

# The production of electrolytic manganese in South Africa

by M. HARRIS\*, Pr. Eng., B.Sc. (Eng.) (Fellow),  
D. M. MEYER\*, Pr. Eng., B.Sc. (Mech. Eng.) (Visitor), and  
K. AUERSWALD\* (Visitor)

## SYNOPSIS

The decision to construct the first electrolytic manganese plant in South Africa was important and far-reaching. After evaluating the results of the pilot plant operation, the first South African producer, Electrolytic Metal Corporation (Emcor), established a plant in Krugersdorp. Initially, there were many process problems that had to be investigated, and, after these had been solved and many operating parameters had been established, manganese was successfully produced.

When the Delta Manganese plant in Nelspruit was planned, cognizance was taken of the fact that, if peak efficiencies were to be maintained, the process must be operated between fairly narrow parameters. Instrumentation was therefore installed to control the process automatically wherever possible.

The main features of the Delta Manganese operation are outlined, with a brief description of each stage of the process from ore milling through to electrowinning and packing of the metal.

It is concluded that much benefit can be obtained from further research work into process improvements and into the exact effect of certain variables on plant and current efficiency.

## SAMEVATTING

Die besluit om die eerste elektrolitiese mangaanaanleg in Suid-Afrika te bou was 'n belangrike en verreikende een. Nadat die resultate van die bedryf van 'n proefaanleg geëvalueer is, het die eerste Suid-Afrikaanse produsent, Electrolytic Metal Corporation, 'n aanleg in Krugersdorp gevestig. Daar was aanvanklik baie prosesprobleme wat ondersoek moes word en nadat hulle opgelos en baie bedryfsparameters vasgestel is, is mangaan suksesvol geproduseer.

Toe die aanleg van Delta Manganese in Nelspruit beplan is, is daar rekening gehou met die feit dat die proses tussen betreklike nou parameters bedryf moet word om toepredementte te handhaaf. Daar is dus instrumentasie geïnstalleer om die proses, waar moontlik, outomaties te beheer.

Die hoofaspekte van die bedryf van Delta Manganese word in breë trekke bespreek met 'n kort beskrywing van elke stap van die proses vanaf die maal van die erts tot by die elektrolitiese herwinning en verpakking van die metaal.

Die gevolgtrekking is dat daar groot voordeel uit verdere navorsingswerk in verband met verbeterings aan die proses en die presiese uitwerking van sekere veranderlikes op die aanleg en die huidige rendement getrek kan word.

When the uranium industry was established in South Africa in the mid-fifties, it created a major demand for manganese dioxide (pyrolusite) as an oxidizing agent. It was initially concluded that sufficient manganese dioxide was not available locally, and all the uranium producers planned to install plants for the recovery of manganese from the solutions for the production of manganese (III) oxide.

In these plants, the pH value of the uranium effluent was raised to between 6 and 7 by the addition of lime to precipitate all the iron. The pH value of the iron-free solution was then raised to 9 by the addition of lime to precipitate the manganese as manganese (II) hydroxide. The underflow of manganese (II) hydroxide from the thickeners was pumped into pachucas and then aerated to convert the manganese hydroxide to manganic hydroxide according to the old Weldon process, which is used in the production of chlorine.

The demand for pyrolusite initiated a search for these ores, and in due course large tonnages of low-grade deposits that could be mined economically were discovered in the Western Transvaal. The manganese recovery plants proved uneconomic and were then used for the precipitation of all the dissolved metals in the solution prior to disposal of the effluent.

At that time, Technimetals, a private company (shareholders J. A. Hahn, W. D. McGarvy, P. W. Sceales, M. Harris, and D. M. Meyer), decided to investigate the possibility of producing electrolytic manganese

metal, instead of manganese (IV) hydroxide, from the precipitated manganese (II) hydroxide. Mr D. Millin, Senior Lecturer at the University of the Witwatersrand, was appointed consultant, and experiments to prove whether electrolytic manganese could be economically produced from the uranium effluent were carried out by M. Harris and D. Millin at the University of the Witwatersrand.

Initially, owing to secrecy, manganese (II) hydroxide could not be obtained from the uranium plant, and the first electrolytic manganese metal in South Africa was produced from manganese ore in 1954. The experimental cell consisted of two cathodes and three anodes, each cathode having a plating area of 1 ft<sup>2</sup>. The d.c. current was supplied by a motor generator set. All the technical information on which this production in South Africa was based was obtained from a U.S. Bureau of Mines publication on the production of electrolytic manganese (obtained free of charge from the U.S. Bureau of Mines).

Following the success of the initial experiments at the University, General Mining agreed to allow Technimetals to erect a pilot plant on West Rand Consolidated Mine that would use, as a source of manganese, the manganese (II) hydroxide produced from the uranium effluent. For allowing the pilot plant to be erected on one of their mines, General Mining were given the option of shares in the commercial plant that would be established if the pilot plant promised success for the venture.

Electrolytic Metal Corporation (Emcor) was then formed with the following shareholders: Technimetals, Anglo Vaal, and A. Johnson & Co. (a Swedish producer

\*Delta Manganese (Pty) Ltd, Nelspruit, Transvaal.

of stainless steel). A pilot plant to produce  $\frac{1}{2}$  t/d, which could be expanded to 2 t/d, was installed in 1955. The pilot plant was successfully commissioned and operated without any technical assistance from overseas by M. Harris and his team of 29 assistants. After a year's results on the pilot plant, the production of electrolytic manganese from manganese (II) hydroxide originating from uranium effluent proved to be a viable venture.

During the operation of the pilot plant, the following problems were resolved.

- (a) A successful filter was developed for the manganese (II) hydroxide. (Filtration of this material was considered to be highly doubtful by eminent metallurgists in the mining industry.)
- (b) Unknown impurities that vitally affected the electrowinning operation were identified, and a method of analysis was developed for them. Among these impurities were cobalti cyanides, which are anionic and cannot be removed from solution on a continuous basis by the normal method used for cationic cobalt. These complexes were formed during the gold cyanidation process. The effect of this problem was almost catastrophic, and production was not possible for six weeks while the reasons for the non-deposition of manganese on the cathode were being investigated. It should be borne in mind that analytical instruments for the determination of cobalt in anionic or cationic form were not available at that time.
- (c) Parameters were established for the production of manganese (II) hydroxide that was free of excess amounts of cobalti and other heavy-metal cyanides. Briefly, this involved the by-passing of the first half-hour's flow of uranium barren solution from the regenerated ion-exchange columns.
- (d) Parameters were established for the design of the anode, cathode, and cell. The following illustrates how a relatively minor change in the production of manganese (II) hydroxide had an absolutely disastrous effect on the pilot-plant operation. The lime for adjustment of pH in the uranium effluent was changed for economic reasons from a lime low in magnesium to one high in magnesium, resulting in a manganese (II) hydroxide high in magnesium. The pilot plant did not incorporate steps for the removal of magnesium, and the magnesium salts precipitated out in the pipe lines, completely stopping the flow of solution and, consequently, the production. The length of the stoppage was approximately ten days.

General Mining, after careful and thorough investigation of the results of the 2 t/d pilot plant, decided to exercise their option and provided sufficient loan capital for the erection of the first commercial plant in South Africa for the production of electrolytic manganese. The planned output of the plant was 7 t/d, and production commenced in April 1960. In 1968, owing to continued problems with the cobalti cyanide impurities in the manganese (II) hydroxide, it was decided to use manganese ore from the northwestern Cape as the sole source of manganese. However, the high iron content of these ores (10 to 12 per cent) meant that new tech-

niques had to be developed for their use. In other countries, the producers of electrolytic manganese use manganese ores with an iron content of 1 to 2 per cent, it being uneconomical and unpractical to use ores high in iron.

If the problems connected with the processing of South African manganese ores had not been resolved, it is doubtful whether there would have been any production of electrolytic manganese in South Africa. Production was increased in stages to meet the increased demand, and at present Emcor has a production capacity of 16 500 t/a.

In 1973, Delta Manganese established a 28 000 t/a electrolytic manganese plant at Nelspruit with an initial production capacity of 14 500 t. Production commenced in June 1974; in October 1975 the capacity was increased to 16 500 t/a, and since then the plant has been operating at rated capacity.

At present, South Africa produces 50 per cent of the world's electrolytic manganese and supplies 75 to 80 per cent of the metal available for free trade. (U.S.A. and Japan consume the major portion of their production, and this amount is thus excluded from the metal available for free trade.) From 1955 until December 1975, 140 000t of electrolytic manganese was produced in South Africa. It was forecast that sales of electrolytic manganese during 1976 would earn between R20 million and R22 million, and by 1980 between R40 million and R45 million.

### Delta Manganese Operation

The flowsheet of the Delta Manganese plant at Nelspruit is given in Fig. 1. The process consists essentially of four main steps:

- (a) reduction of the ore from manganese (IV) to manganese (II) to solubilize it in sulphuric acid,
- (b) leaching of the reduced ore in spent electrolyte by the reverse-leaching technique to minimize the dissolution of iron,
- (c) purification of the leach liquor to remove all the elements that will adversely affect the electro-deposition of manganese, and
- (d) electrolysis of the purified solution.

