**Figure 2.**  
Polarization of lead-antimony anodes, mol%: 1, Pb; 2, Pb-Sb (70–30); 3, Pb-Sb (50–50); 4, Pb-Sb (30–70); 5, Sb.

of 773 K in the current density interval of 0.001–2 A/cm<sup>2</sup>. **Figure 3** illustrates the lead-bismuth electrode polarization measurements.

Analogous to the Pb-Sb alloys, the potentials of the Pb-Bi alloys are located between the potentials of individual lead and bismuth. In addition, the potentials of bismuth are significantly more positive than those of lead. The alloys containing 40.7, 67.5, and 82.9 mol% of bismuth (**Figure 3**, curves 2–4) demonstrate the constancy of measured potentials at the anode current density increase to 0.2 A/cm<sup>2</sup>. Within the current density interval of 0.2–2.0 A/cm<sup>2</sup>, the anode potential shifts noticeably to the region of electropositive values. The anode potential of the working electrode containing 97 mol% of Bi reaches the electropositive values of bismuth dissolution potentials (**Figure 3**, curve 5). This is the only composition of the working electrode that has the following values.

The polarization of antimony-bismuth working electrodes Sb-Bi (25–75), Sb-Bi (94–04), and Sb-Bi (99–01) was measured at the temperature of 773 K in the current density interval of 0.001–2 A/cm<sup>2</sup>. **Figure 4** illustrates the measurement results.

The potentials of the Sb-Bi alloys are located between the potentials of individual antimony and bismuth, and the bismuth potential is more positive than that of



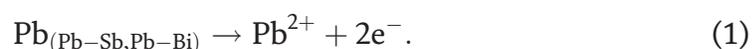
**Figure 3.**

*Polarization of lead-bismuth anodes, mol%: 1, Pb; 2, Pb-Bi (59.3–40.7); 3, Pb-Bi (32.5–67.5); 4, Pb-Bi (17.1–82.9); 5, Pb-Bi (3–97); 6, Bi.*

antimony. Polarization curves of all alloys under analysis demonstrate the platform of the limiting diffusion current of antimony ionization. The numerical value of the limiting diffusion current density decreases as the concentration of the more positive alloy component, i.e., bismuth, increases.

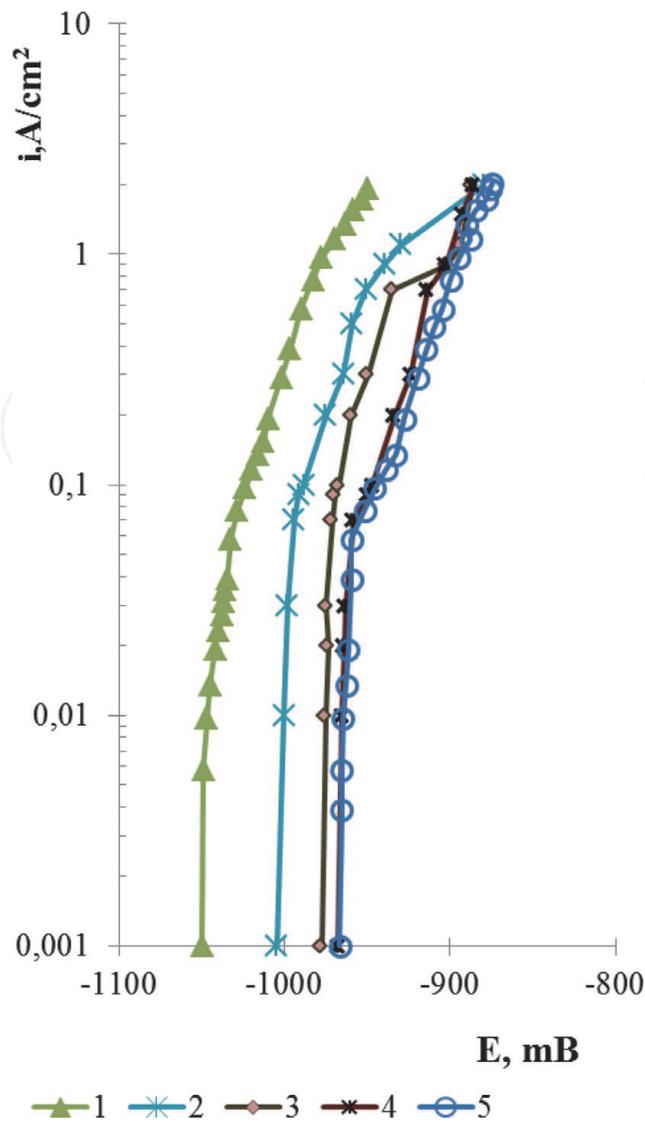
The analysis of the general form of the polarization dependencies of double metallic systems allows us to predict that the metal ionization from the alloys proceeds selectively in diffusion regime. The mechanism of dissolution may be described by the following electrode reactions. The most negative metal ionizes on the regions of polarization curves, corresponding to the insignificant deviations of polarization from the alloy equilibrium potentials.

