ELECTROLYSIS AS A LINK BETWEEN SOME METALLURGICAL AND CHEMICAL INDUSTRIES

(SOME NEW PROCESSES OF HYDROELECTROMETALLURGY)

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As requirements for the quality of products (metals, gases, etc.) and the productivity of labor increase, along with the increase of available energy, electrochemical processes are used more and more in industry because they allow automation and make it possible to use raw materials of low quality. However, the modern methods of electrolysis used in chemistry and metallurgy are characterized by a number of fundamental drawbacks: the mechanization and productivity of these processes are low; the anodes are insufficiently resistant and the anode potentials are high; utilization of the secondary products of electrolysis is low. To improve the whole operation, one must try to improve the separate processes. However, in each area of knowledge and technique there are fundamental problems which are significant for all the separate processes. Successful solutions for such general problems always lead to an advancement in large areas of science and technology. It appears to us that the group of drawbacks in the electrochemical industry which we have referred to represent just such a complex of problems; these problems need special attention, and when solved they will allow us to accomplish the following:

a) To substitute for the old method of electrolysis (with stationary, suspended, dense electrodes working at low current densities and requiring a large expenditure of man hours for unloading the cathode metal and loading the bath) a method which would make it possible to apply high current densities through the use of porous, movable, temperature-controlled electrodes;

b) To use anodes which would be resistant or made resistant by modifications of the processes which destroy them, or by replacing these processes with others; in this way anode potentials could be decreased;

c) To utilize the anodic product in most hydroelectrometallurgical processes; to do this it is necessary to replace the production of oxygen on lead anodes (which is formed during electrolysis of sulfates) with the production of chlorine, for example, which forms on graphite anodes during electrolysis of chloride solutions, etc.

The problems involved in increasing the productivity and mechanization of the electrochemical industry were considered in another report, based on the electrolytic production of zinc [1].

Problems concerning the anode and the secondary products of electrolysis are closely interwoven and form the so-called problem of the anode [2], which presents in a new light the link between the electrochemical and metallurgical industries through electrolysis.

Anodes made of lead or lead alloys are used for the electrolysis of acid solutions of copper sulfate, zinc sulfate, cadmium sulfate, etc., i.e., in hydroelectrometallurgical industries producing a great variety of products simultaneously: a) As the result of electrolysis the production of sulfuric acid is accompanied by the "manufacture" of oxygen. This oxygen is not now utilized by anyone because to "gather" it from the present electrolytic bath is more expensive than to let it escape into the atmosphere. b) About 80% of the energy used for electrolysis is lost because of the high positive potential (about 2 v) needed during electrolysis, which is about 80% of the potential used in the bath. c) These losses are expensive in themselves, and furthermore they cause the contamination of pure cathode metals with lead. The numerous attempts to increase the resistance of the anodes [3] and decrease their potential have not given any encouraging results.

Graphite anodes, used in the electrolysis of chloride solutions, work considerably better: they are much cheaper, they do not appreciably contaminate the products of electrolysis, and their anode potential is lower. The anode product—chlorine—is in increasingly wider demand. We believe that in many cases the present hydroelectrometallurgical industry must be reconstructed. Lead anodes must be replaced by graphite anodes (and sometimes, in the case of alkaline solutions, by iron and nickel-plated anodes); to accomplish this (aside from depolarization by sulfurous gases, see below), it is necessary to replace the sulfate electrolytes with chloride electrolytes; then the chlorine, which can be easily utilized, will be evolved at the anode; the expenditure of electrical energy will be decreased, and there is no reason to believe that any complications will arise as the cathodic process is intensified.

Industrial electrolysis of aqueous solutions of chlorides of heavy metals is described in the literature—in the case of electrolysis of $ZnCl_2$ solutions (Gepfner process) [4]. The main drawbacks of the process, as determined after several years of industrial operation in Germany and England, were the following: the cathode current intensity must be low, and the yield of zinc is low; the carbon anodes, which were broken off from gas plant converters without reworking, were insufficiently stable; diaphragms must be used, complicating the equipment and are rapidly destroyed; and there was no demand for pure zinc. At present the situation has changed drastically. There exist very good graphite anodes, techniques for using higher current densities [1], and the demand for pure zinc is very high; as to the diaphragms, we now have many resistant materials which can be used; however, it is better to work without diaphragms. To do so it is better to evacuate the chlorine evolved at the anode through the body of the anode together with the electrolyte, and this is possible if the graphite anode is sufficiently porous [5]. A series of preliminary experiments and calculations [6] with $ZnCl_2$ solutions confirms the possibility of conducting the electrolysis without diaphragms. For the electrolysis of alkaline chloride solutions for the ordinary electrolytic production of chlorine and alkali it is also possible under certain conditions to use more porous graphite anodes, through the body of which the bath can be fed with the solution, etc. [7].