The manganese ore is received in the form of fines with a grading analysis of 98 per cent minus 12 mm mesh. A typical analysis is given in Table I. The ore is dried during the milling operation in a Babcock and Wilcox vertical spindle mill. Production rates of 10 t/h have been achieved from this air-swept mill at a fineness of 80 per cent minus 74  $\mu$ m.

TABLE I  
TYPICAL ANALYSIS OF MANGANESE ORE

	%
Manganese (total) .....	48,0
Iron .....	10,0
Silica .....	5,2
Nickel .....	0,07
Cobalt .....	0,02
Zinc .....	0,10
Calcium oxide .....	1,2
Magnesium oxide .....	0,56
Aluminium oxide .....	0,35
Moisture .....	0,4 to 5,0

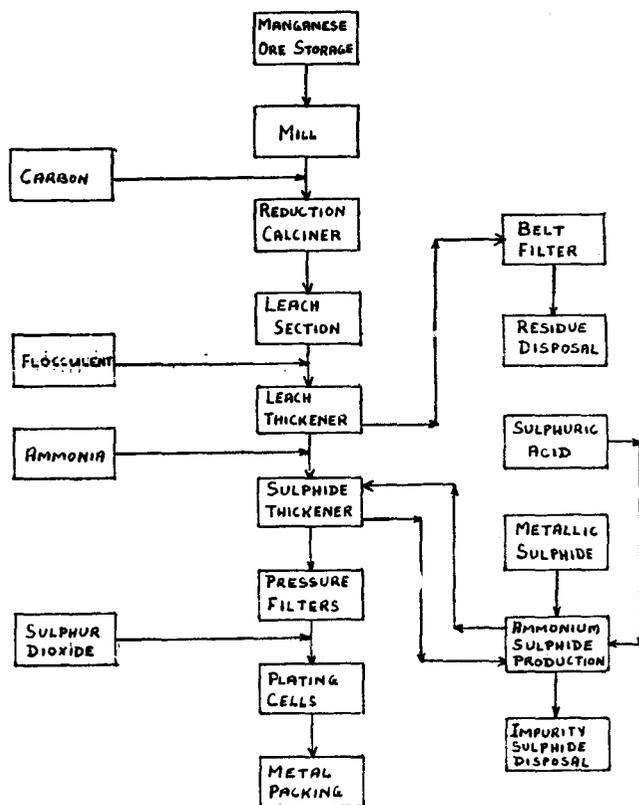


Fig. 1—Flowsheet for the production of electrolytic manganese at Delta Manganese

In the ore-reduction process, the ground ore is mixed with carbon in the form of ground coal and is then fed into a rotating stainless-steel calciner that is externally heated by electrical elements to between 850 and 900°C. By careful control of the amount of reductant and the temperature, the manganese can be preferentially reduced to manganese (II) oxide, leaving the bulk of the iron in a form that is insoluble in dilute sulphuric acid. If too much iron is reduced to iron (II) oxide, two problems are created.

- (1) The large amount of iron that dissolves must be oxidized and precipitated as iron (III) hydroxide to prevent serious problems in the subsequent purification procedures.
- (2) The precipitated iron (III) hydroxide is bulky and is difficult to filter and wash efficiently, thus increasing losses of soluble salts.

The effect of carbon on the solubility of manganese and iron at 830°C is shown in Fig. 2.

In the leaching section, the reduced ore and the anolyte from the cell house, which contains 35 g/l sulphuric acid and 125 g/l ammonium sulphate, are mixed in agitated tanks under controlled conditions to maintain a pH of between 5,2 and 6,2. Leaching at these pH values minimizes the dissolution of iron and results in manganese leaching efficiencies of 88 to 94 per cent. Any iron (II) in solution at that stage must be oxidized with air to levels of less than 50 mg/l. The precipitation of iron in the leaching section plays an important part in the purification of the solution since

any chromium or copper and most of the arsenic, molybdenum, phosphorus, and silica are co-precipitated with the iron. After leaching, the gangue is separated from the solution in a thickener of 19 m diameter. The underflow, which has a solids content of 50 per cent, is then fed to a 30 m<sup>2</sup> Landskrona belt filter, where, after washing, the gangue is discarded. The analysis of the residue is given in Table II.

TABLE II  
ANALYSIS OF LEACH RESIDUE

	%
Total manganese .....	7,0
Water-soluble manganese .....	0,1
Ammonium sulphate .....	0,7
Moisture .....	40,0

All metals more noble than manganese, if present in quantities above certain critical limits, will decrease the current efficiency at which manganese can be plated. Since the only metals less noble than manganese are aluminium and the alkali and alkaline earth metals, practically all the other metals present will have a deleterious effect on the current efficiency. Good current efficiencies are therefore largely a function of electrolyte purity. Since the control of impurities in concentrations of milligrams or fractions of milligrams per litre is not an easy task, the precise measurement of the effect of other factors on current efficiency is not always possible.

The commercially accepted method for the purification of manganese solutions is based on the precipitation of impurities as insoluble sulphides with ammonium sulphide<sup>1, 2</sup>. The maximum levels of some impurities that can be tolerated in the cell feed solution without affecting the current efficiency are given in Table III. It has been proved that a combination of impurities often has a greater negative effect than any one impurity

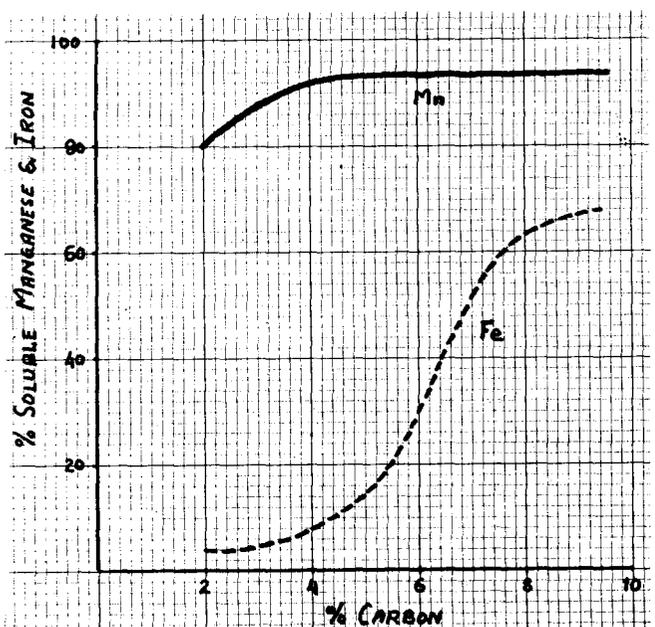


Fig. 2—Effect of carbon content on the reduction of manganese ore at 830°C

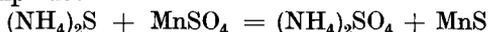
alone. This is especially the case with cobalt, which on its own has the greatest negative effect of all the impurities listed.

TABLE III

MAXIMUM LEVELS OF IMPURITIES IN CELL FEED SOLUTION	
	mg/l
Nickel*	1
Cobalt	0,3
Iron (ferrous)*	15
Silicon	10
Copper*	5
Zinc	10

\*Quoted from Jacobs *et al.*<sup>3</sup>

The pH value of the overflow from the leach thickener is adjusted to between 6,8 and 7,2 with ammonia and, after the addition of the required amount of 20 per cent ammonium sulphide to precipitate the impurities, is pumped to a sulphide thickener of 19 m diameter. The following reactions take place after the addition of the sulphide:

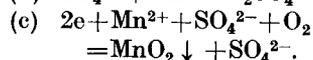
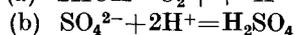
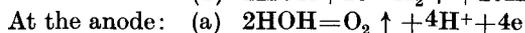
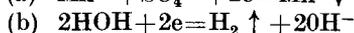
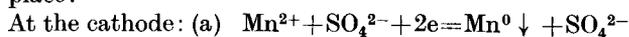


If the above reactions are to take place at a reasonably fast rate, it is important to ensure that a suitable excess of manganese is present in the precipitated sulphide sludge. The sludge is removed from the thickener and treated for the recovery of the manganese and hydrogen sulphide. The overflow from the sulphide thickener is pumped through either a 40 m<sup>2</sup> Funda filter or a 38 m<sup>2</sup> Stellar filter that has been precoated with a diatomaceous earth filter aid. It is essential that a clear filtrate is maintained since any solid particles will affect the deposition of metal in the following ways.

- (i) They can be occluded in the deposit, thus contaminating the purity of the metal and increasing the sulphur content to unacceptable limits.
- (ii) They can be absorbed onto the surface of the deposit, where the hydrogen overvoltage will then be lowered, resulting in the evolution of hydrogen at that spot and the re-dissolution of the deposited manganese metal.

