



Behaviour of multicomponent lead–tin alloys under cathodic polarization in a sodium hydroxide melt

A.A. OMELCHUK¹, O.G. ZARUBITSKII^{1,*}, V.P. OPANASYUK¹, N.F. ZAKHARCHENKO¹
and V.Ye. D'YAKOV²

¹Institute of General and Inorganic Chemistry of the Ukrainian National Academy of Sciences, 32/34 Pr. Palladina, 03680 Kyiv 142, Ukraine

²Tin plant, 630033 Novosibirsk, ul. Mira 62, zRussia

(* author for correspondence, e-mail: zarub@ionc.kar.net)

Received 6 March 2002; accepted in revised form 15 December 2002

Key words: cathodic polarization, electrode processes, lead–tin alloys, sodium hydroxide melt

Abstract

The results of investigations of the electrochemical behaviour of multicomponent lead–tin alloys under cathodic polarization in a sodium hydroxide melt are presented. It has been shown that as a result of the formation of intermetallic compounds, such elements as antimony, tin, bismuth and arsenic are extracted from the cathode to the anode. The electrolysis product on the cathode is lead with a total percentage of the above impurities of 0.065–0.070%. The extraction kinetics have been studied, the dissolution rate constants for each of the alloy components have been determined and a mechanism of mass exchange between the electrodes has been proposed. The current consumption for the extraction of metals from the melt has been determined.

1. Introduction

When heavy nonferrous metals, such as tin and lead, are produced and refined, a large number of multicomponent alloys are formed [1–6]. The composition of these alloys is very diverse and depends both on the composition of the raw materials to be processed and on the method of their processing. For example, the production of high-purity tin is accompanied by the formation of a large number of alloys containing up to (wt%): 30–40 tin, 10 bismuth, 5–6 antimony, 3–5 copper, 0.1–0.2 silver, 0.3–1.5 arsenic, 0.3 iron, 0.1–0.2 indium, and the rest is lead [4]. Such compositions are a valuable source for the production of a number of nonferrous metals and alloys for special purposes (e.g., solders etc). It was shown earlier [5–9] that cathodic refining enables the selective extraction of components from nonferrous alloys. The essence of the method is the electrodeposition of an alkali metal M (in this particular case, M=Na), which forms intermetallic compounds with most nonferrous metals M_i:



on the surface of the metals or alloy to be refined. Individual molten alkali metal hydroxides or their mixtures are usually used as the electrolyte. Under definite conditions (temperature, current density etc), these compounds transfer from the cathodic metal to the

electrolyte. By changing the electrolysis conditions, alloy components can be extracted selectively. The conditions for the selective extraction of the metals from an alloy have been described [5–7].

This paper presents the results of an investigation of the electrochemical behaviour of lead–tin alloys, containing accompanying metallic impurities, in the case of cathodic polarization in molten sodium hydroxide. The kinetics of extraction of alloy components have been studied as a function of the quantity of electricity passed, and the current yield of the metals in electrolysis has been estimated.

2. Experimental details

The electrolysis was conducted in a reactor, depicted in Figure 1. A cylindrical tank (1) 0.4 m in diameter and 0.3 m in height made of $(5-6) \times 10^{-3}$ m thick corrosion-resistant steel 12Kh18N10T contained molten sodium hydroxide and served as a receiver for electrolysis products formed on the anode. Within, a nickel anode (2) and a tank (3) for the cathodic alloy (11) were mounted concentrically. To stir the cathodic metal and electrolyte, there was an electrically driven stirrer (7) in the reactor. The temperature conditions of the electrolysis were maintained by means of nichrome heaters (6) with a total power of 8 kW. The electrolysis temperature was controlled by means of a temperature control

