NONFERROUS METALLURGY:

DISCUSSION

Electrolysis as a Link Between Some Metallurgical and Chemical Industries by V. V. Stender

Yu. V. Baimakov. V. V. Stender's presentation of the future development of electrolysis in metallurgy commands attention. The use of chloride solutions for the precipitation of heavy metals makes it possible to replace lead anodes with graphitized anodes, which are easier to obtain, and also to utilize the anodic product and obtain very pure metals without lead and sulfur impurities. The drawbacks of the present methods of electrolysis of molten cryolites for the production of aluminum are described quite correctly. However, improvement of aluminum production methods will not be based on the use of metal oxide anodes but rather on electrothermic production of aluminosilicate alloys, with subsequent purification; for this purpose organic electrolytes are of particular interest.

S. A. Zaretskii. V. V. Stender has described very well the problem of electrolysis as a link between the metallurgical and chemical industries. I will give another example of the fruitfulness of such a link: contaminated hydrochloric acid -- the voluminous waste product from the synthesis of organic halogene derivatives -- can be used for the production of chlorine and metallic manganese. According to the well known Sheele reaction between hydrochloric acid and manganese oxide ore, half the chlorine is obtained in the elementary state and the other half in the form of manganese chloride:

$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O.$$

If the $MnCl_2$ solution is subjected to electrolysis one obtains metallic manganese and the second half of the chlorine from the original hydrochloric acid:

$$MnCl_2 + 2e \rightarrow Mn + Cl_2.$$

By linking these two reactions through electrolysis one solves two important problems of the chemical and metallurgical industries.

O. A. Khan. Anodes are the most important problems of hydroelectrometallurgy of ferrous and nonferrous metals. The investigations of the electrolysis of zinc chlorides and other chloride solutions with highly porous graphite anodes performed by V. V. Stender and his colleagues have a great theoretical and practical importance. In our hydrometallurgical laboratory of the Altai Mountains Metallurgical Institute of the Academy of Sciences Kaz.SSR we have investigated the electrolysis of lead chloride solutions, using soluble iron and cast iron anodes. [O. A. Khan and L. A. Saltovskaya, Byull. Tekhn. Inf. Ust'-Kamenogorsk Lead-Zinc Combine, August, 1956.] This process fits easily into the present hydrometallurgical chloride method of treating products containing lead. For the heavy hydrometallurgy of lead ores the use of highly porous graphite anodes is of great interest.

Amalgam Metallurgy: Cementation with Amalgams by M. T. Kozlovskii

P. P. Tsyb. The application of the amalgam method in metallurgy is particularly interesting for the production of rare metals or highly pure metals.

Our investigations of the electrolysis of different salts with a mercury cathode and anodic oxidation of the amalgams obtained have revealed a series of anomalous phenomena. Figure 1 represents the variation of the cathode potential as a function of the current density during electrolysis of aqueous acid solutions of some sulfates. The shape of the curves indicates that the deposition of iron, nickel, cobalt, and chromium requires more energy than their deposition on solid electrodes. During electrolysis of thallium salts the cathode potential is almost independent of the current density. Further, while the normal potential of indium is equal to -0.34 v and it dissolves in mercury without any absorption of energy, it is deposited from indium sulfate on a mercury cathode at a potential of 0.7 to -0.9 v.

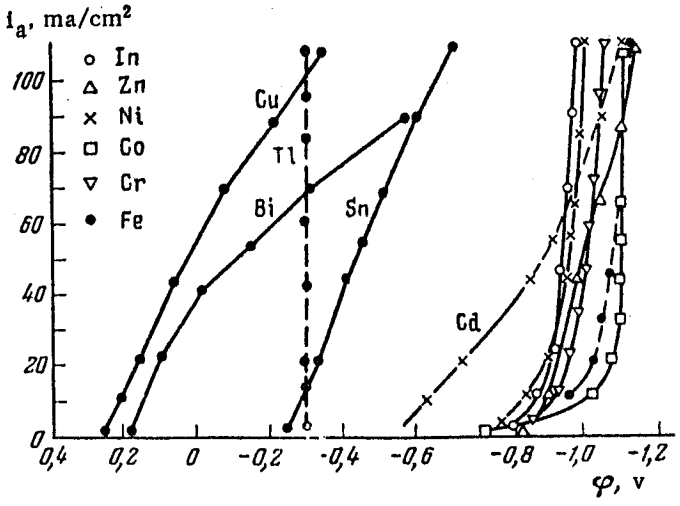

Fig. 1. Variation of the cathode potential as a function of current density.