In spite of the fact that graphite electrodes are very widely used, there have been few investigations of their structure and their properties. These circumstances led to a series of experiments in our laboratory concerning this problem [8], with particular attention given to the more porous systems. Some results of this investigation are summarized in the table.

The real current density on a porous graphite electrode is considerably different from that calculated according to the geometric dimensions of the electrode. The results concerning this problem and also the potentials and the effective thickness of the electrode are described in another article [9]. Here we can note only that aside from purely electrochemical characteristics of the highly porous graphite anodes, we have also studied their filtering capacities. It was shown that chlorine evolved on the surface of such electrodes can be evacuated through the porosities together with part of the electrolyte. To evacuate the chlorine completely, even at current densities of the order of several thousand amp/m^2, only relatively small amounts of electrolyte are needed (0.5-2.0 $m^3/m^2 \cdot hr$). The best electrodes for evacuation are those with the most homogeneous structure, a total porosity of 40-50%, with the average diameter of pores about 30-40 microns, and a minimum of surface. On the basis of the experimental results we arrived at an empirical formula allowing a rough calculation of the amount of electrolyte ($\underline{v}$) necessary to eliminate the gas evolved on the cathode

$$v = AC^{-1/2} i \ \mathrm{m^3/m^2 \cdot hr.}$$

Here C is the solubility of the gas, g/liter; $\underline{i}$ is the current density, amp/m^2; A is a constant depending on the type of electrode and on the process occurring in the electrode. A is of the order of $1\text{-}3 \cdot 10^{-3}$ for different porous electrodes in the case of deposition of chlorine. Experiments concerning the feeding of electrolyte into the bath through the pores of the graphite anode show that the increase of the concentration of chloride by this method makes it possible to increase the anode resistance by 20-40% or to increase the degree of transformation of chloride up to 70-80% and, correspondingly, increase the concentration of the alkali, the degree of destruction of graphite remaining normal. Hydrodynamic investigation of highly porous graphite anodes shows that it is possible to use them as electrode-diaphragms in a number of processes of industrial electrolysis and in the production of current by chemical means.

It appears possible to solve the problem of industrial production of a series of metals on a different basis, namely, using an aqueous solution of chloride as electrolyte, highly porous graphite anodes, evacuation of chlorine together with electrolyte from the anode, very high current density at the cathode, and devices for automatic removal of cathodic metal, e.g., in the form of a ribbon from cathode drums [1] or in powder form. We believe that with these methods one can obtain zinc, lead, manganese, and possibly iron, chromium, and other metals.

Type of electrode	Density	Porosity, %	Specific electrical resistance, ohm • cm • 10^3	Coefficients of sinuosity of pores	Resistance of the electrolyte in the porosities, ohm • cm
"Dense"					
DEZ 51 x 51	1,65	25,0	0,80	4,7	460
Acheson 51 x 51 . . .	1,52	31,0	0,85	3,9	255
DKhTI-DEZ-1p	1,45	32,1	2,66	3,5	220
"Porous"					
PT-6	1,18	46,0	7,8	2,0	46
Ts-27	1,27	42,0	3,0	1,8	41
SS-14	1,18	46,0	2,8	3,0	100
DKhTI-DEZ-8p	0,66	69,3	8,8	1,8	27,4

Our point of view [5] has been supported in a book by a well known Viennese electrochemist, Billiter, [10] who considers that in the near future considerable amounts of chlorine will be obtained by electrolysis of solutions of chlorides of heavy metals, including zinc chloride, and "the replacement of zinc sulfate electrolytes with zinc chlorides is only a question of time."