The following electrode reaction describes the dissolution mechanism of the lead-antimony and lead-bismuth electrodes:



This reaction describes the mechanism for the antimony-bismuth alloys:





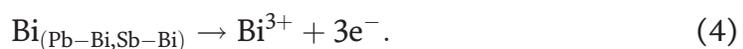
**Figure 4.**  
 Polarization of antimony-bismuth anodes, mol%: 1, Sb; 2, Sb-Bi (25-75); 3, Sb-Bi (04-94); 4, Sb-Bi (01-99); 5, Bi (100).

As the value of the polarization current increases, the abrupt shift of the potential to the values corresponding to ionization of more electropositive metal in the alloy is observed. The polarization jump is caused by the lack of the electronegative metal at the surface of the alloy, because the transport rate of the electronegative metal to the reaction spot from the electrode bulk is lower than the ionization rate. This results in the increase in the electropositive metal concentration at the alloy surface. The value of the working electrode potential shifts to the region of positive values, which create the conditions for dissolution of the second component of the alloy.

The following reaction takes place in the lead-antimony electrode:



and this reaction proceeds in the antimony-bismuth electrode:



The value of the limiting diffusion current of the metal may be used to evaluate the thickness of the diffusion layer in the liquid metal anode [18]:

$$\delta_{\text{Pb-Sb-Bi}} = \frac{nFDC_{\text{Me}}}{i_{\text{Me}}}, \quad (5)$$

where  $\delta_{Pb-Sb-Bi}$  is the thickness of the alloy diffusion.

$n$  is the number of electrons.

$D$  is the coefficient of metal atom diffusion in the electrode.

$C_{Me}$  is the concentration of the diffusing atom.

$i_{Me}$  is the limiting diffusion current of metals atoms from the alloy.

The values of lead diffusion coefficients  $D_{Pb} = 7.67 \cdot 10^{-5} \text{ cm}^2/\text{s}$  in the electrode ( $T = 773 \text{ K}$ ) and antimony  $D_{Sb} = 5.3 \cdot 10^{-5} \text{ cm}^2/\text{s}$  in the alloy ( $T = 773 \text{ K}$ ) are provided in the reference book [19]. Results of the diffusion layer thickness are provided in **Table 1**.

The thickness of diffusion layer in lead liquid alloys with antimony and bismuth of the same order for diffusing lead and antimony is close to the value of diffusion layer in molten salt under self-convection conditions [20]. The presence of clearly marked areas of limiting diffusion currents of ionization of electronegative components in the regions of their small concentrations proves high selectivity of the dissolution of individual elements of the alloys. As the concentration of the electronegative component in the melt (lead or antimony) decreases, the limiting current of its dissolution decreases. Therefore, the limiting current of ionization of the alloy electronegative component may be used to control the alloy separation degree.

The separation of the elements in electrochemical processes with participation of metallic alloys in molten salts was assessed quantitatively on the basis of thermodynamic data for Pb-Sb, Pb-Bi, and Sb-Bi double alloys.

A theoretic possibility to separate elements from the alloys may be evaluated according to the values of equilibrium potentials of alloys of the definite composition in the chloride melt [21]. In our case the Pb-Sb-Bi system in the KCl-PbCl<sub>2</sub> melt was used. According to the Nernst equation, the equilibrium potential of the alloy is composed of the value of the standard electrode potential of the potential-determining metal and its ions in the electrolyte ( $E_{Me^{n+}/Me}^0$ ) and a summand, which is determined by the metal ion activity in the electrolyte ( $a_{Me}$ ) and atom activity in the alloy ( $a_{Me(\text{alloy})}$ ).