Before the solution is electrolysed, sulphur dioxide is added to the extent of 0,2 to 0,4 g/l. According to Dean<sup>2</sup>, manganese is first deposited in the gamma modification. Deposition in this form cannot proceed for very long before the current efficiency drops to unacceptable levels unless very pure solutions are used. To make the production of electrolytic manganese a commercial proposition, the manganese must be deposited in the alpha form so that the current efficiencies are maintained over deposition periods of more than 24 hours. The added sulphur dioxide performs the function of transforming the initial gamma deposit into a fine-grained alpha deposit that gives the deposited metal a duplex structure.

During electrolysis, the following reactions take place:



The amount of manganese plated from the solution is replaced by an equivalent amount of sulphuric acid, which is then used to dissolve more manganese from the reduced ore in the leach section.

The successful electrolysis of purified manganese sulphate solution depends upon a combination of many factors such as cell design, concentrations of manganese and ammonium sulphate in the solutions, current density, pH of the electrolyte, cell solution temperature, composition and treatment of anodes and cathodes, and rate of flow to the cells.

At the Delta plant, the electrolytic cells are made of fibreglass, the anodes and cathodes being supported and located in frames of Rhodesian teak. The cathode frame is covered with a cotton diaphragm cloth of 620 g/m<sup>2</sup>. The 70 cathode frames and 71 pairs of anode timber stiles are alternately clamped together by means of stainless-steel rods to form a timber cell frame, which rests on a shelf in the fibreglass cell. Feed solution enters a common compartment surrounding the timber frame, enters each cathode frame compartment through slots in the side of the frames, flows past the cathode and through the cotton diaphragm into the anode compartment, and then passes the anode and leaves the anode compartment through an opening at the bottom into a common anolyte sump. From the sump the solution flows up through an adjustable raiser pipe, which controls the cell level, and leaves the cell through an overflow weir box. Each cell holds 11,5 m<sup>3</sup> of solution. Since the temperature of the cell solution is an important operating parameter, each cell is also equipped with stainless-steel cooling coils for circulating the cooling water. For each kilamp of power input, 14 200 kJ of heat must be removed from each cell.

In the electrowinning of metals, it is essential that the anodes should have the following properties:

- (1) they should be insoluble in the solutions used,
- (2) they should be good conductors of electricity, and
- (3) they should not be chemically conducive to anodic reactions that will interfere with the economical operation of the process.

After extensive experimentation with various metals and alloys, it was determined that an alloy of 99 per cent lead and 1 per cent silver was the most practical anode material<sup>4</sup> for the production of manganese. With this silver-lead alloy anode at a current density of between 9,70 and 15,00 A/dm<sup>2</sup>, less than 1,5 per cent of the manganese input was lost as MnO<sub>2</sub> in the anode sludge.

Cathodes used in the manganese electrowinning operation must

- (a) be insoluble in the catholyte,
- (b) be insoluble in the dilute sulphuric acid used for cleaning,
- (c) have a low electrical resistance,
- (d) have good flexibility,
- (e) have a high hydrogen overvoltage, and
- (f) have surfaces from which the manganese deposit can easily be removed.

The most widely used cathode material is type

316 AISI stainless steel, although titanium is being used by some plants. When stainless steel is used, the cathode, after being thoroughly cleaned and buffed to a high polish, is treated with sodium silicate solution, which, after rinsing, leaves a thin film on the cathode that prevents the plated manganese from adhering too tightly to the surface of the cathode. The plating area of each cathode is 980 mm by 680 mm per side. Cathode current density varies between 4,30 and 5,40 A/dm<sup>2</sup>.

The composition of the solution fed to the cells is given in Table IV.

TABLE IV  
COMPOSITION OF CELL FEED SOLUTION

	g/l
Manganese as manganese sulphate	30-34
Ammonium sulphate	120-130
Sulphur dioxide	0,2-0,4
pH value	6,7-7,2

The feed to each cell is controlled by a flowmeter at a rate that will give a manganese concentration in the catholyte of approximately 12 g/l, which means that approximately 20 g/l of manganese has been stripped from the feed solution. The effect of catholyte manganese concentration on current efficiency is given in Table V.

TABLE V  
EFFECT OF CATHOLYTE MANGANESE CONCENTRATION ON CURRENT EFFICIENCY  
(Mn in feed solution: 32 g/l)

Catholyte Mn g/l	Current efficiency
	%
6	47,0
8	56,3
12	62,3
15	59,8
21	43,5

The ideal concentration of ammonium sulphate is between 120 and 130 g/l. During electrolysis, the solution surrounding the cathode becomes more alkaline, which would result in the precipitation of manganese (II) hydroxide if the solution were not buffered by the ammonium sulphate to a pH value between 8,2 and 8,8. The ammonium sulphate also increases the conductivity of the solution and activates the surface of the manganese deposit.

As the cathode current density is increased, the manganese deposit becomes more nodular. At current densities of more than 5,9 A/dm<sup>2</sup>, tree formation becomes prevalent. If all the relevant factors are taken into account, the optimum cathode current density is between 4,3 and 5,4 A/dm<sup>2</sup>. The operating current density will determine the optimum deposition time.

It has been found that current efficiency decreases with an increase in temperature above 36 to 38 °C, which, owing to an increase in the conductivity of the solution, offsets any advantage from the lower power consumption. Below this range, the deposit becomes dark in colour with a fine-grained, highly stressed structure, and it normally cracks and falls off the cathode.

The maximum limits of some impurities have been given in Table III. The presence of impurities is indi-

cated in various ways. The most usual indication is the re-dissolution of the manganese deposit, which starts at the outer edges and progresses inwards with time. This leaves a typical black border around the deposit, which can be seen in Figs. 3 and 4. As the impurity level increases, the deposit cracks and peels off the cathode. Impurities can also result in the formation of extremely nodular deposits, or deposits that are very brittle or extensively pin-holed and difficult to remove from the cathode. In extreme cases, the cathode turns black and it is difficult to initiate a deposit at all or the deposit cracks and peels off the cathode within a few hours.

The cathodes, after the required deposition period, are removed from the cells by a specially designed stripping machine. The manganese deposit is removed from the cathode by being struck with a rubber mallet. The metal flakes fall into a sodium dichromate bath, from which a submerged rubber belt transports the flakes to a conveyor-belt system that transports the flakes to the metal-handling section. Here the flakes are washed, dried, and packed as low-oxygen grade or treated for the removal of the occluded hydrogen and then packed as

