
**METALLURGY
OF NONFERROUS METALS**

Electroextraction of Lead from a Lead Trilonate Solution

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Abstract—Laboratory studies of the cathode process of the electroextraction of zinc from the trilonate electrolyte obtained after the purification of solutions after leaching lead cakes of zinc production are performed. The potential scan rate is determined by recording potentiodynamic curves; the optimal electrolyte acidity, the composition, and the temperature are established. Values of activation energy confirming the concentration nature of process polarization are found.

Keywords: lead, Trilon, electroextraction, potential, activation energy, polarization

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The method of extracting lead into a solution from lead cakes of zinc production and the removal of metal impurities from the thus prepared solution were suggested in [1, 2]. We used a complex former, namely, disodium salt of ethylenediamine acid known as Trilon B, as the leaching reagent. The processing technology of the lead cake is described in [3]. The finishing operation is the electroextraction of lead from the purified solution by leaching.

The electroreduction of various metals from complex electrolytes is described in many publications. However, the data presented in them have either academic or strictly specialized characters. In connection with this, we investigated the regularities of the electroreduction of lead from trilonate electrolytes under various conditions. We varied the potential scan rate, the concentration of the lead cation, the pH of the electrolyte, and the process temperature.

The cathode reduction of lead from the trilonate solution was studied by recording the polarization curves using an IPC-Pro M potentiostat connected to a personal computer. The tests were performed in a standard thermostated electrochemical cell. Mixing of the working solution in the cell with a constant rate for all the experiments was performed using a magnetic stirrer established under the cell. We used a silver–chlorine half-cell as the reference electrode. The working electrode with an area of 0.5024 cm², which was fabricated from stainless steel and pressed into a vinyl-plastic holder, was separated from the reference electrode using an electrolytic key. The platinum electrode was an auxiliary electrode. To hold the temperature of the working solution, water from a thermostat was passed through the jacket of the electrochemical cell.

A working solution in an amount of 100 cm³ was poured into the electrochemical cell, electrodes and cables were connected, and stirring was switched on. The necessary parameters of the potential scan rate and the ranges of potentials and currents were specified; the current–voltage dependence was fixed. The data were processed in Microsoft Excel recalculating cathode currents into the current density.

The potentiodynamic discharge curves of metal cations were recorded for a solution with the averaged composition (pH = 7, Pb²⁺ of 20 g/dm³) at various potential scan rates ($V_p = 5, 10, 20,$ and 50 mV/s) in the E range from -500 to -2500 mV by fixing the cathode currents with recalculation into the current density with the help of special software using a personal computer. Before each experiment, the working electrode was carefully cleaned and polished. To ensure the reproducibility of results, each experiment was repeated sixfold averaging the results. Further, averaged curves were combined into a common plot (Fig. 1).

The increase in i_c at $E = -1500$ mV is smoothed in the curves at $V_p = 20$ and 50 mV/s (Fig. 1, curves 3 and 4); diffusion limiting is not distinguishable. An increase in the current density and a variation in the slope angle of the curve are also noted for the rates of 5 and 10 mV/s (Fig. 1, curves 1 and 2). A small segment of the limiting diffusion current is also observed. Under these conditions, the value $V_s = 5$ mV/s is unreasonable because curve recording is prolonged. Thus, we performed further investigations at a potential scan rate of 10 mV/s.

We studied reduction of lead from a trilonate solution with various acidities (pH = 4, 7, and 10) with the selected scan rate.

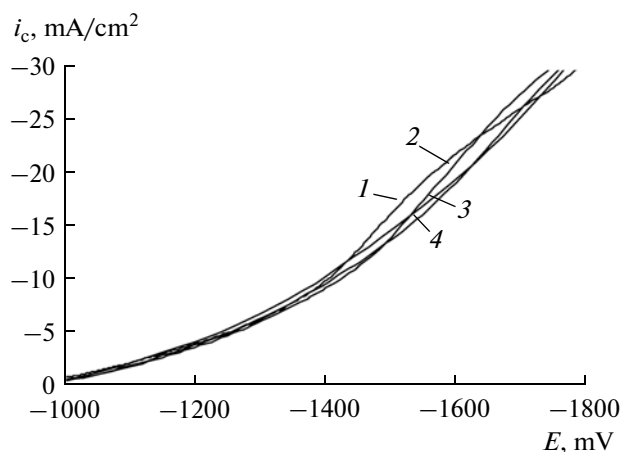


Fig. 1. Dependence of the cathode current density on the potential scan rate. V_s : (1) 5, (2) 10, (3) 20, and (4) 50 mV/s.