The following equation is written for the Pb-Sb alloy:

$$E_P = E_{Pb^{2+}/Pb}^0 + \frac{RT}{2F} \ln \frac{a_{Pb^{2+}}}{a_{Pb(Pb-Sb)}}. \quad (6)$$

This equation is used for the Pb-Bi alloy:

$$E_P = E_{Pb^{2+}/Pb}^0 + \frac{RT}{2F} \ln \frac{a_{Pb^{2+}}}{a_{Pb(Pb-Bi)}}. \quad (7)$$

The equilibrium potential of the Sb-Bi alloy is determined as follows:

$$E_P = E_{Sb^{3+}/Sb}^0 + \frac{RT}{3F} \ln \frac{a_{Sb^{3+}}}{a_{Sb(Sb-Bi)}}. \quad (8)$$

The separation coefficient ( $\theta$ ) is convenient to express the degree of the electrochemical purification of the selective metal dissolution from the alloy. The

Diffusing element	Alloy composition, mol%	$C_{Me}$ , mol/cm <sup>3</sup>	$i_{Me}$ , A/cm <sup>2</sup>	$\delta$ , cm
Pb	Pb-Sb (30.0–70.0)	0.00104	0.05	0.031
Pb	Pb-Bi (3.0–97.0)	0.00165	0.09	0.027
Sb	Sb-Bi (4.0–96.0)	0.00122	0.7	0.018

**Table 1.**

*Thickness of the diffusion layer in liquid alloys at 773 K for double Pb-Sb, Pb-Bi, and Sb-Bi alloys.*

separation coefficient is normally written as the quotient of atomic fractions of the separated metals in the electrolyte and in the alloy:

the Pb-Sb alloy:

$$\theta_{Pb/Sb} = \frac{c_{Pb} \cdot c_{Sb^{3+}}}{c_{Pb^{2+}} \cdot c_{Sb}}, \quad (9)$$

the Pb-Bi alloy:

$$\theta_{Pb/Bi} = \frac{c_{Pb} \cdot c_{Bi^{3+}}}{c_{Pb^{2+}} \cdot c_{Bi}}, \quad (10)$$

the Sb-Bi alloy:

$$\theta_{Sb/Bi} = \frac{c_{Sb} \cdot c_{Bi^{3+}}}{c_{Sb^{3+}} \cdot c_{Bi}}. \quad (11)$$

In the majority of cases in the molten salts, when the concentrations of ions of potential-determining metals in the electrolyte have such values that the ion activity coefficients remain constant, the values of standard conditional potentials may be used, at that the equations used to calculate the separation coefficients transform as follows:

for the Pb-Sb alloy:

$$\ln \theta_{Pb/Sb} = \frac{-F \cdot E_p + 3F \cdot E_{Sb^{3+}/Sb}^* - 2F \cdot E_{Pb^{2+}/Pb}^*}{RT} + \ln, \quad (12)$$

for the Pb-Bi alloy:

$$\ln \theta_{Pb/Bi} = \frac{-F \cdot E_p + 3F \cdot E_{Bi^{3+}/Bi}^* - 2F \cdot E_{Pb^{2+}/Pb}^*}{RT} + \ln \frac{\gamma_{Pb}}{\gamma_{Bi}}, \quad (13)$$

for the Sb-Bi alloy:

$$\ln \theta_{Sb/Bi} = \frac{3F \cdot \left( E_{Bi^{3+}/Bi}^* - E_{Sb^{3+}/Sb}^* \right)}{RT} + \ln \frac{\gamma_{Sb}}{\gamma_{Bi}}. \quad (14)$$

The equilibrium potentials and element activity coefficients in the alloys of the Pb-Sb and Pb-Bi systems are provided in papers [22, 23]. The antimony and bismuth activity coefficients are reported in paper [24]. The temperature dependencies of the conditional standard electrode potentials of metals are taken from the papers [25–27]. **Figure 5** elucidates calculation results of possible separation coefficients of lead and antimony, of lead and bismuth, as well as of antimony and bismuth according to Eqs. 9–11.