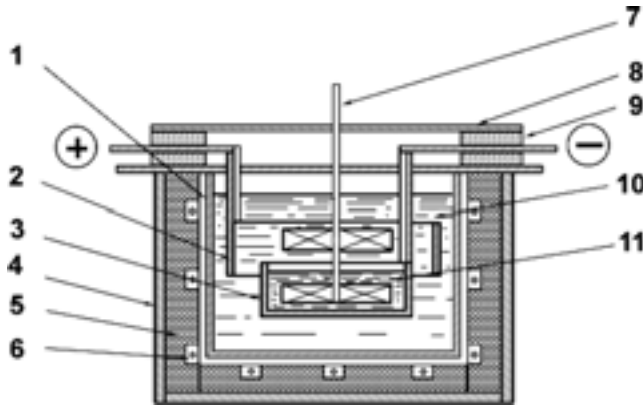


Fig. 1. Electrolyser for the cathodic refining of metals in hydroxide melts: (1) electrolytic tank, (2) nickel anode, (3) cathode tank with the metal, alloy being refined, (4) electrolyser casing, (5) refractory, (6) heaters, (7) stirrer for stirring the cathodic metal and electrolyte, (8) electrolyser cover, (9) dielectric, (10) electrolyte and (11) cathodic alloy.

potentiometer and a chromel–alumel thermocouple to within ± 10 degrees. Analytically pure molten sodium hydroxide was used as the electrolyte (10). Samples of the metals on the electrodes and the electrolyte were taken at regular intervals and their quantitative composition was determined by chemical and atomic absorption analysis. The electrolysis was conducted at a current load of 250 A, at 430–450 °C for 116 h. During electrolysis, the cathodic metal was stirred with a stirrer, whose rotational speed was constant in all experiments at 15 rpm. The effect of the rate of stirring of the cathodic metal on the extraction rate of the alloy components (arsenic, antimony, tin, bismuth) was not studied.

3. Results and discussion

Electrolysis results are listed in Table 1. It is seen from the table that under the given cathodic refining conditions, all metals accompanying lead are practically wholly removed from the starting alloy. On the cathode, lead was obtained as a result of electrolysis (78–80% of the mass of the starting alloy), which contained, as a whole, no more than 0.065–0.070% heavy nonferrous metallic impurities and up to 5% sodium. This metal is easily removed from lead under anodic polarization. On the anode, a lead–bismuth alloy with a higher bismuth content as compared to the starting alloy and sludgelike products were obtained. The ratio of the amounts of the heavy nonferrous metals accompanying lead is much the same in the anodic sludgelike products and in the starting alloy. This indicates that a transfer of the alloy components accompanying lead from cathode to anode mainly occurs during electrolysis. The amount of the anodic alloy is 7.2% and that of sludgelike products 19.3% of the mass of the starting alloy loaded on to the anode.

The laws governing the mass exchange between the electrodes during the cathodic refining of metals, the

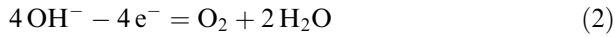
Table 1. Results of the electrolysis of lead–tin alloys in molten sodium hydroxide under cathodic polarization parameters: $t = 430$ °C, $I = 250$ A, $U = 4.6$ V, $Q = 29\,000$ Ah, rotary speed of the stirrer: 15 rpm

| Electrolysis products | Content | | | | | | | | | | | | | |
|-----------------------------|---------|-------------|-------|------|-------|-------|---------|------|----------|-------|---------|------|--------|-----|
| | Name | Wzeight /kg | Lead | | Tin | | Bismuth | | Antimony | | Arsenic | | Sodium | |
| | | | % | /kg | % | /kg | % | /kg | % | /kg | % | /kg | % | /kg |
| Starting alloy (S) | 41.4 | 87.47 | 36.2 | 1.93 | 0.8 | 5.73 | 2.37 | 4.76 | 1.97 | 0.074 | 0.03 | – | – | |
| Cathodic alloy (C) | 32.3 | 97.2 | 31.4 | 0.03 | 0.01 | 0.005 | 0.002 | 0.02 | 0.01 | 0.01 | 0.003 | 4.22 | 1.36 | |
| Anodic alloy (A) | 3.0 | 90.6 | 2.73 | 0.06 | 0.002 | 8.3 | 0.25 | 0.78 | 0.02 | 0.073 | 0.0002 | 0.4 | 0.012 | |
| Anode sludge (AS) | 18.0 | 7.5 | 1.35 | 3.5 | 0.63 | 11.0 | 1.98 | 6.34 | 1.14 | 0.078 | 0.014 | – | – | |
| Cathodic metal samples (CS) | 1.1 | – | 0.99 | – | 0.01 | – | 0.03 | – | 0.03 | – | 0.0004 | – | – | |
| Electrolyte (E) | 44.0 | – | – | – | – | – | – | – | – | – | – | – | – | |
| (a) loaded | 30.0 | 0.05 | 0.02 | 0.02 | 0.01 | 0.05 | 0.015 | 1.40 | 0.42 | 0.05 | 0.015 | – | – | |
| (b) unloaded | 5.0* | – | –0.29 | – | 0.138 | 0.093 | 0.35 | – | – | – | – | – | – | |
| Difference: | | | | | | | | | | | | | | |
| S–(C+A+CS+AS+E) | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | |

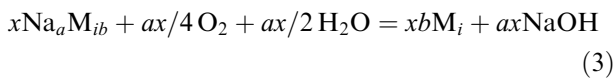
* Difference: S–(C+A+CS).

mechanism and kinetics of the electrode reactions proceeding during this process are described in detail elsewhere [4, 5].

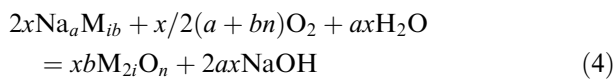
The metal is obtained on the anode by a number of electrochemical reactions, which may be represented schematically in a simplified form as follows. The main electrode reaction on an inert nickel anode in a sodium hydroxide melt is the discharge of hydroxide ions:



The intermetallic compounds Na_aM_{ib} that have transferred from the cathode into the molten electrolyte are oxidized on the anode by Reaction 2 products to form metal M_i :



At high current densities or in the case of long electrolysis, the metal M_i deposited on the anode can oxidize [5, 6] to oxides:



where $\text{M}_{2i}\text{O}_n = \text{Bi}_2\text{O}_3, \text{SnO}, \text{Sb}_2\text{O}_3, \text{As}_2\text{O}_3, \text{PbO}$ etc., on which the sludgelike products are based.

Figure 2 shows the dependence of the variation of the amount of cathodic alloy components on electrolysis time. This dependence is of both scientific and practical interest since it is possible to assess the interrelation between the rate of transformations on the cathode and the parameters determining them, to obtain a mathematical model of this process and hence to determine the electrolysis time up to the production of metal of

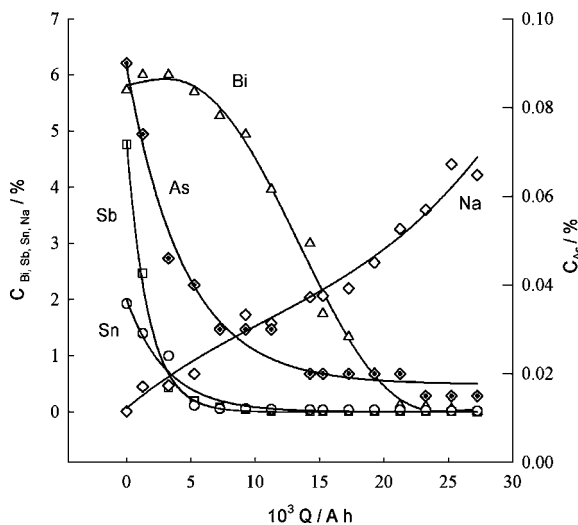


Fig. 2. Impurity content of the cathodic metal as a function of the quantity of charge passed ($I = 250 \text{ A}$, $i_c = 5 \times 10^3 \text{ A m}^{-2}$, $i_a = 2 \times 10^3 \text{ A m}^{-2}$, $t = 450 \text{ }^\circ\text{C}$, $U = 4.6 \text{ V}$; metal loaded into the cathode tank: 41.4 kg, electrolyte loaded: 51.1 kg).