It was shown previously [2] that the ligand configuration changes at various pH of the ethylenediaminetetraacetate solution, namely, ions H_3EDTA^- and H_2EDTA^{2-} are present in the solution at pH = 4; H_2EDTA^{2-} ions are preferentially observed at pH = 7; and $EDTA^{4-}$ ions prevail at pH = 10. In connection with this fact, the electroreduction process itself depends on the strength of existing complexes, on their charge, and on the electrical conductivity of the electrolyte (which decreases in the alkali medium proportionally to the concentration of hydrogen ions).

For each value of pH, the results of six identical experiments with their subsequent averaging were registered. Voltammetric curves were drawn in a common plot (Fig. 2).

Gas bubbles (hydrogen) started to vigorously liberate themselves at pH = 4 on the working electrode from the potential of -600 mV and above; at pH = 7, the process started from -900 mV. The process-onset potential is more electronegative for the solution with pH = 10 compared with pH = 4. Lead almost was not isolated, and its collection from the working electrode surface was hampered. The most probable interpretation is the prevalence of the reduction reaction of hydrogen over the reduction of lead, which is caused by the smaller strength of lead-trilonate complexes in weakly acidic (pH = 4) and neutral (pH = 7) media. Simultaneously, the concentration of hydrogen ions in weakly acidic and neutral media is higher than in the alkali medium; in connection with this, the overvoltage of hydrogen liberation is correspondingly lower.

For the electrolyte with pH = 10, we observed a variation in the slope angle of the potentiodynamic curve near -1500 mV. Until the potential of -1500 mV was reached, no liberation of gas bubbles was fixed similarly to the case of pH = 4 and 7. Consequently, we

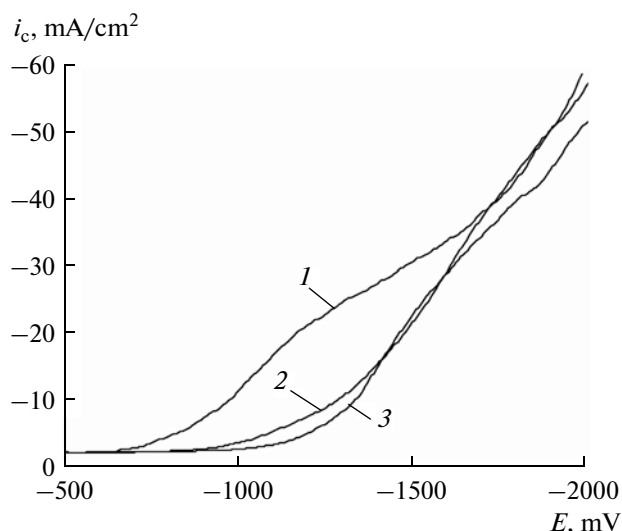


Fig. 2. Influence of pH on the electroreduction rate of lead. (1) pH = 4, (2) pH = 7, and (3) pH = 10.

can assume that the region of reduction of lead ions without the preliminary liberation of hydrogen is the potential range from -750 to -1500 mV.

The calculation of the standard potential of electroreduction of lead allowing for the instability constant with the invariable complexon concentration (i.e., allowing for the true concentration of free dissociated Pb^{2+} ions in the solution) shows that this magnitude constitutes -667 mV (relatively to the standard hydrogen electrode); i.e., its value on the potential scale relative to the silver-chlorine half-cell is determined as -440 mV:

$$E_{Pb(\text{compl})} = E_{Pb(H_2O)}^0 + (0.059/2) \log [K_{\text{inst}} C_{[PbEDTA]}] \\ = -0.136 + (-0.531) = -0.667 \text{ B (n.h.e.)}. \quad (1)$$