Figure 2 represents the variation of the anode potential as a function of current density during electrolytic decomposition of the amalgams. The exceedingly low polarization of the gallium, indium, and thallium amalgams is rather remarkable; the behavior of iron, cobalt, nickel, and chromium amalgams is also remarkable; in spite of the fact that these amalgams are metastable, their oxidation potentials are positive. This phenomenon has great interest from the point of view of the theory of passivation of metals.

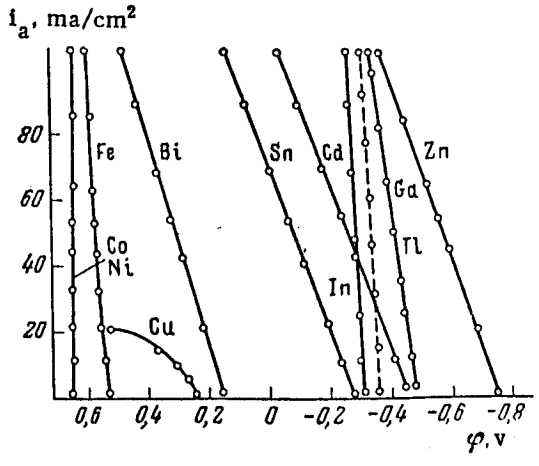

Fig. 2. Variation of the anode potential as a function of current density.

Mechanism of the Reduction of Galenite from a Suspension in a Molten Mixture of Potassium and Sodium Chlorides on a Liquid Lead Cathode by I. T. Gul'din and A. V. Buzhinskaya

V. P. Mashovets. I. T. Gul'din incorrectly explained the cathode process of sodium ion discharge with subsequent chemical reduction of the lead. In the case examined when the cathode is electron-conducting PbS under the cathode potential, the reduction of lead ions in the PbS lattice should be regarded as the first process. An equivalent amount of S^{2-} ions are then freed from the sulfide lattice and pass into the solution and this explains the subsequent anode liberation of sulfur. It seems to me that this mechanism for the cathode process explains the observed phenomena more accurately.

I. T. Gul'din. I do not deny the possibility of the process mechanism pointed out by V. P. Mashovets. However, it would be necessary to carry out additional experiments to confirm it. It seems to me that the fraction of the lead obtained at high current densities due to the discharge of lead ions from solution, where the solubility of galenite is very low, is insignificant. On the basis of the experiments carried out it may be assumed that sodium ions are discharged on ionized, cathodically polarized galenite both in the solid state and dissolved in lead.

Investigation of the Potentials and Anode Polarization of Metal Sulfides and Their Alloys by D. M. Chizhikov and V. N. Kovylina

O. A. Khan. In connection with the report by D. M. Chizhikov, I would like to note the importance of the physicochemical state of the metal alloy used as the soluble anode in electroplating or refining metal by electrolysis. We have shown [A. A. Bulakh and O. A. Khan, Zhur. Priklad. Khim. 27, 111 (1954); Izvest. Akad. Nauk Kaz.

SSR, Ser. Khim. 7, 96 (1953)] that heat treatment of the alloy consisting of a continuous series of solid solutions decreases the amount of slime formed at the anode. Thus during electrolysis annealed copper-nickel anodes having an equilibrium polyhedral structure are dissolved much more regularly and with much less formation of slime than cast alloys having a nonequilibrium dendritic structure.

The Decomposition Voltage of Nonferrous Metallurgy Slags and Their Properties by S. E. Vaisberg and U. L. Kheifets

S. E. Vaisberg. In our report we emphasized the fundamental difficulties in the determination of the activity of FeO in slags, which are connected with the presence of trivalent iron. In recording the different content of it in the slags of two compartments of a concentration cell without transfer, we were not considering the potential at the slag--metal boundary, but the potential jump at the slag 1—magnesium oxide diaphragm—slag 2 boundary, arising due to the different activity of oxygen in the slags.