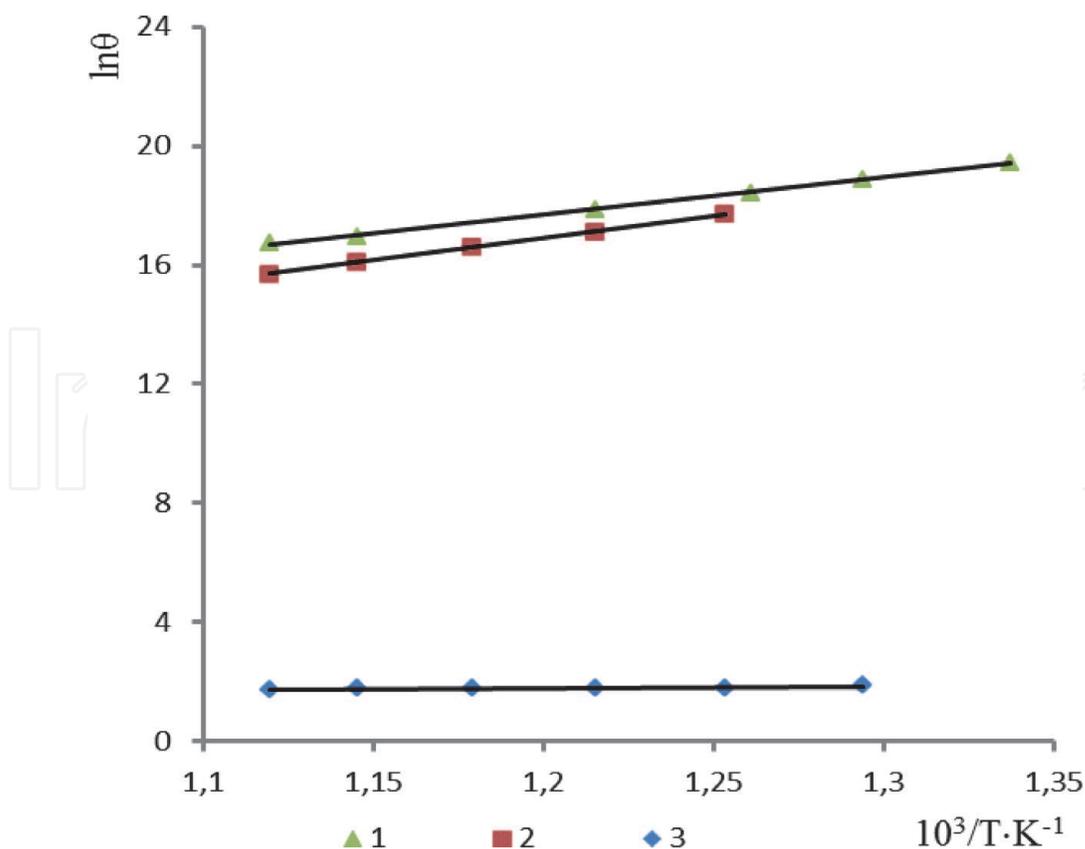
Linear dependencies may be described using the following equations:

the Pb-Sb alloy:

$$\ln \theta_{Pb/Sb} = 2.63 + \frac{12547}{T}, R^2 = 0.99 \quad (15)$$

the Pb-Bi alloy:

$$\ln \theta_{Pb/Bi} = -0.94 + \frac{14858}{T}, R^2 = 0.99 \quad (16)$$



**Figure 5.** Dependence of the separation coefficients of metals in double systems on the reverse temperature in the  $KCl-PbCl_2$  (50–50 mol%) melt: 1, Pb/Bi; 2, Pb/Sb; 3, Sb/Bi.

the Sb-Bi alloy:

$$\ln \theta_{Sb/Bi} = 0.73 + \frac{941}{T}, R^2 = 0.93 \quad (17)$$

The obtained calculation results of the separation coefficients of the double systems according to the experimental values of the equilibrium potentials for the Pb-Sb and Pb-Bi alloys in the temperature range of 748–873 K are  $6.5 \cdot 10^6$ – $1.5 \cdot 10^8$  for a single stage. The values of separation coefficients allow us to predict a deep selective separation of lead from antimony and bismuth from double alloys. The separation coefficients for the Sb-Bi alloys in the temperature range of 773–873 K are by 6–8 orders of magnitude lower and are located within the range of 5.5 and 6.6. Separation of antimony and bismuth is possible from theoretical point of view if the anode potential is under constant control and the anode current density is readjusted.