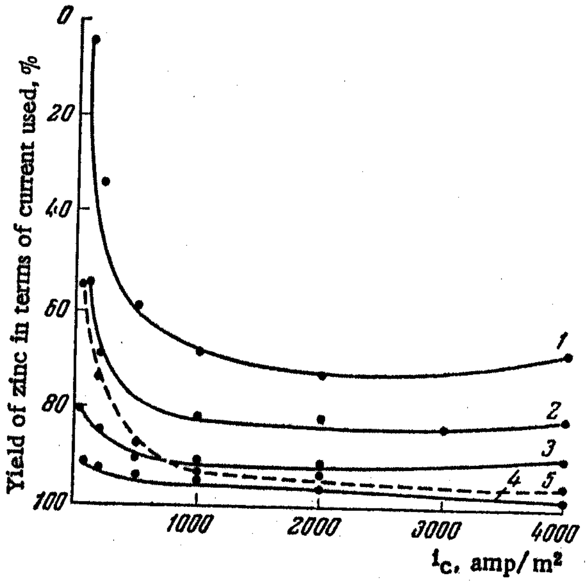
Chlorides for electrolysis can be obtained by various means. $ZnCl_2$ or $MnCl_2$ can be obtained from oxides by the reaction between the oxide and $CaCl_2$, with CO_2 blown through the solution [4]

$$ZnO + CaCl_2 + CO_2 \rightarrow ZnCl_2 + CaCO_3.$$

S. M. Ivanov and M. B. Kartsynel, of the Dnepropetrovsk Chemicotechnological Institute, have made a preliminary investigation of this reaction; it showed that a high yield of chlorides can be obtained at 90 deg C over a period of 3-5 hours provided there is a considerable excess of $CaCl_2$. If a reverse current is used, the $CaCl_2$ is utilized much more efficiently. The technical-economic calculations made by E. A. Kalinovskii showed that this way of obtaining $ZnCl_2$ is advantageous in cases where the raw materials are cheap carbonic acid and $CaCl_2$ (as a byproduct of calcination of sodium hydroxide by the ammonia method or of saponification of organic halogene derivatives). Another way of obtaining zinc chloride solutions (manganese, iron) could be the as yet incompletely studied method of chlorination of ores and concentrates, and also the use of excess hydrogen chloride as a byproduct of chlorination of hydrocarbons. If cheap hydrochloric acid is available it can be used to extract metals from ores and concentrates; this method is particularly effective in the case of extraction of manganese. Chlorination and use of hydrochloric acid will probably be more suitable than the method proposed in 1929 by Kangro and Flügge [11] for the treatment of iron ores with chlorine at 900-1000 deg C to obtain iron chloride, with subsequent dissolution of iron chloride and electrolytic reduction up to the ferrous salt and metal. According to a scheme proposed by Kangro, the powder-like iron formed in this process is used for reproduction of alloyed steel; the expenditure of energy for 1 ton of iron is 5,400 kw-hr; the authors consider these conditions satisfactory. E. A. Kalinovskii [6] has investigated the electrolysis of a $ZnCl_2$ solution, and we present his data as an example of the electrolysis of chlorides of heavy metals. He studied the yield of zinc and the quality of the deposit as functions of current density (100-400 amp/m^2), concentration of zinc (10-160 g/ liter), concentration of hydrochloric acid (0.1-50 g/ liter), temperature (7-60 deg C), and concentration of impurities: $CaCl_2$, NaCl, and copper ions. Some of the results of this investigationare presented in the figure. It was shown that a good quality cathodic zinc with high yield can be obtained when the concentration of zinc is no lower than 20 g/liter, hydrochloric acid no higher than 30-40 g/ liter, current density up to 4000 amp/m^2, the temperature up to 50 deg C, $CaCl_2$ and NaCl up to 50 g/ liter, and copper ions up to 25 mg/ liter.

An investigation of the electrolysis of solutions of manganese, chromium, and iron chlorides at high cathodic current densities with a porous graphite anode is being made in our laboratory.