predetermined purity. In the general case, the rate of Reaction 1 may be represented [5, 6] by the equation:

$$W_i = k[\text{Na}]^{n_1}[\text{M}_i]^{n_2} \quad (5)$$

where k is the rate constant, and n_1, n_2 are the reaction orders for sodium and some alloy component, respectively. The overall order of the reaction, n_0 , is

$$n_0 = n_1 + n_2 \quad (6)$$

It should be noted that in most cases the numbers n_0, n_1 and n_2 are not identical to the values of the stoichiometric coefficients of chemical equations. This is due to the fact that the formal notation of a chemical equation does not reflect elementary steps of the mechanism of the transformations that take place. The reaction order is a strictly experimental quantity, which characterizes the dependence of the rate of a particular reaction on the reactant concentration.

The kinetic equation of any reaction may be represented in the general form as follows:

$$-\frac{dC}{dt} = kC^n \quad (7)$$

By integrating Equation 7, the reaction order with respect to some component and the rate constant can be determined. For first-order kinetic equations, integrating Equation 7 yields:

$$\ln C_t = \ln C_o - kt \quad (8)$$

and for second-order equations:

$$\frac{1}{C} = \frac{1}{C_o} + kt \quad (9)$$

It follows that if the reaction is of first order, the plot of C against t must give a straight line in $\ln C_t$ against t coordinates, and if it is of second order, the plot must give a straight line in $1/C$ against t coordinates. The slope of this straight line must correspond to the rate constant k . An analysis of the experimental data obtained (Figure 3) showed the plot of the concentration of the alloy components against the electrolysis time in $\ln C_t$ against t coordinates to give a straight line with a kink, the kink in the kinetic plots for each of them being observed approximately in the same time interval, which corresponds to the passing of 15 000–16 000 Ah of electricity. This may indicate that in the course of electrolysis, a change in the dissolution mechanism of alloy components takes place in a certain period; on the whole, however, the rate of their extraction is described by a first-order kinetic equation. Since heavy nonferrous metals are extracted at the interface, it is expedient to characterize the moment of the change in the kinetic plot by electricity consumption per unit surface area and mass of the starting alloy. In this particular case, the moment of the change in the shape of the kinetic plot

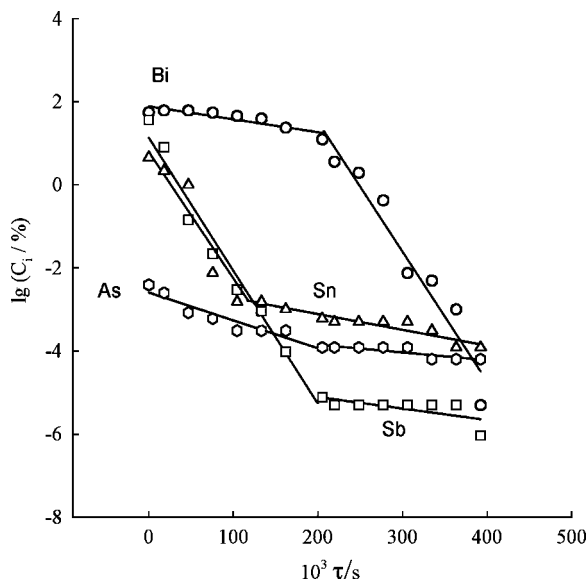
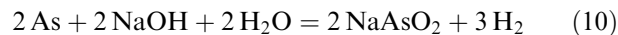


Fig. 3. Logarithm of impurity concentration as a function of electrolysis time in the cathodic refining of lead-tin alloy ($I = 250$ A, $i_c = 5 \times 10^3$ A m $^{-2}$, $i_a = 2 \times 10^3$ A m $^{-2}$, $t = 450$ °C, $U = 4.6$ V; metal loaded into the cathode tank: 41.4 kg, electrolyte loaded: 51.1 kg).

corresponds to the value $(6.3\text{--}6.7) \times 10^3$ Ah m $^{-2}$ kg $^{-1}$. During this electrolysis time, the lead concentration in the starting alloy increased by 10%, and the extraction ratio of the accompanying components was: antimony, 99%; tin, 98%; bismuth, 70%; arsenic, 60%. A typical plot of cathodic alloy component concentration against electrolysis time in $\ln C_i$ against t coordinates is shown in Figure 3, and the values corresponding to the electrochemical reaction rate constants at each of the electrolysis stages are listed in Table 2. The same table lists the initial dissolution rates of the alloy components, which were calculated from the slope of tangents to the kinetic C_i against t plots (Figure 2).