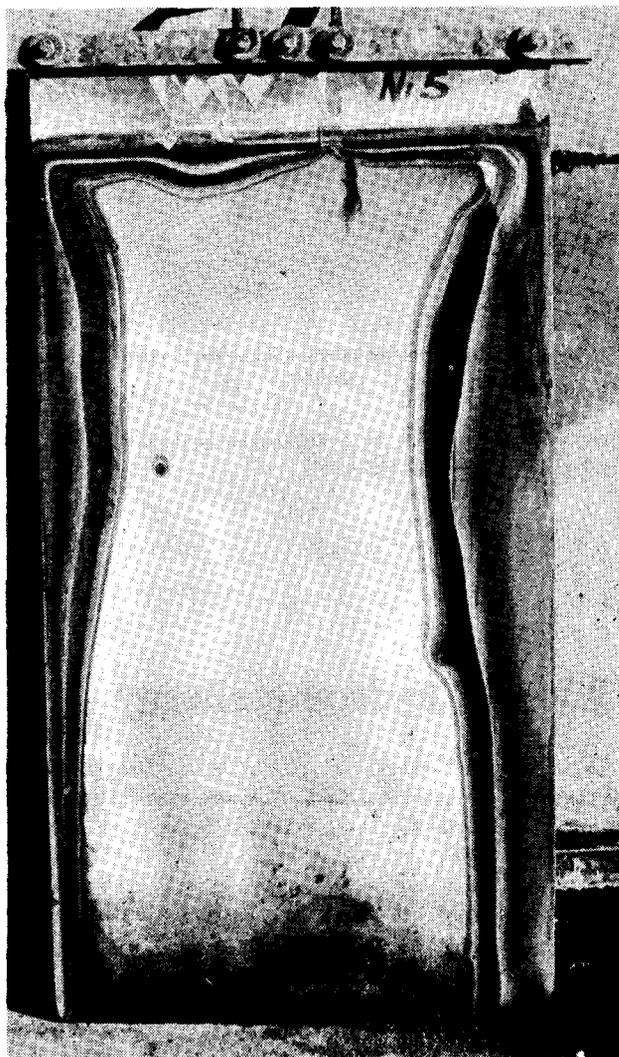


Fig. 3—Manganese plated from a solution containing 5 mg/l nickel

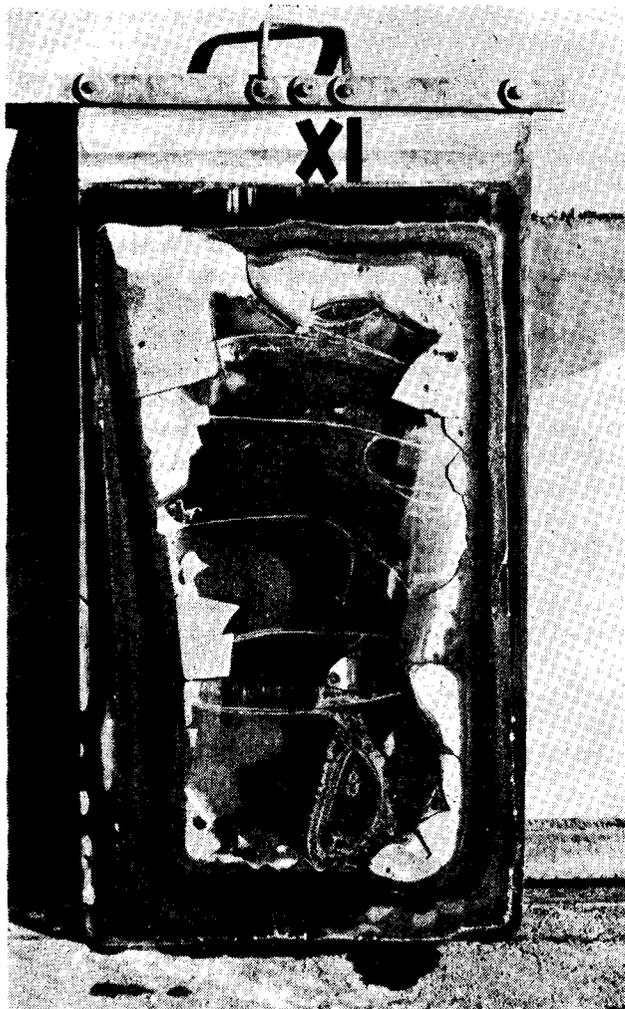


Fig. 4—Manganese plated from a solution containing 3 mg/l cobalt

low-hydrogen grade. The typical analyses of the two grades are shown in Table VI.

TABLE VI  
TYPICAL ANALYSIS OF ELECTROLYTIC MANGANESE

	Low-oxygen grade %	Low-hydrogen grade %
Manganese	99,82	99,65
Sulphur	0,024	0,026
Iron	< 0,001	< 0,001
Carbon	0,006	0,006
Oxygen	0,08	0,30
Hydrogen	0,018	0,0006

In conclusion, it can be stated that, after the usual commissioning and minor process problems had been solved, the Delta plant in Nelspruit operated most satisfactorily at its rated capacity of 16 500 t/a of manganese at current efficiencies of 68 per cent. In the design of the plant, the control of chemical processes has been automated as far as possible. Since it is realized that tremendous benefit can be derived from further research work, research programmes are being undertaken on improvements in the ore-reduction, leaching, and purification processes.

An interesting research programme at present being undertaken is a detailed investigation into the effects of various impurities on current efficiency. A laboratory cell has been constructed in which all the plant operating conditions can be simulated. In the tests completed so far, the comparative current efficiencies indicate that a similar cell could be used as a control instrument to monitor the efficiency of the purification process. At present, the effects of cobalt and nickel on the current efficiency of the cell are being investigated.

#### References

1. WANAMAKER, E. M., and MORGAN, W. D. Purification in electrowinning of manganese. *U. S. Pat.*, 2325723. 1943.
2. DEAN, R. S. *Electrolytic manganese and its alloys*. New York, Ronald Press, 1952.
3. JACOBS, J. H., HUNTER, J. W., CHURCHWARD, P. E., and KNOCKERBOCKER, R. G. Operation of the electrolytic manganese pilot plant at Boulder City, Nevada. *U. S. Bur. Mines Bull.* 463. 1946.
4. HENLEY, H. R., and JACOBS, J. G. Method of electrowinning manganese. *U. S. Pat.* 2439805. 1948.

## Chloride hydrometallurgy

Benelux Metallurgie is to hold an international symposium devoted to chloride hydrometallurgy. This meeting will take place in Brussels from 26th to 28th September, 1977.

The main topics of the meeting will be as follows:

Ore dressing: specific chemical treatments pertaining to the chlor-hydric route (chloridizing roasting, chloridizing volatilization)

Ore leaching

Purification of solutions (precipitation, cementation, ion exchange, solvent extraction, membranes)

Metal recovery from purified solutions (cementation, electrolysis, hydrogen reduction)

Eventually, recovery of a pure compound

Antipollution waste disposal.

The introductory plenary lecture will be given by Professor E. Peters, British Columbia University (Vancouver, Canada).

Copies of the First Circular can be obtained from Dr E. Schalch, National Institute for Metallurgy, Private Bag X3015, Randburg, 2125 South Africa (tel. 48-9470 ext. 474 and 490).

# Electrowinning of nickel at the Bindura Smelting and Refining Company

by H. T. BROWN\*, B.Sc. (Member) and P. G. MASON\*, B.Sc. (Member)

## SYNOPSIS

After a brief discussion of theoretical considerations in the electrowinning of nickel, an account is given of the electrowinning process and plant used at the Bindura Smelting and Refining Company.

## SAMEVATTING

Na 'n kort bespreking van die teoretiese oorwegings in verband met die elektrowinning van nikkell, word daar verslag gedoen oor die elektrowinningsproses en -aanleg wat deur die Bindura Smelting and Refining Company gebruik word.

## Introduction

The refinery at the Bindura Smelting and Refining Company (B.S.R.), Rhodesia, treats the nickel-copper-sulphide alloy that is produced in its pyrometallurgical smelting plant. The design of the refinery circuit was formulated by Outokumpu Oy, and the nickel and copper products are electrowon from solution. The control of the refinery circuit is based on the rate at which nickel is plated out of solution. New nickel-copper alloy must be added to match that rate, and allowances must be made for the sulphide content, or 'non-leaching' fraction, in the calculation.

Copper is essential to the process, and care has to be taken with the addition rate of the alloy, as well as with the copper-plating rate, if the circuit is not to be denuded of copper.

This paper examines the theoretical aspects of the electrowinning of nickel, and describes the equipment used at B.S.R. and some of the problems that have been encountered.

## Theoretical Considerations

The nickel is electrowon with insoluble anodes and nickel cathodes in a diaphragmed compartment from a purified nickel sulphate solution containing boric acid.

The cell potential can be considered to be made up of three potentials:

$E_{cell}$ , the cell potential,

$E_A$ , the anode electrode potential, and

$E_C$ , the cathode electrode potential.

$E_{cell} = E_A - E_C + E_R$ , where

$E_R$  = potential across the electrolyte.

The anode and cathode electrode potentials,  $E_A$  and  $E_C$ , are made up of further potentials:

E.P. (electrode potential) = R.P. + C.P. + A.D.

E.P. is the driving force required for a reaction to occur at a given electrode-electrolyte interface. It is the voltage between the electrode and the adjacent electrolyte and depends on composition of electrode and electrolyte, temperature, and current density.

R.P. (reversible potential) is the voltage that can be theoretically measured across the interface when no current is flowing. It is independent of whether the

electrode is an anode or cathode. Standard reference reversible potentials are available.

C.P. (concentration polarization) is the voltage necessary to overcome the effects of gradients in the concentration of reacting ions. These gradients are produced in the electrolyte layer adjacent to the electrode by operating at practical current densities. The concentration polarization increases with current density.

A.O. (activation overvoltage) is necessitated by some slow step in the electrode reaction. The transfer of an electron in the initial ion discharge at the cathode and the incorporation of the nickel atom in the crystal lattice are slow steps and require an overvoltage. The activation overvoltage increases with current density.

In electrowinning, the electrons are discharged from the cathode and collected onto the anode. The electrode potential for the various reactions that take place at the anode or cathode are best represented by the electro-motive series of Table I. The more negative the potential, the more readily the reaction takes place at the anode; and the more positive the potential, the more readily the reverse reaction takes place at the cathode.

TABLE I  
STANDARD ELECTRODE POTENTIAL AT 25°C

Element	Anodic reaction	Reversible electrode potential, V
Zinc	$Zn = Zn^{2+} + 2e$	-0,76
Iron	$Fe = Fe^{2+} + 2e$	-0,44
Cobalt	$Co = Co^{2+} + 2e$	-0,28
Nickel	$Ni = Ni^{2+} + 2e$	-0,25
Lead	$Pb = Pb^{2+} + 2e$	-0,13
Hydrogen	$H_2 = 2H^+ + 2e$	0,00
Copper	$Cu = Cu^{2+} + 2e$	+0,34
Oxygen	$2H_2O = O_2 + 4H^+ + 4e$	+1,23

## The Cathodic Reaction

Comparison of the reversible electrode potentials indicates that hydrogen would be evolved at the cathode, its potential being more positive than that of nickel. This does not occur because the hydrogen electrode potential is made substantially more negative than the nickel electrode potential by the following.

- (1) The concentration of hydrogen ions in the cathode compartment is kept low by the use of a diaphragm bag, thus inducing a high concentration polarization.
- (2) The deposition of hydrogen on nickel requires a high liberation overvoltage.

\*Bindura Smelting and Refining Company, Bindura, Rhodesia.