The electrolytic cell of original construction was used in the experiments [28].

The experimental electrochemical refining of secondary lead, containing bismuth as a basic admixture, was carried out during 14 days. The range of technological parameters that were tested at the processing of bismuth drosses, which are formed during the lead purification from bismuth by pyrometallurgical method, is as follows:

- Anode current density from 0.2 to 0.35 A/cm<sup>2</sup>
- Cathode current density from 0.4 to 0.7 A/cm<sup>2</sup>
- Mass fraction of bismuth in the anode from 2 to 14%

- Current from 300 to 500 A
- Total voltage of the electrolytic cell 8–10 V
- Temperature from 500 to 530°C

Zinc and silver admixtures are always present in the secondary lead. Zinc being the most electronegative metal transfer to the electrolyte first and silver accumulates in the anode metal.

During the electrorefining, lead ions discharge at the cathode to the metallic phase. The bismuth concentration in the cathode metal changes within the range of 0.008–0.011 wt% (**Table 2**) during the whole period of the experiment under the chosen conditions.

Antimony, bismuth, arsenic, and silver accumulate at the anode. The concentration of bismuth at the anode increased from 1 to 13.5 wt% (**Table 3**). In addition,

$i_c, A/cm^2$	t, day	Components concentration, wt%						
		Sb	Sn	Bi	Fe	As	Ag	Zn
0.4	5	0.001	0.0006	0.008	<0.0003	<0.0005	<0.0005	0.001
	6	0.001	0.0006	0.007				0.001
0.5	7	0.001	0.0005	0.008				0.0008
0.6	8	0.001	0.0004	0.008				0.0007
0.7	9	0.001	0.0006	0.009				0.001
	10	0.0008	0.0004	0.008				0.001
	11	0.0006	0.0005	0.009				0.0009
	12	0.0007	0.0006	0.009				0.006
	13	0.0004	0.0006	0.01				0.001
	14	0.0005	0.0007	0.011				0.001

**Table 2.**  
 Lead chemical composition (cathode) at bismuth dross processing.

$i_a, A/cm^2$	t, day	Components concentration, wt%						
		Sb	Sn	Bi	Fe	As	Ag	Zn
0.2	5	0.022	0.002	5.0	<0.0003	0.001	0.03	0.0005
	6	0.029	0.002	5.5		0.001	0.032	0.0005
0.25	7	0.035	0.002	6.0		0.001	0.038	0.0005
0.3	8	0.41	0.002	6.5		0.001	0.045	0.0005
0.35	9	0.047	0.001	7.0		0.001	0.051	0.0007
	10	0.06	0.002	7.5	0.0030	0.0012	0.057	0.0008
	11	0.08	0.003	8.5	<0.0003	0.0015	0.067	0.0005
	12	0.102	0.002	10.0	<0.0003	0.0017	0.08	0.0007
	13	0.126	0.002	11.5	0.0005	0.0022	0.09	0.0005
	14	0.13	0.0018	13.5	0.0005	0.0041	0.1	0.0005

**Table 3.**  
 Chemical composition of the anode metal at bismuth dross processing.

the bismuth concentration at the cathode was by 2–3 orders of magnitude lower, which is in agreement with the theoretical calculations and the polarization studies. The silver concentration increased to 0.011 wt% (**Table 3**).

The zinc concentration does not exceed 0.001 wt% both at the cathode and at the anode. Zinc being the most electronegative metal ionizes first and transfers from the anode to the melt in the form of two valence ions. The zinc ions accumulate in the electrolyte. During the test, the experimental batch of lead of 350 kg was obtained.

The experimental electrochemical refining of secondary lead, containing antimony as a basic admixture alloy, was carried out during 18 days. Black lead, which was obtained by the reducing melting from accumulator scrap, was used as a raw material.

During the electrolytic refining, the antimony concentration in the cathode metal was lower than 0.002 wt% (**Table 4**), and it did not change at the further electrolytic cell operation in the chosen technological regime.