It is evident that antimony and tin possess the highest extraction rate at the initial electrolysis stage. At the second electrolysis stage, the extraction rate constant for practically all components, except bismuth, decreases.

When analysing experimental data it must be taken into account that under certain conditions molten sodium hydroxide can react with alloy components to form corresponding oxygen-containing compounds (arsenates, antimonates etc). According to [2, 6, 10], arsenic reacts with sodium hydroxide with hydrogen evolution:



In the presence of oxidants, compounds of arsenic in the highest oxidation states are formed:



Both water and oxygen are products of Reaction 2 and can get in some measure into the cathode chamber. Antimony, tin and bismuth react weakly and lead hardly reacts with thoroughly dehydrated molten sodium hydroxide, but they oxidize readily in the presence of oxidants in the following order: arsenic > tin > antimony > bismuth > lead. The standard free energies of formation of the corresponding oxygen-containing compounds at 450 °C are: -304.47 kJ mol $^{-1}$ for Na $_3$ -AsO $_4$, -300.20 kJ mol $^{-1}$ for Na $_2$ SnO $_3$ and -287.10 kJ mol $^{-1}$ for Na $_3$ SbO $_4$ [10]. Thus, arsenic is a reductant for oxygen-containing tin, antimony, bismuth and lead compounds. Tin is a reductant for antimony, bismuth and lead compounds etc. An oxidant for all elements is lead plumbite. If alloy components were removed by oxidation and formation of oxygen-containing compounds according to reactions similar to Reaction 11, arsenic, then tin, antimony etc would be extracted in the first place from the alloy in the fullest measure. The observed order of the extraction of components from a cathodically polarizable alloy is somewhat different (Table 2). Since the main electrode process at the cathode is the discharge of sodium ions:



the oxidation of alloy components in the presence of such a strong reductant as sodium is hardly probable. The main process, which removes alloy components, is the formation of intermetallic compounds and their subsequent transfer into the salt phase. According to [5, 6], the intermetallic compounds having the highest heat of formation and the highest melting point must be removed from the alloy in the first place. One of the necessary conditions for the extraction of such compounds from a cathodic alloy is that they form a solid phase in it.

Table 3 lists the standard free energies of formation [11] and melting points [11, 12] of some intermetallic compounds of sodium with heavy nonferrous metals.

Table 2. Rate constants and initial rates of the electrochemical extraction of intermetallic compounds of lead-tin alloy components under cathodic polarization in molten sodium hydroxide
Parameters: $t = 430$ °C, $I = 250$ A, $U = 4.6$ V, $Q = 29$ 000 Ah, rotary speed of the stirrer: 15 rpm

| Rate constant, k/s^{-1} | Alloy component | | | | |
|-------------------------------------|----------------------|-----------------------|----------------------|----------------------|----------------------|
| | Lead | Antimony | Tin | Bismuth | Arsenic |
| First region | 4.3×10^{-7} | 4.6×10^{-4} | 4.1×10^{-4} | 1.4×10^{-5} | 1.5×10^{-4} |
| Second region | 5.2×10^{-9} | 1.5×10^{-18} | 5.3×10^{-5} | 4.5×10^{-4} | 3.9×10^{-5} |
| Initial rate /g-at s $^{-1}$ | – | 8.5×10^{-4} | 2.3×10^{-4} | 1.5×10^{-6} | 1.6×10^{-5} |