It can be mentioned here that certain organic chemicals, e.g., amines from boiler-water chemicals and lubricating oils, are considered to lower the overvoltage to such an extent that hydrogen is evolved at the cathode in place of nickel deposition. Thus, at the cathode the reaction can be taken as



At 225 A/m<sup>2</sup> and 65°C, an electrode potential of -0,56 V would be made up of the following voltages, which are estimates from rough measurement to serve only as a guide:

Reversible potential	-0,25 V
Deposition overvoltage	-0,15 V
Concentration overvoltage	-0,16 V.

Some hydrogen is evolved, but this is probably due to the reaction



The hydroxyl ion could raise the catholyte pH and cause the nickel to precipitate. To prevent this, boric acid is introduced as a buffer. Boric acid, which is a weak acid, normally forms complexes with nickel ions, preventing the precipitation of the nickel hydroxide.

Because of the high electrode potential, it is necessary to purify the catholyte of metal ions such as copper, cobalt, lead, iron, and zinc that would otherwise plate with the nickel.

### The Anodic Reaction

Because insoluble anodes are used, the reaction must involve either the decomposition of water or the oxidation of the anion if current is to pass. The electrode potential for the oxidation of the sulphate anion is greater than that for the decomposition of water, and oxidation therefore becomes the principle anodic reaction:



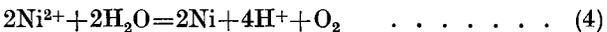
At 225 A/m<sup>2</sup> and 65°C, an electrode potential of +1,99 V was made up of

Reversible potential	+1,23 V
Oxygen overvoltage	+0,76 V.

The potential is high enough for hydroxyl ions to be oxidized at the anode but, because their concentration in acid solution is low, they consume very little anode current.

### The Overall Cell Reaction

Reactions (1) and (3) combine to give the overall cell reaction



or



The combined potentials are

$E_A = +1,99 \text{ V}$
$E_C = -0,56 \text{ V}$
$E_R = +1,05 \text{ V}.$

$$E_{\text{cell}} = E_A - E_C + E_R$$

$$= 1,99 - (-0,56) + 1,05$$

$$= 3,60 \text{ V}.$$

It should be noted that  $E_R$  includes a voltage drop across the diaphragm bag of 0,25 V.

## The Plant

### Cells

The cells are constructed in pairs, and are of reinforced concrete with an acid-resistant lining.

#### Cell measurements

6,6 by 1,15 by 1,2 m internal

#### Cell linings

Original : 4% antimonial lead. Testing : pure lead, fibreglass, Telcovin (thermoplastic), neoprene. (It has been necessary to replace antimonial lead linings every 2 to 3 years.)

#### Cathodes

39 trimmed nickel starting sheets or stainless-steel blanks.

#### Anodes

40 6 mm pure-lead plates (originally 4% antimonial lead).

#### Spacing

160 mm anode to anode.

#### Cathode compartment

Fibreglass cathode bag frame with terylene diaphragm bag. Catholyte distributed to each compartment.

#### Unscreened plating surface

Starting sheets: 1000 mm by 855 mm. Cathodes: 990 mm by 805 mm.

#### Fume

Anodes are bagged and the cloth effectively filters the gases.

### Power Source

The d.c. power to the cells is obtained from silicon rectifiers connected to a 24 phase 4800 kV.A transformer arrangement. On load tap-changing and transducers are used to provide constant current output up to a maximum of 15 000 A. The voltage range is 40 to 280 V.

### The Process

Nickel is first plated at a current density of 210 A/m<sup>2</sup> onto stainless-steel blanks to form three-day starting sheets, which are trimmed and have nickel loops welded to them. Thinner sheets may be used but would require rigidizing. The stainless-steel blanks are sanded with a 270 grit emery cloth, and need only a thin coating of shellac.

The trimmed and looped starting sheets are placed in an etching tank of 20 g/l sulphuric acid, and the current is reversed for about 30 minutes. The etched sheets are removed and, without being dried, are placed in a 10 to 15 g/l boric acid solution in a holding cell to await transfer to the commercial cells. In this manner, passivation of the etched starting sheets is avoided, and a clear *wettable* sheet is made available for plating, thus reducing the tendency for split or pitted cathodes.

Plating at a current density of 225 A/m<sup>2</sup> continues in the commercial cells for a further six days to provide cathodes within a specified thickness. The tankhouse is currently operating at 14,5 kA, with current efficiency in the region of 95 per cent.

The cathodes are pulled, washed, sheared into squares, packed, and despatched. Some whole cathodes are sold.

## Process Control

Current density, catholyte flow, nickel concentration, pH, purity, and temperature are the most important control parameters.

Depletion of nickel ions in the liquid film adjacent to the cathode increases the concentration polarization, and thus the electrode potential. If this is taken to the extreme, excessive evolution of hydrogen may occur. Replenishment of the nickel ions in this liquid film depends on electromigration and diffusion. The rate of diffusion is controlled by the concentration of nickel in the bulk of the electrolyte, which in turn is dependent on the concentration in the catholyte, the catholyte flow, and the plating rate (current density).

It is evident therefore that the current density, the nickel concentration in the catholyte, and the drop in nickel concentration (on which the flow is based) are interdependent. It is current practice at B.S.R. to operate with a drop in nickel concentration of 28 g/l (from 96 g/l in the catholyte) at a current density of 225 A/m<sup>2</sup>.

Liberation of hydrogen at the cathode is inhibited by the high concentration overvoltage. However, if the pH is allowed to drop by the back diffusion of hydrogen ions, excessive liberation of hydrogen may occur. To prevent this, a suitable diaphragm membrane is required so that a hydraulic head, preferably 25 mm, is maintained in the cathode compartment. On the other hand, if the pH is too high, nickel can precipitate at the cathode surface, affecting the quality of the deposit.

The pH of the catholyte is controlled to 3.5 by the addition of acid, and boric acid is added to prevent nickel precipitation. An indication of the pH of the electrolyte can be gained by inspection of the froth layer on the solution surface. Suspect bags are checked and changed as necessary.

As most metal ions will be deposited at the cathode at the high potentials employed, cathode purity is directly related to the efficiency of catholyte purification. The following are typical analyses.

	Catholyte p.p.m.	Cathodes p.p.m.
Cu . . . . .	1	10
Co . . . . .	1-2	40
Pb . . . . .	1	10
Fe . . . . .	1	5
Zn . . . . .	1	2

Owing to the lack of sensitivity of catholyte analyses,

no correlations have been possible between catholyte and cathode impurity at this level.

The temperature of the solution affects the stresses in the cathode deposit, the stresses being relieved once the temperature is above about 55°C. As PVC piping in the circuit limits the upper temperature to 65°C, the catholyte temperature is normally controlled at 62°C. After long shutdowns, it is essential that the temperature should be raised before plating commences if the cathodes are not to split.

The plating current can be interrupted for several hours without adverse effect to the cathodes. It is not the practice at B.S.R. to hold with a trickle current. After a long shutdown, the current is reversed for a short period before normal plating is commenced, but it is uncertain whether this achieves anything other than heating of the electrolyte. However, cells that are shorted out and left loaded become passive, and current reversal is essential prior to normal plating.

## Problems

### *Pitting of the Cathode*

Sodium lauryl sulphate is added to the catholyte to prevent pitting of the cathode surface. This additive may act as a wetting agent; or it may increase the hydrogen overvoltage, or form complexes with organic material, particularly oil, present in the catholyte.

### *Nodules on the Cathode*

Particulate matter adhering to the cathode forms nodules. For this reason, the catholyte is clarified in Stellar filters, and a turbidimeter has been installed to cause the filtrate to recycle if breakthrough occurs. Because precipitation of nickel at the cathode can also result in the growth of nodules, the pH of the catholyte is reduced.

### *Current Distribution*

Uneven distribution of current between the cathodes can result in wide variation of current density and cathode quality. Cells are regularly steam-cleaned, and a close watch is kept on the busbar contacts.

### *Catholyte Distribution*

The flow of catholyte to each bag is adjusted by the action of a screw clamp on flexible PVC pipe, and is measured by rotameter. The system is far from ideal, and there are large variations between the flows. This naturally affects the drop in nickel concentration, and thus the quality of the nickel cathode. An improved method of flow distribution is being sought.

# The electrolytic extraction of zinc at the Zinc Corporation of South Africa Limited

by C. J. VAN NIEKERK\*, B.Sc. (Hons.) (Potch.), M.Sc. (Unisa) (Fellow)  
and D. R. ALLEN\*, A. Met. (Sheffield) (Member)

## SYNOPSIS

This paper gives a brief account of some modifications that were made to the process of zinc electrowinning practised by the Zinc Corporation of South Africa Limited. Some changes in the materials of construction are also described.

## SAMEVATTING

Hierdie referaat doen kortliks verslag oor 'n paar wysigings wat in die proses vir die elektrowinning van sink soos dit deur die Sink Korporasie van Suid-Afrika Beperk toegepas word, aangebring is. 'n Paar veranderings in die konstruksiemateriale word ook beskryf.