$i_c, A/cm^2$	t, day	Components concentration, wt%						
		Sb	Sn	Bi	Fe	As	Ag	Zn
0.3	2	0.0008	0.0006	0.0005	0.0003	0.0005	0.0003	0.0006
	4	0.0006	0.0006	0.0005	0.0003	0.0005	0.0003	0.0004
0.4	6	0.0007	0.0005	0.001	0.0006	0.0003	0.0003	0.0008
	8	0.0004	0.0004	0.001	0.0006	0.0003	0.0005	0.0007
0.5	10	0.001	0.0006	0.0007	0.0005	0.0005	0.0004	0.0005
	12	0.002	0.0004	0.0005	0.0005	0.0005	0.0005	0.0004
	14	0.002	0.0005	0.0008	0.0003	0.0003	0.0003	0.0009
	16	0.0015	0.0006	0.001	0.0005	0.0005	0.0005	0.0006
	18	0.0011	0.0006	0.001	0.0003	0.0005	0.0005	0.001

**Table 4.** Chemical composition of the cathode metal at the processing of black lead obtained by reduction melting from battery scrap.

$i_a, A/cm^2$	t, day	Components concentration, wt%						
		Sb	Sn	Bi	Fe	As	Ag	Zn
0.3	2	2.3	0.002	0.06	<0.0003	0.03	0.005	0.0008
	4	5.5	0.002	0.13	0.0005	0.08	0.012	0.0003
0.4	6	6.7	0.002	0.16	0.0005	0.10	0.014	0.0007
	8	8.6	0.002	0.20	0.0005	0.14	0.017	0.0005
0.5	10	5.7	0.002	0.13	0.0005	0.09	0.008	0.0008
	12	6.4	0.002	0.14	0.0030	0.10	0.009	0.0008
	14	13.2	0.002	0.29	<0.0003	0.22	0.022	0.0006
	16	22.9	0.002	0.36	<0.0003	0.25	0.040	0.0007
	18	26.5	0.002	0.43	0.0025	0.31	0.040	0.0005

**Table 5.** Chemical composition of the anode metal at the processing of black lead obtained by reduction melting from battery scrap.

The antimony concentration in the anode metal during the test increased to 26.5 wt%, bismuth concentration increased to 0.43 wt%, arsenic concentration grew to 0.31 wt%, and silver concentration reached 0.04 wt% (**Table 5**).

The experimental batch of cathode lead (250 kg) was obtained.

The test of the electrochemical separation of Pb-Sb and Pb-Bi alloys demonstrated that lead is effectively separated from metal admixtures. The end product, i.e., grade lead, was obtained on the cathode, and alloys of lead with the excess concentrations of bismuth and antimony were obtained on the anode.

#### 4. Conclusions

Anode dissolution of Pb-Sb, Pb-Bi, and Sb-Bi alloys in the KCl-PbCl<sub>2</sub> melt at the temperatures of 773–873 K in wide interval of current densities was studied. The anode dissolution of Pb-Sb and Pb-Bi alloys proceed according to the two-electron scheme in the whole interval of current densities (0.07–2.00 A/cm<sup>2</sup>), i.e., the anode dissolution of lead takes place. The anode dissolution of Sb-Bi alloys proceeds according to the three-electron scheme in the whole interval of current densities, i.e., the anode dissolution of antimony takes place. The polarization curves illustrate the limiting diffusion current of lead ionization for Pb-Sb and Pb-Bi alloys, and at the Sb-Bi alloy dissolution, the antimony dissolution limiting current is observed.

The thickness of diffusion layer in the liquid metal anode was evaluated according to the limiting diffusion current of the metal. The thickness of the diffusion layers in liquid Pb-Sb, Pb-Bi, and Sb-Bi alloys are of the same order for diffusing lead, and antimony atoms and their values are close to that of the diffusion layer in the molten salt.

The experimentally obtained values of the equilibrium potentials of Pb-Sb, Pb-Bi, and Sb-Bi alloys in the temperature interval of 748–873 K were used to calculate the separation coefficients of double systems. According to the obtained values of separation coefficients, it was found that lead extraction from the Pb-Sb and Pb-Bi alloys is highly effective ( $6.5 \cdot 10^6$ – $1.5 \cdot 10^8$ ), whereas the process of bismuth and antimony separation is complex and not effective (5.5–6.5).

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