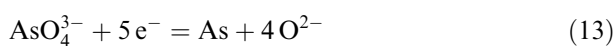
Table 3. Standard free energies of formation and melting points of intermetallic compounds of sodium with some heavy metals

| Metal | Intermetallic compound | Standard free energies of formation [11], $\Delta G_{298.15}^{\circ}$ /kJ mol ⁻¹ | Melting point [11, 12] /°C |
|----------|----------------------------------|---|----------------------------|
| Arsenic | NaAs | -89.12 | - |
| | NaAs ₂ | -98.32 | - |
| | Na ₃ As | -196.23 | - |
| Antimony | NaSb | -67.78 | 465 |
| | Na ₃ Sb | -205.85 | 1010 |
| Bismuth | Na ₃ Bi | -167.36 | 848 |
| Tin | NaSn | -62.85 | 578 |
| | Na ₂ Sn | -56.90 | 478 |
| Lead | NaPb | -41.36 | 372 |
| | NaPb ₃ | -46.38 | 320 |
| | Na ₉ Pb ₄ | -258.61 | 403 |
| | Na ₁₃ Pb ₅ | -284.46 | 391 |
| | Na ₁₅ Pb ₄ | -250.87 | 386 |

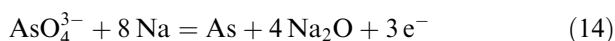
It is seen from the data that there is a certain correlation between the standard free energies of formation, melting points, order and rate of the extraction of intermetallic compounds (Table 2). Antimony intermetallide (Na₃Sb) has the highest melting point, and tin intermetallides have the highest standard free energies of formation. Hence these compounds are removed from the alloy first. In spite of the fact that lead intermetallides possess a high heat of formation, they have a low melting point. The high-melting intermetallic compounds of bismuth are characterized by lower standard free energies of formation and hence are extracted later from the cathodic alloy. The change in the shape of the kinetic $\ln C_t$ against t plots must be due to the occurrence of the following reactions.

The oxides formed by the anodic oxidation of intermetallic compounds (according to Equation 4) interact with molten sodium hydroxide. This interaction results in the formation of oxygen-containing compounds. As pointed out above, these compounds are also formed on the direct interaction of heavy nonferrous metals with molten sodium hydroxide (Equations 10 and 11) in the following order according to the variation of standard free energies of formation [10]: Na₃AsO₄, Na₂SnO₃, Na₃SbO₄, Na₃BiO₄, NaPbO₂.

As a result of the forced convection of the electrolyte, these compounds enter the cathode chamber during electrolysis and are reduced to metal on the cathodic alloy surface either by the action of direct current or by the action of sodium. For example,



or



Thus, in a certain period the conditions are attained under which metal transfers in the opposite direction,

from anode to cathode, takes place. It is this circumstance that gives rise to a change in alloy component extraction kinetics in the course of electrolysis. Among the components of the alloy under investigation, arsenic possesses [10] the greatest ability to interact with molten sodium hydroxide. Accordingly, its extraction from the cathode to the anode is small. This element seems to 'circulate' between the cathode and anode. As pointed out above, antimony and tin react weakly with alkali melts, and hence the transfer in the opposite direction from anode to cathode is less pronounced.

The considerable (about 30-fold) increase in bismuth dissolution rate constant at the second electrolysis stage is due to the fact that by this time bismuth becomes practically the main cathodic alloy component that accompanies lead.

At the moment of change in kinetic dependence (Figure 3), the antimony content of the cathodic alloy is 0.05%, tin content 0.037%, arsenic content 0.03%, whereas the bismuth content is 1.75%. It is not improbable that the alloy component extraction kinetics are influenced by hindrances in the transport of heavy nonferrous metals from the bulk of the alloy to its surface, where sodium ions are discharged, and intermetallic compounds are formed.

An important characteristic of any electrochemical process is current consumption. Therefore, we have estimated the relative quantity of electricity that is consumed for the extraction of one or another alloy component. The calculation was made according to the equation:

$$\eta_i = \frac{Fn_i}{Q} \quad (15)$$

where F is the faradaic constant, n_i the quantity of reacted component (g equiv.), Q the quantity of passed electricity and η_i the formal current efficiency.