The shift of the electroreduction potentials of lead to the electronegative region at all tested pH indicates a considerable retardation of the process, i.e., the overvoltage of the reduction of lead. Since this phenomenon is associated with the stability of trilonate complexes and, consequently, with the concentration of dissociated Pb^{2+} ions, then the polarization during the reduction of lead from a complex electrolyte is exclusively concentration. It is noteworthy that, as the pH of the solution increases, polarization rises because the anion charge and, consequently, its concentration in the near-cathode space increase, which in turn increases electrode screening. When considering this phenomenon, it should be noted that the declared values of pH of the solution correspond to the starting state (before switching on the current). An essential increase in electrolyte alkalinity occurs in the near-cathode region during the electrolysis due to the reduction of hydrogen ions; therefore, it is impossible to note the true value of pH of the discharge.

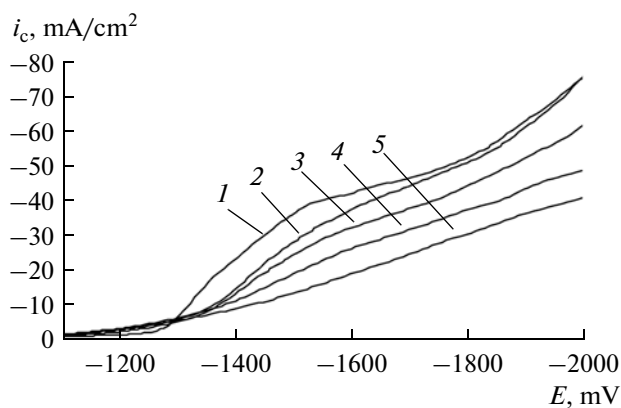


Fig. 3. Influence of the solution composition on the electroreduction rate of lead. Pb^{2+} concentration: (1) 40, (2) 30, (3) 20, (4) 10, and (5) 1 g/dm³.

The density of the limiting diffusion current at $\text{pH} = 4$ is also largest (Fig. 2, curve 1); it is conditioned by the maximal concentration of dissociated lead ions in this solution compared with solutions in neutral and alkali media.

The reduction of hydrogen at $\text{pH} = 4$ introduces the largest contribution to the total electrochemical reaction, and the smallest contribution is introduced at $\text{pH} = 10$, which is caused by a maximal concentration of dissociated hydrogen ions in a weakly acidic medium and minimal concentration (in an alkali medium).

A decrease in the magnitude of the limiting current with an increase in pH of the solution is associated with the delivery of complex lead ions to the electrode surface being hampered and their destruction.

Thus, the solution with $\text{pH} = 10$ has a series of advantages for obtaining metal lead:

(i) the highest stability of trilonate lead complexes allows us to obtain more dense compact precipitates;

(ii) the high overvoltage of hydrogen liberation in the alkali solution retards the undesirable reaction of its reduction, which provides a high current yield for lead.

The investigation into the electrolyte composition on regularities of the electroreduction of lead were performed at a potential scan rate of 10 mV/s, $\text{pH} = 10$, and a temperature of 20°C. The concentration of lead ions in experiments was 1, 5, 10, 20, and 40 g/dm³. In the potential range from -1000 to -2000 mV, the density of the cathode current across the working electrode made of stainless steel (X18H10T) was detected. All measurements were performed sixfold, and their averaged values are presented in Fig. 3.

It is established that lead is reduced with the largest limiting current and a lower electronegative potential at a concentration of lead ions of 40 g/dm³. The limit-

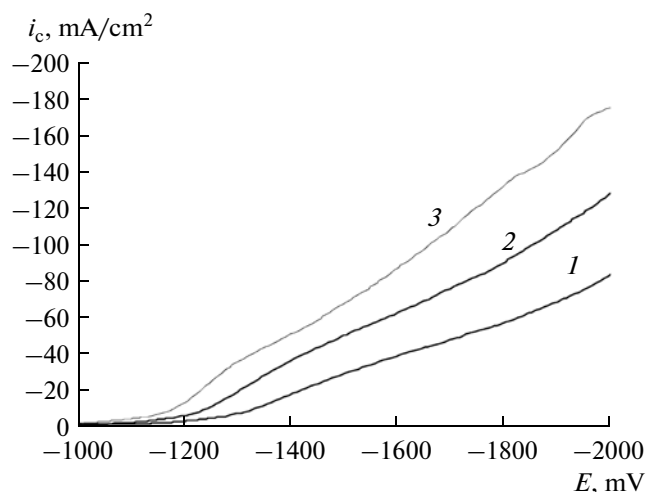


Fig. 4. Influence of temperature on the electroreduction rate of lead. t : (1) 20, (2) 50, and (3) 80°C.

ing cathode current density decreases as it decreases (Fig. 3), while the onset potential of reduction of lead shifts to the electronegative region. A decrease in the Pb^{2+} content in the solution leads to the formation of powderlike precipitates. This phenomenon also indicates the concentration nature of process polarization.