## Introduction

The hydrometallurgical extraction of zinc became possible through the electrolysis of zinc solutions, which was accomplished during the decade 1870 to 1880. The first patent dealing with the electrolysis of zinc from sulphate solution appeared in 1883, and the first two commercial plants were built in 1915. The hydrometallurgical process has steadily replaced the earlier (pyrometallurgical) methods of zinc extraction, so that today approximately 70 per cent of all zinc is produced electrolytically.

The raw material in the electrolytic process is zinc oxide, which may be in the form of a calcine obtained after roasting of the sulphide, or in the form of a fume obtained from a fuming process.

The various steps in the conversion of the impure raw material to pure metal are as follows. The oxide is leached with dilute sulphuric acid, referred to as spent electrolyte, in order to convert the zinc oxide to zinc sulphate. The resultant zinc sulphate solution is separated from the insolubles by thickening and filtration, and is then purified and electrolysed to yield zinc metal on the cathode whilst oxygen is liberated from the anodes. The sulphuric acid released is recycled to the leach.

## The Process at Zincor

### Leaching

At the Zinc Corporation of South Africa Limited (Zincor), leaching was initially carried out batch-wise in air-agitated pachucas of 300 m<sup>3</sup> capacity, but the formation of agglomerates of unleached calcine was a problem. These agglomerates formed when the calcine, which contains approximately 10 per cent zinc sulphate (anhydrous), was added rapidly to the leach slurry. Wetting of the calcine results in the hydration of the zinc sulphate, which in turn acts like a glue in cementing particles together. A faster rate of agitation did not materially improve the situation. A similar problem was encountered during the continuous leaching of Waelz oxide fume, but here the agglomeration was probably

due to the presence of calcium oxide, which reacted with the sulphuric acid to form calcium sulphate. Wet milling of the Waelz oxide to minus 100 mesh Tyler and the addition of milled slurry to the leach reduced the formation of these agglomerates.

Leaching of the calcine was changed later from batch to continuous operation, the latter having the advantage of a slow addition rate for the calcine, and thus easier control. Continuous leaching resulted in a reduction of agglomerate formation, but the problem was not entirely solved and the leaching tanks still had to be drained of the coarse material from time to time.

The continuous leach now consists of two pachucas, 300 m<sup>3</sup> each, in series, and coarse material is drained into a third agitator (of 20 m<sup>3</sup> capacity) on a daily basis. This coarse material is allowed to dissolve and disperse in spent electrolyte, which is an approximately 15 per cent solution, for 24 hours before it is returned to the continuous leach.

The method of leaching used is generally referred to as neutral leaching because of the small amount of free acid present during the leach. The concentration of free acid in the first pachuca is only between 1 and 2 g/l.

Zinc plants usually allow a certain amount of iron to dissolve during leaching. On neutralization, this iron precipitates as ferric hydroxide and absorbs impurities such as arsenic and antimony.

Neutral leaching dissolves very little iron, and at one time Zincor added iron in the form of ferrous sulphate. This practice was later discontinued without any ill effect on the final electrolysis.

### Separation

The liquid-solid separation step after leaching was initially carried out by countercurrent thickening followed by two-stage filtration. The control of this plant was difficult, and the loss of soluble zinc amounted to approximately 1 per cent. Later, one-stage filtration was introduced, but more wash water was applied to the filter and the thickening was done in one stage. The control of the plant solution inventory was much easier, and the loss of soluble zinc was maintained at a level of 0,3 per cent.

\*The Zinc Corporation of South Africa Limited, Springs, Transvaal.

## Purification

The impure zinc sulphate solution was formerly purified by heating of the solution to approximately 90°C, followed by the addition of arsenic trioxide, copper sulphate, and zinc dust to precipitate impurities such as cobalt, nickel, germanium, antimony, copper, and arsenic. The solution was then filtered, and cadmium was cemented out by a further addition of zinc dust and a small amount of copper sulphate. It was found later that a reduction of temperature to between 75 and 80°C during the first-stage purification, while not reducing the current efficiency, led to a saving in steam and an increase in the production capacity of the purification plant. Many problems were experienced with the corrosion of materials of construction in the purification plant and the impure storage tanks. The impure storage tanks were equipped with copper steam-heating coils, which corroded rapidly in the impure solution from the Waelz oxide but gave, and are still giving, very good service in the first-stage purification tanks.

The copper coils in the impure storage tanks were replaced by 316L stainless-steel coils, but these had a life of only about three months. Failure was found to be due to stress-corrosion, and heat treatment of these coils, relieving the bending stresses, increased the life to approximately two years.

The impure storage tanks are fabricated in mild steel and are rubber lined. The rubber lining does not stand up well to the temperatures of 70 to 80°C, and the tanks have to be rubber lined once every eight years or so. Intermittent patching of the rubber lining is also required during service life.

A third impure storage tank has now been fabricated in 316L stainless steel and has been in operation for eight months with no visible evidence of corrosion.

The first-stage purification tanks were of lead-lined mild steel. The lead lining was unsuccessful, and leaks developed owing to creeping and cracking of the lead. The lead lining was removed and replaced by a rubber lining, which, owing to the high temperature and strong agitation of the solution, kept coming loose from the tank. At that stage it was decided to re-build the tanks in 316L stainless steel.

These tanks have been in service for the past three years and are showing no signs of corrosion. In addition, they do not appear to have had any ill effect on the electrolysis.

## Cell House

Changes in operation of the cell house and in the materials of construction were also brought about.

Two electrolytic circuits are operated at Zincor, the reason being that the Waelz oxide received from Kiln Products Limited has a fluorine content of approximately 0,03 per cent. The fluorine dissolves during leaching and accumulates in the plant solution to reach an operating level of between 100 and 150 mg/l. Fluorine causes severe sticking of the plated zinc to the aluminium cathodes, and the cathodes have therefore to be treated in some way in order to prevent sticking. Initial practice was to strip only from the circuit high in fluorine. This was done by plating for 12 hours in the low-fluorine

solution, followed by 12 hours plating in the high-fluorine solution, and then stripping off the deposited zinc. It was later found that this preplating period of 12 hours could be reduced to as little as 10 minutes, and that the zinc plated onto the cathode during this brief period was sufficient to prevent sticking during subsequent plating for 24 hours in the high-fluorine circuit.

Sticking of zinc to the cathodes to the extent where stripping became impossible was experienced at times on the sulphide circuit, where the fluorine concentration is generally less than 5 mg/l. A small amount of potassium antimony tartrate (0,01 to 0,02 mg of antimony per litre) added daily to the electrolytic circuit has proved beneficial, and no sticking has occurred since December 1972.

The presence of magnesium in some of the raw materials has forced the plant to use a compromise electrolyte. The zinc concentration of the electrolyte had to be reduced from the customary level of between 60 and 70 g/l to 45 g/l, and the sulphuric acid from 200 g/l down to approximately 130 g/l. This reduction in zinc and sulphuric acid concentrations allows enough room in the electrolyte to operate at a magnesium concentration of 20 g/l. The magnesium is controlled by continuous bleeding of a portion of the electrolyte, and neutralizing this with lime slurry to a pH value of 8, followed by filtration. The filtrate, which contains 0,03 g of zinc per litre and all the magnesium, is discarded. The zinc hydroxide is filtered off, slurried, and returned to the leach.

Before the erection of this neutralization plant, magnesium in the electrolyte was controlled by reducing the zinc content of the solution to between 10 and 15 g/l by electrolysis and then discarding the whole of the solution, which resulted in large losses of zinc.

The magnesium control plant can also be used to control manganese in solution. At a pH value of 8, manganese is oxidized and precipitated as insoluble manganese dioxide in the presence of a suitable oxidant such as oxygen or air. The manganese can be precipitated down to solution levels of less than 0,02 g/l.

The presence of manganese in the electrolyte is of extreme importance. Manganese is oxidized at the anodes and precipitates on the anodes as manganese dioxide, which forms a protective layer that prevents corrosion. The anode consumption was found to be four times higher for an electrolyte containing manganese at 1 g/l than when the manganese content was 3 g/l. It was also observed that the cell-house atmosphere improved when the manganese concentration was at a higher level, probably owing to oxidation of chlorides to perchlorates in the presence of permanganate. The absence of manganese in solution allows chlorides to be oxidized to free chlorine, which escapes and pollutes the cell-house atmosphere.

Air sparging of the anodes and cathodes resulted in a smoother zinc deposit but did not improve the current efficiency at the current densities tested. These were all below 700 A/m<sup>2</sup>. A slight decrease in the lead content of the deposited zinc was observed, as reported by Martin and his co-workers<sup>1</sup>.

TABLE I

LIMITS OF CONTAMINANTS IN ZINC ELECTROLYSIS<sup>2</sup>

Authors	Contaminant, mg/l							
	As	Sb	Fe	Ge	Cd	Cu	Co	Ni
Billiter, Ralstan	10	0,3-1	30					
Eger, Tafel	1	1	20-30	1	12	10	1	
Loskutow, Shurnikow	0,1	0,1	30					
Hannay, Bryden	5	0,15	70	0,15				
Scacciate				0,2			3	
Salin	1	1	12	0,5	12	7-10	1	2-4
Wolkowa, Pachonova	0,1		50			0,2	3-4	
Orlowa								
Hansel	1	0,5	50	0,05	10	1	3	3
Wever		0,02					10	0,1

Various reagent additions are made to the electrolytic circuit. The addition of a suspension of strontium carbonate to the electrolyte results in the precipitation of lead from solution, and zinc cathodes containing approximately 0,0015 per cent lead can be produced. Another chemical often used for the suppression of lead is barium carbonate, but at Zincor it was found to be less effective than the strontium carbonate.

