Electrolytic Recovery of Iron from Waste Pickle Liquors with the Simultaneous Production of Manganese Dioxide

By V. ARAVAMUTHAN, S. VISVANATHAN AND N. BALASUBRAMANIAN.

Central Electrochemical Research Institute, Karaikudi

INTRODUCTION

It is well known that the electrolytic production of two different products, one at the cathode and the other at the anode simultaneously would reduce the electric energy requirements. However, the choice of such processes is limited. This is because of the fact that the temperature conditions, current, density, pH etc., vary for the anodic and cathodic processes and the need for the use of a diaphragm also exists. In addition, the contamination of the anolyte in the catholyte and vice versa should not bring down unduly the purity of the anode and cathode products formed.

Taking all these factors into consideration, it was concluded that the use of ferrous salt solutions obtained as by product in the pickling of iron and steel could be conveniently employed as catholyte for the electrodeposition of iron, and manganese sulphate or nitrate solutions as anolyte for the electrodeposition of manganese dioxide in a diaphragm cell. It is known that sheet deposits of iron could be obtained from ferrous chloride or sulphate or mixtures of these solutions by electrolysing at high temperatures, and the presence of manganese salt is advantageous in the deposition of iron. It is also known that for the electrodeposition of manganese dioxide high temperature is very favourable. Hence a temperature of about 85°C was chosen for the simultaneous production of iron at the cathode and manganese dioxide at the anode. Porcelain diaphragms were employed as none of the other diaphragms viz., microporous rubber, P.V. C. etc., could withstand this temperature.

Our earlier experiments both with sulphate and nitrate baths for the electrodeposition of manganese dioxide have indicated that at the temperature of 85°C an anode current density of 10 amp/ sq. ft was optimum keeping in view the quality of the product to be obtained and to minimise the loss of chemicals in cyclic process. We have also established that manganese sulphate or nitrate solution of 16-17 % concentration at a pH 4-5 was favourable for electrolysis and we could deplete conveniently upto 11 % of manganese sulphate or nitrate. Under these conditions the current efficiency was even better than in commercial cells (75%) wherein manganese sulphate is employed in a non-diaphragm cell for the production of manganese dioxide.

Our experiments on deposition of iron independently gave the clue that sheet iron deposits could be obtained from iron chloride or sulphate or mixtures of these solutions in the presence or absence of alkali metal chlorides like potassium chloride or sodium chloride at a temperature of 80 to 90°C, and we could conveniently deplete the iron concentration from 7 to 4 % realising a current efficiency of 80 to 90 %. Incorporating the above conditions in a single set-up, the present process for electrodepositing iron at the cathode and manganese dioxide at the anode has been worked out.

EXPERIMENTS AND RESULTS

The anolyte was prepared by reacting sulphuric or nitric acid with manganese carbonate or roast reduced ore till a pH of 4.5 was obtained and the clear filtrate was used as the anolyte. Ferrous chloride or sulphate pickle liquor was treated with scrap iron to react with the free acid and the clear filtrate of ferrous chloride or sulphate having a pH of 2 was employed as catholyte. One litre of anolyte was taken in a 3 litre Pyrex beaker and was heated to 85°C over an electric heater with thermostatic control. 800 cc of the catholyte was separately heated to 85°C and was taken in a medium porosity porcelain diaphragm, of 3″ diameter. The diaphragm was placed centrally in the beaker and anolyte and catholyte levels adjusted to be equal. Two graphite anodes of size 8″ × 3″ × 1/8″ thick and one stainless steel

	Anolyte	Catholyte	Current density, amp/sq. ft. Anode	Cathode	Current efficiency% Anode	Cathode	Cell Voltage V.
1.	$MnSO_4$ 15.7%	$FeSO_4$ (7.7%)	10	61	76	82	2 95
2.	$Mn(NO_3)_2$ 21.6%	$FeSO_4$ 8.2%	10	61	76	85	2.8
3.	$MnSO_4$ 21.8%	$FeSO_4$ (7.7% Fe) KCl 20%	10	61	81	93	2.4
4.	$Mn(NO_3)_2$ 16.1%	$FeSO_4$ 9.1% Fe KC l 20%	10	61	78	8,	2.4
5.	$MnSO_4$ 17.9%	$FeCl_2$ (6.3% Fe) KC l 20%	10	61	80	91	2.4
6.	$Mn(NO_3)_2$ 17.9%	$FeCl_2$ 8.2% Fe KC l 20%	10	61	76	98	2.4

cathode of size 8″ × ½″ × 1/32″ thick were used, immersed in the respective electrolytes to a depth of 6″. A cathode current density of 61 amp/sq. ft corresponding to anode current density of 10 amp/sq. ft was employed. The typical experimental results for a 12 hour run are given below.