Another example of the combination of chemical and metallurgical industries through electrolysis is the utilization of the sulfurous gases produced as a byproduct in copper and lead mills, and other plants. Up to now these gases have usually been released into the atmosphere because the concentration of SO_2 in them is only a fraction of a per cent. In 1943-1944[12] we developed an experimental setup, under plant conditions, for catalytic oxidation of SO_2 by solutions of manganese salts, with subsequent production of dilute solutions of H_2SO_4 which was used at the plant for treatment of oxides and mixed ores, for example. This proposal has not yet been practically applied and gases lean in SO_2 have not yet been made use of. Another purely electrochemical scheme is the utilization of sulfurous gases for depolarization of the anode during electrolytic extraction of copper from solutions resulting from the treatment of ores [13]. Instead of using a difference of potential of 2 v and allowing oxygen to evolve on the ordinary lead anodes used in sulfate solutions we propose using another anodic process: a highly porous graphite anode and oxidation of sulfurous acid into sulfuric acid at the anode. The potential at the anode can be lowered to 1.0–1.2 v, and the expenditure of energy in this process is thus decreased 1.5–2 times. The sulfuric acid obtained is used to replace the losses during treatment of copper ores. This method is not yet developed to the point where it can be used on a large scale. An analogous process was tested by G. Z. Kir'yakov and I. A. Korchmarek for electrolysis of zinc sulfate solutions. However, at the difference of potential used the SO_3^{2-} ion is easily reduced to elementary sulfur or even hydrogen sulfate at the zinc cathode, which prevents the formation of good quality zinc.



Yield of electrolytic zinc from $ZnCl_2$ solution. Concentration of zinc, 40 g/ liter. Temperature, 20 deg C. Concentration of HCl: 1) 45 g/ liter; 2) 22.5 g/ liter; 3) 10 g/ liter; 4) 0.6 g/ liter 5) "Standard" $ZnSO_4$ solution.

Utilization of the anodic product—oxygen—during electrolysis of sulfate solutions is practically impossible with the present equipment; the anode oxygen can be utilized only if the current density is high and the electrolytic baths are mechanized and enclosed [1].

The gases evolved at the anode—mainly CO and CO_2—in the present type of electrolysis of molten cryolites are very difficult to utilize because of the present arrangement of the electrolytic bath. It seems more advantageous to avoid the formation of carbon oxides at the anode, i.e., oxidation of the anode. An economy of a fraction of a volt, i.e., about 2000 kw-hr/ ton of aluminum, cannot justify the burning of 600 kg of carbon anodes which cost 2-3 rubles/ kg. It is better to avoid using carbon anodes in the present process of electrolytic extraction of aluminum and replace them with metal oxide anodes. The increased expenditure of electrical energy which accompanies this replacement should not be a factor, since the noncarbon anode allows a decrease of the labor force, i.e., an increase of labor productivity. We have not yet sufficiently investigated the new anodes for electrolysis of molten media.

A brilliant example of the combination of the chemical and metallurgical industries through electrolysis is the new area of so-called amalgam metallurgy [14].

In the modern industrial use of electrolysis, particularly in the metallurgy of nonferrous metals, usually only one of the products of electrolysis is utilized—the cathode metal—while the second product—the gas(oxygen) —is almost never utilized. The same situation is very often true in pyrometallurgy, where the metals are utilized while the byproducts, particularly SO_2, are released into the atmosphere. On the other hand, the chemist producing pure $ZnCl_2$, for example, dissolves metallic zinc in hydrochloric acid without thinking that all the electric, human, and other types of energy spent to obtain this metal are lost during this process, and that the same pure zinc chloride can be obtained from the natural raw material or waste material, bypassing the high energy state of the metal. This waste results from lack of attention to the connections between the chemical and metallurgical industries.

The examples of industrial electrolysis described are characterized by the fact that the main drawbacks of the present processes are eliminated. In order to utilize a number of anodic products of the hydroelectrometallurgical industry, we recommend a change from sulfate solutions to chloride solutions and the collection of chlorine on graphite anodes instead of oxygen on lead anodes. This change makes the anodic material cheaper, decreases the expenditure of electrical energy, and makes it possible to obtain very pure cathodic metal. In other cases it is possible to use the anodic process for the oxidation of SO_2, the byproduct of pyrometallurgical operations. Here again a graphite anode can replace the lead anode and the anode potential (i.e., the expenditure of electrical energy) can be decreased. The utilization of anodic oxygen becomes possible if the electrolysis of sulfates is intensified.

In inorganic and organic syntheses, electrolysis of nonchloride molten substances, etc., a great number of electrolytic products are not being satisfactorily utilized. This is a large field for electrochemical engineers [15, 16]. In most cases these problems are connected with the processes occurring at the anode.

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