A mixture of cresylic acid and gum arabic is being added to the electrolyte cells to prevent acid mist by the formation of a froth layer on the surface. This method of mist suppression is rather inefficient, however, and other chemical additions are being tried at the present time.

#### Impurities in the Electrolyte

The effect of impurities in the electrolyte on the current efficiency has been extensively reported in the literature, but there is little agreement on the levels that can be tolerated in the cell house.

Kruger and Winterhager<sup>2</sup> have summarized the findings of various authors, which are listed in Table I.

Bratt's results<sup>3</sup> are given in Table II, and those of Ault and his co-authors<sup>4</sup> in Table III.

TABLE II

EFFECT OF IMPURITIES ON CURRENT EFFICIENCY<sup>3</sup>

Impurity	Effect on current efficiency, % (+Gain -Loss)
Hg	+1 at 10 mg/l. +5 at 10 mg/l.
Pb	+5 at 3 mg/l.
Cd	-6 at 1 000 mg/l. +4 at 12 mg/l.
Tl	No effect at 5 mg/l. Gain at 1 mg/l. Loss at 10 mg/l.
Sb	-36 at 1 mg/l. Gain at 0,15 mg/l. Loss at 0,25 mg/l.
Sn	-20 to -25 at 0,5 mg/l.
Au	-0,8 at 1 mg/l.
Cu	-2 at 10 mg/l. -3,9 at 1 mg/l. -6 at 1 mg/l.
Fe	-3 at 10 mg/l.
Ni	-16 at 10 mg/l. -5 at 1 mg/l. -12 at 10 mg/l.
Co	-15 at 10 mg/l.
Ge	-56 at 1 mg/l. High loss at 1 mg/l.

From the published work and also from experience at Zincor, it is known that a high-quality solution can be ensured only by thorough purification of the zinc sulphate solution. The quality of the solution is generally determined from analyses for certain impurities.

The quality of the purified solution fed to the cells at Zincor was in the past determined by analysis of the

solution for the following elements: cobalt, nickel, arsenic plus antimony, and germanium. A high-quality solution was considered to be one that did not exceed the following maximum levels: cobalt 0,3 mg/l, nickel 0,1 mg/l, arsenic plus antimony 0,02 mg/l, and germanium 0,01 mg/l. It was often found that, even though a purified solution complied with this specification, there was no assurance that the solution was of a high quality from a current efficiency point of view.

The National Institute for Metallurgy has developed and constructed an instrument with which the quality of a solution can be measured. The total time required to make one measurement is less than five minutes, and Zincor, having now discontinued the determination of nickel, arsenic, and germanium, has purchased such an instrument for the determination of solution quality in the laboratory. The current efficiencies obtained from measurements on purified solution from the sulphide circuit correlated well with current efficiencies as measured on the plant over a period of one month (Fig. 1).

However, very poor correlation was obtained for the oxide circuit. This means that certain changes are taking place in the oxide electrolyte that cannot be accounted for by the quality of the purified solution alone. A possible explanation is that, owing to the high magnesium concentration of that circuit (20 g/l), electrolyte control becomes more sensitive. This is best illustrated by a few examples.

For an electrolyte that contains no magnesium, the zinc concentration may be as high as 63 g/l at an acid concentration of 200 g/l. This gives an electrolyte with a molarity of 3,0 (viz  $H_2SO_4=2,04$  M and  $Zn=0,96$  M). An electrolyte of 3,0 M has acceptable viscosity and good plating properties. At higher concentrations, the deposited zinc becomes uneven and rough owing to the evolution of hydrogen, and there is a consequent drop in current efficiency.

In comparison, for an electrolyte containing 20 g of magnesium per litre, the concentration of acid plus zinc must not exceed a molarity of 2,17 (Mg 20 g/l=0,83 M). If the zinc concentration is a minimum of 45 g/l (equivalent to 0,69 M), the maximum for acid becomes 145 g/l. Now, any small decrease in zinc concentration will cause a drop in the current efficiency owing to the starvation of zinc at the cathode surface, and any small increase in concentration will have the same effect because the practical concentration

TABLE III  
THE EFFECTS OF CONCENTRATION INCREASE ON CURRENT EFFICIENCY

Impurity	Typical concentration mg/l	Increase in concentration mg/l	Average $\Delta$ C.E.	Max. $\Delta$ C.E.	Min. $\Delta$ C.E.
Co	10	2	-1,41	-1,81	-1,10
Ni	0,3	0,3	-0,98	-1,13	-0,77
Cd	0,2	0,8	-0,78	-1,05	-0,50
Cu	0,05	0,06	-1,66	-2,76	-1,00
Cl <sub>2</sub>	160	40	-1,00	-1,30	-0,79
NH <sub>3</sub>	3000	2000	-2,89	-3,11	-2,56
Fe	0,5	0,6	-1,10	-1,38	-0,83

of salt plus acid (3,0 M) has been exceeded (Fig. 2).

An investigation into the relative size of anodes to cathodes showed that, if the anodes were made 100 mm narrower and shorter than the cathodes, an improvement of 2 to 3 per cent in current efficiency was obtained. The dendrite formation was greatly reduced because the narrower anodes resulted in a lower current density on the edges of the cathodes as a result of the greater cathode-to-anode distance. The practice of having holes punched at 2 inch centres in the anodes was also stopped, since it was found that these holes very rapidly became filled with the manganese dioxide and sludge deposit and, contrary to general belief, played no part whatsoever in enhancing the circulation of electrolyte between anode and cathode.

#### Further Research

Zincor considers that much remains to be learnt about the electrolytic process, and research is continuing on all aspects of the process in an endeavour to achieve a higher recovery of zinc. The Corporation is in the process of erecting a hot-acid leaching plant, which is based on research that it conducted on the treatment of leach residues. It is hoped that this plant will achieve recoveries in the region of 96 per cent.

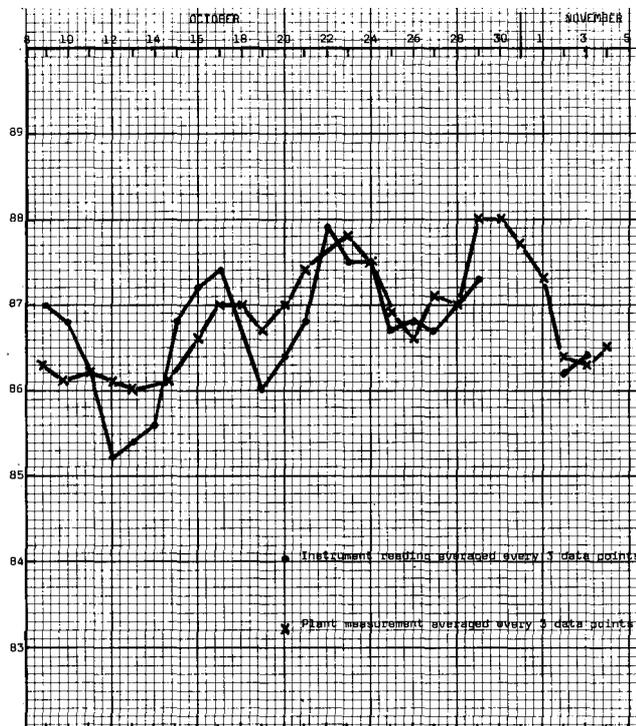


Fig. 1—Correlation between current efficiency and quality of electrolyte on the plant

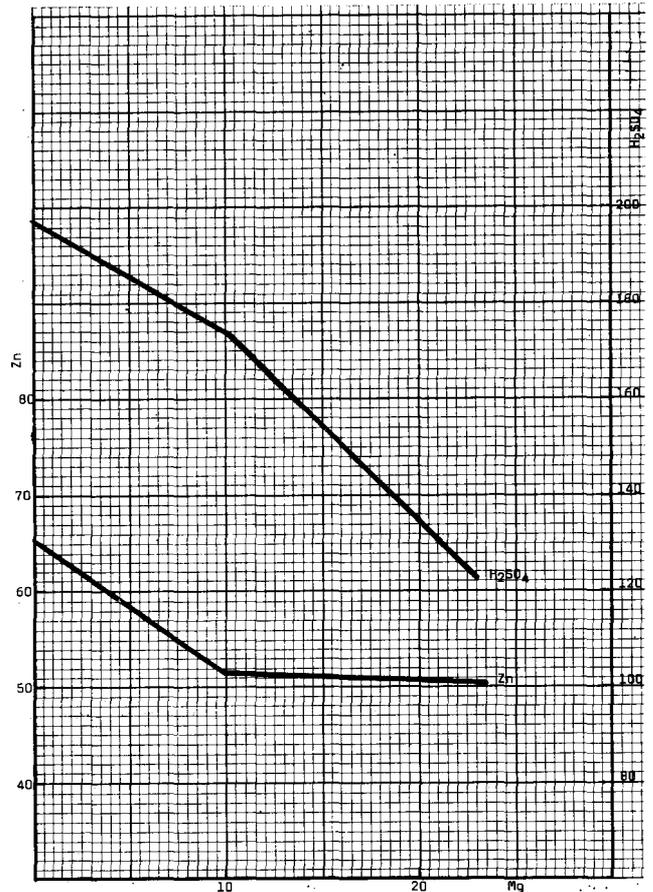


Fig. 2—Composition, in grams per litre, of the cell feed when the manganese concentration in the electrolyte is less than 5,5 g/l

#### Acknowledgement

The authors thank the Directors of the Zinc Corporation of South Africa Limited for permission to publish this paper.