DISCUSSION OF THE RESULTS:

From the table it may be seen that a current efficiency of 75% for the electrodeposition of manganese dioxide has been realised at a cell voltage of 2·4 in experiments 3 to 6. By this procedure 0·83 kw. hrs. of electric energy is required for producing 1 lb., of manganese dioxide and 0 8 lb., of iron. When these processes are conducted separately the electric energy requirements are 1·3 kw hr/lb. for iron and 1·0 kw. hr/lb. for manganese dioxide. The pH of the catholyte remained stable in these experiments when potassium chloride was added to the catholyte. The effect of adding potassium chloride is not only to reduce the electric energy requirements through the reduction in cell voltage but also to keep the pH of the catholyte stable. Experiments 1 and 2 indicate the effects without addition of potassium chloride. Cell voltages ranging from 2·8 to 2·95 have to be used for getting the same current efficiency, the other conditions of the experiments remaining the same.

When potassium chloride is added to the catholyte potassium sulphate is crystallized out by concentrating the catholyte at the end of electrolysis. Thus the sulphate content of the pickle liquor is also fixed profitably. This is especially true when potassium sulphate is to be employed as fertilizer and where it has got specific advantages over potassium chloride such as in tobacco cultivation.

The purity of iron deposit was found to be between 96—99%. The manganese dioxide deposit was found to possess the gamma form as revealed by X-ray diffraction studies. Electron microscopic studies also confirmed it to be a suitable specimen for use in dry cells (Fig. 1).

When the concentration of iron in the anolyte becomes high the iron is removed by reacting with manganese carbonate or with roast reduced ore. Investigations are in progress to determine the maximum amount of ferric iron and or

chloride content permissible to get good deposits of manganese dioxide with over 75% current efficiency.

It is proposed to conduct large scale trials using porous porcelain plate diaphragms fixed to ebonite lined vessels to assess the commercial feasibility of the process.

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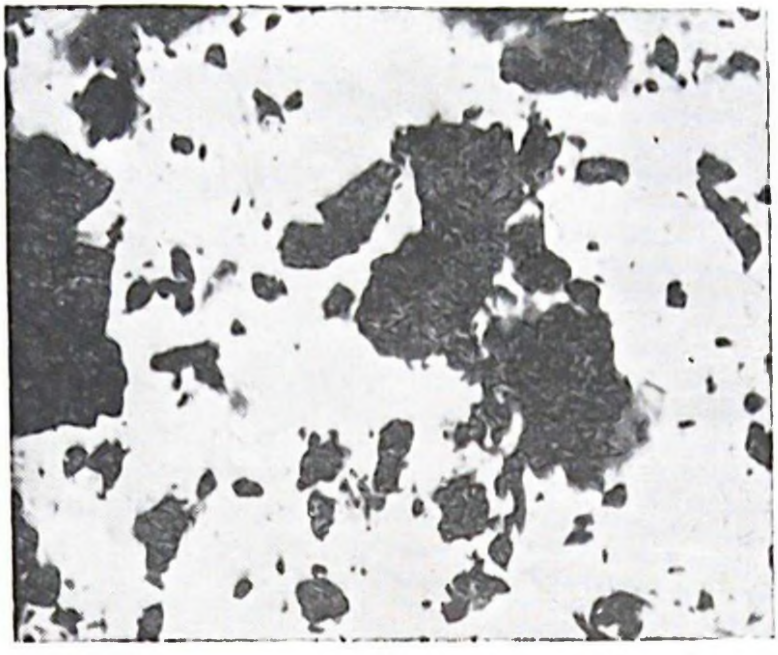


Fig. 1

ELECTRON MICROGRAPH OF
ELECTROLYTIC MANGANESE DIOXIDE

Magnification : X8000/3
Photographic Enlargement : X3

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nate the copper undercoating. Partly this is a matter of cost, and further, there is no doubt that a copper-nickel coating is less corrosion resistant than the same thickness of nickel. Of course, it is not a question of whether copper is desirable, but of whether there is any alternative. One of the attempts in this direction is the sequence embodying a special nickel strike followed by a nickel sulphamate deposit before bright nickel developed at the Battelle Memorial Institute, U.S.A. In practice, however, it has proved difficult to avoid a pitted coating and the process is no less expensive.

An alternative which appears to be rather more promising is the deposition of a first nickel coating from an alkaline pyrophosphate solution. It would not only eliminate the risk of immersion deposition, but also avoid the danger of the dissolution of the zinc from low current density areas. Although tests with such a bath are still in the development stage, there are signs that it may be possible to gain an increased corrosion resistance from the two different nickel coatings which is similar to that obtained by the conventional type of duplex nickel plating process. As there are only two plating stages involved, the process will be less expensive than the copper-duplex nickel sequence.—Electroplating and Metal Finishing, Vol. 14, 355, 1961.

—T.L.R.