A concentration ratio of components of the solution (metal ion : ligand) less than 1 : 1 also affects the overvoltage of the isolation of metal; namely, the higher the content of free EDTA^{4-} ions in the near-cathode space is, the stronger their screening effect on the electrode is and the larger the degree of hampering the reduction of metal is.

The temperature dependence of the cathode reduction of lead was investigated at an electrolyte temperature of 20, 50, and 80°C. For each temperature, the set of curves was recorded; from averaging this set, we can see (Fig. 4) that the potential of the isolation onset of lead shifts to the less electronegative region from -1300 to -1200 mV. The reduction at $t = 20^\circ\text{C}$ is implemented at lower current densities, i.e., with a lower rate, and the region of the potential for the reduction onset of hydrogen at about -1700 mV is clearly seen. An increase in the electrolyte temperature at the same potentials leads to a considerable increase in the current density, i.e., to an increase in the reduction reaction rate on the surface of the working electrode.

The nature of the cathode polarization is confirmed by an analysis of experimental data by the Gorbachev method [4]. Temperature corrections for the apparent activation energy were taken into account for the silver-chlorine half-cell by the equation valid in a temperature range of 0–100°C [5]. The activation energy of the discharge of lead ions of 12.5–20.9 kJ/mol, which is characteristic of the concentration polarization, was calculated by slope tangents of straight lines of the dependence of the current density

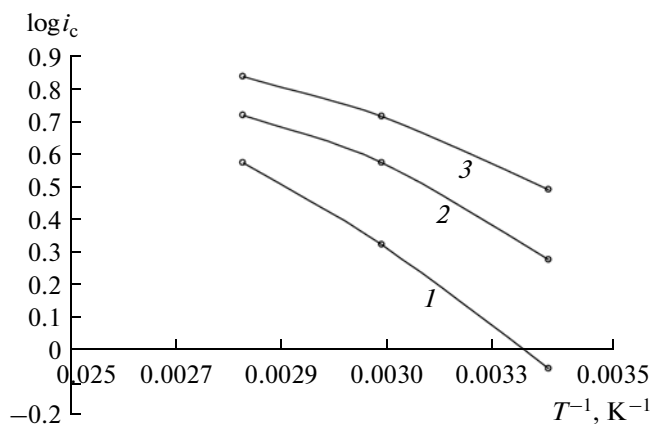


Fig. 5. Dependence $\log i_c - T^{-1}$ for the lead trilonate solution containing $20 \text{ g/dm}^3 \text{ Pb}^{2+}$. $E = (1) -1300$, $(2) -1400$, and $(3) -1500 \text{ mV}$.

logarithm on the inverse temperature at $E = -1300$, -1400 , and -1500 mV (Fig. 5).

Thus, it is confirmed that the polarization of the reduction of lead has mainly a concentration character and the reduction of hydrogen prevails at the working electrode as the temperature increases, which is undesirable. Consequently, it is more favorable energetically to perform the electrolysis at $T = 20^\circ\text{C}$.

CONCLUSIONS

(i) The maximal current yield for lead with the largest overvoltage of hydrogen liberation is implemented in an alkali electrolyte with $\text{pH} = 10$.

(ii) The electrolyte concentration by lead ions should be held at the solubility limit of the complexonate, i.e., of about $40 \text{ g/dm}^3 \text{ Pb}^{2+}$, in order to obtain compact precipitates and a high (up to 95%) current yield.

(iii) Temperature dependences of electroreduction of lead make it possible to calculate the activation energy of the process, the magnitude of which is $12.5\text{--}20.9 \text{ kJ/mol}$, which confirms the hypothesis that the polarization has an almost completely concentration nature.

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