The results obtained are shown in Figure 4. It is seen that most of the current is consumed for the extraction of antimony and tin. In the initial electrolysis stages (electricity consumption, up to 5000 Ah), bismuth is practically not extracted from the alloy, and its concentration increases (negative values of formal current efficiency).

4. Conclusion

The data obtained indicate that the cathodic refining method makes it possible to extract almost completely such elements as antimony, tin, arsenic from multicomponent lead-tin alloys and to obtain cathodic lead with a total percentage of these metals of 0.065–0.070% at an extraction ratio of 78–80%.

The extraction rate of the alloy components is satisfactorily approximated by a first order kinetic equation. The extraction rate of such alloy components as antimony, tin, and arsenic decreases during the course

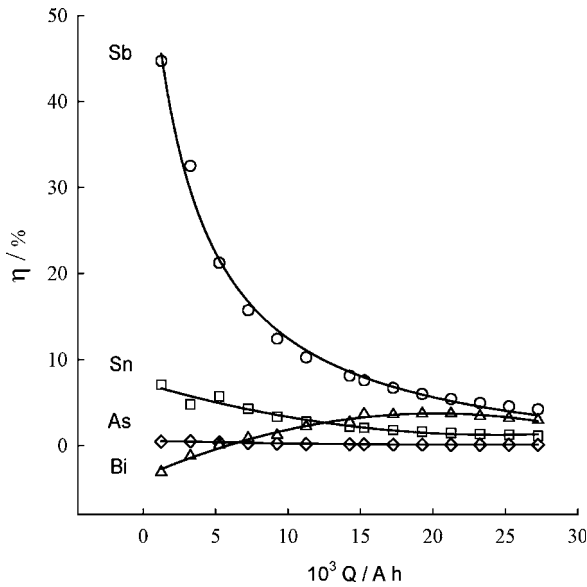


Fig. 4. Formal current efficiency as a function of the quantity of charge passed.

of electrolysis. This is due to the codischarge on the cathode of oxygen-containing compounds (Na_3AsO_4 , Na_2SnO_3 , Na_3SbO_4), which are formed with time near the anode. Rate constants for alloy component extraction in different electrolysis stages have been determined from kinetic relations $\ln C = f(\tau)$.

Information on the extraction kinetics of alloy components can be utilized to optimize the conditions for this process.

References

1. W.H. Dennis, 'Metallurgy of Non-ferrous Metals' (Pitman, London, 1961).
2. P. Paschen and H. Winterhager, *Z. Erzbergbau und Metallhüttenwesen* **21** (1968) 14.
3. T.R.A. Davey, *J. Metals* **8**(3) (1956) 341.
4. O.G. Zarubitskii, A.P. Dugelnyi, A.A. Omelchuk, V.Y. Dyakov and V.T. Melyokhin, *Tsvet. Metally* **3** (1991) 30 (in Russian).
5. Y.K. Delimarskii and O.G. Zarubitskii, 'Electrorefining of Heavy Nonferrous Metals in Melts' (Metallurgiya, Moscow, 1975), (in Russian).
6. O.G. Zarubitskii, 'Refining of Metals in Alkali Melts' (Metallurgiya, Moscow, 1981), (in Russian).
7. O.G. Zarubitskii and N.F. Zakharchenko, *Bull. Bismuth Institute* **21** (1978) 5.
8. W.T. Denholm, R. Dorin and H.J. Gardner, in M.J. Bones (Ed.), 'Advances in Extractive Metallurgy and Refining' (IMM, London, 1977), p. 239.
9. C. Grange and L. Heerman, *J. Appl. Electrochem.* **4** (1974) 279.
10. V.S. Lovchikov, 'Alkali Refining of Lead' (Metallurgiya, Moscow, 1964), (in Russian).
11. V.P. Glushko (Ed.), 'Thermodynamic Constants of Substances', issue X, part 1 (Moscow, 1981), (in Russian).
12. M. Hansen and K. Anderko, 'Constitution of Binary Alloys', 2nd edn (McGraw-Hill, New York, 1958).