#### References

- MARTIN, J. P., LOVEDAY, B. K., PAULSEN, H., and JOCHENS, P. R. The application of air-sparging techniques to the industrial electrodeposition of zinc from acidic zinc sulphate solutions. Johannesburg, National Institute for Metallurgy, Report No. 1782. Mar. 1976.
- KRUGER, J., and WINTERHAGER, H. Contribution to the question of zinc refining by electrolysis. *Z. Erz. Metallhüttes.*, Nov. 1965.
- BRATT, G. C. Impurity effects in the electrowinning of zinc and cadmium. *Electrochemical Technology*, vol. 2, no. 11-12. Nov.-Dec. 1964. pp. 323-326.
- AULT, A. R., BAIN, J. H., PALMER, D. J., and PULLEN, J. B. Recent investigations into some cellroom problems at Risdon. *The Australia I.M.M. Conference, South Australia*. Jun. 1975. pp. 225-234.

## Book review

*Proceedings of the Symposium on Mining Methods.* London, Institution of Mining and Metallurgy, 1974. 160 pp.

The Symposium was held from 30th October to 1st November, 1974, and the papers include an interesting range of subjects in coal-mining operations, covering the improvements achieved to date, current practice, and required development for the future.

*Constraints in Planning* includes comment on geology, design, policy, law, markets, and their part in planning, the objective being to optimize safety, efficiency, and profit.

*High Speed Tunnelling* considers the requirements of tunnelling for NCB mines. The authors are directors in the NCB's R & D Division, who have designed a machine for coal headings that is described in the paper. The requirements of high speed tunnelling over the next ten years are considered.

*Rapid Drivages with Continuous Miners* includes comment on ancillary equipment, materials handling, ventilation, manning, supervision, and control systems, and the importance of maintenance is highlighted.

The third paper on this subject, *Drivages with Dosco Roadheaders*, describes the modifications made to the machine to improve its performance, its future development, and application.

Falls of ground and their prevention are considered in *The Prop Free Front and Its Development*. The effects of the introduction of powered support on accidents is discussed. A similar paper, *Support on the Face*, briefly

reviews a history of face supports and suggested areas for improvement.

Two further papers on support are *New Techniques in Roadway Support*, which covers the importance of design, strength of strata, and characteristics of support systems, and a paper on *Mechanical Packing Systems* dealing with the development, application, and experiences with various packing machines.

Longwall operations are considered in two papers: *Longwall Machinery Development and Current Practice with Special Reference to Scotland* reviews the development of power loading up to the present continuous mining operations, and the paper on *Longwall Equipment Development* looks to possible future developments in coal face equipment.

The text of the discussions arising from these papers is included, as are the opening and closing addresses.

Salamon, M.D.G., and Oravec, K. I. *Rock Mechanics in Coal Mining*. 119 pp.

This book has a fund of information and practical application for coal-mining officials and mining engineers.

The subject is covered in chapters on Fundamentals and Basic Concepts, Design of Bord and Pillar Workings, Pillar Extraction, Longwalling, Support in Workings, and Surface Subsidence. These aspects are clearly explained, and practical examples are given.

This handy-sized, well-produced book provides the industry with an excellent manual for both the operating production official and the mining engineer for planning and design.

D. E. M.

## NIM reports

The following reports are available free of charge from the National Institute for Metallurgy, Private Bag X3015, Randburg, 2125 South Africa.

### Report no. 1822

*Stability constants and linear free-energy relations for the platinum-group metals.* (22nd Oct., 1976).

The formation constants of Pd(II) and Pt(II) with eight ligands each are reported, together with stability constants for Ir(III) and Rh(III) SCN<sup>-</sup>. All the determinations of stability constants were based on the use of appropriate metal electrodes. It is shown that a linear free-energy relation exists for the free energy of formation of the Pd(II) and corresponding Pt(II) complexes with a wide variety of ligands. Similar, but less well established, relations were observed for Au(III) and Pt(IV) stability constants plotted against the corresponding Pd(II) constants. The formation constants of Pd(III) were plotted against the corresponding Ag(I) formation constants, and it is shown that the expected break-up

into hard and soft ligands occurs as for the d<sup>10</sup> metal ions. Owing to the difficulty of determining stability constants for Rh(III) and Ir(III), sufficient evidence for the existence of linear free-energy relations for these ions was not obtained.

### Report no. 1852

*A revised method for the dissolution of platinumiferous materials by the sealed-tube technique.* (18th Oct., 1976).

Revised procedures are given for the dissolution of platinumiferous materials ranging from lead-cupellation prills to matte-leach residues and individual noble metals. The procedures are based on pressure dissolution with different acid media and heating to temperatures of between 200 and 270 °C.

### Report no. 1828

*γ-picoline adducts of the nickel, copper, and zinc chelates of 2-thenoyltrifluoroacetone.* (26th Nov., 1976)

The extraction of metals by the formation of organic

soluble complexes improves dramatically in the presence of certain neutral ligands. Where these synergistic adducts occur as crystals, the phenomenon can be investigated by crystallographic methods.

This report deals with the synthesis, crystallization, and synoptic crystallographic examination of the  $\gamma$ -picoline adducts of the nickel, copper, and zinc chelates of 2-thenoyltrifluoroacetone.

#### Report no. 1847

*A pilot-plant investigation of a kinetic model for flotation.* (19th Nov., 1976)

The flotation behaviour of phoscorite from the Phosphate Development Corporation was measured in a pilot plant, the flotation cells in the plant being varied in configuration so as to operate with or without circulating loads. The ore was floated in a batch cell so that the

parameters for a kinetic model could be estimated, and these parameters were then used in a flotation-plant simulator, which is based on the kinetic model, in the prediction of the performance of a pilot flotation plant operating on phoscorite. The simulator predictions compare well with the measured performance of the ore in the pilot plant, but the comparison shows that the kinetic model is not completely adequate for the prediction of performance in continuous flotation plants. The model is weakest in its ability to model the behaviour of the froth phase. The flotation behaviour of the ore could be adequately described when it was assumed that the apatite and gangue each consist of floatable and unfloatable components.

The effect of particle size on the specific flotation rate constant of apatite was found to have a maximum at 85  $\mu\text{m}$  and to fall to zero at 400  $\mu\text{m}$ ; that for the gangue had a maximum at 50  $\mu\text{m}$  and was zero at 350  $\mu\text{m}$ .

---

## Company Affiliates

The following members have been admitted to the Institute as Company Affiliates.

AE & CI Limited.

Afrox/Dowson and Dobson Limited.

Amalgamated Collieries of S.A. Limited.

Apex Mines Limited.

Associated Manganese Mines of S.A. Limited.

Billiton Exploration S.A. (Pty) Limited.

Blackwood Hodge (S.A.) Limited.

Blyvooruitzicht G.M. Co. Ltd.

Boart International Limited

Bracken Mines Limited.

Buffelsfontein G.M. Co. Limited.

Cape Asbestos South Africa (Pty) Ltd.

Compair S.A. (Pty) Limited.

Consolidated Murchison (Tvl) Goldfields & Development Co. Limited.

Deelkraal Gold Mining Co. Ltd.

Doornfontein G.M. Co. Limited.

Durban Roodepoort Deep Limited.

East Driefontein G.M. Co. Limited.

East Rand Prop. Mines Limited.

Engineering Management Services (Pty) Ltd.

Envirotech (Pty) Ltd.

Free State Saaiplaas G.M. Co. Limited.

Fraser & Chalmers S.A. (Pty) Limited.

Gardner-Denver Co. Africa (Pty) Ltd.  
Goldfields of S.A. Limited.

The Grootvlei (Pty) Mines Limited.

Harmony Gold Mining Co. Limited.

Hartebeesfontein G.M. Co. Limited.

Highveld Steel and Vanadium Corporation Limited.

Hubert Davies Heavy Equipment (Pty) Ltd

Impala Platinum Limited.

Ingersoll Rand Co. S.A. (Pty) Ltd.

Johannesburg Consolidated Investment Corp. Ltd.

Kinross Mines Limited.

Kloof Gold Mining Co. Limited.

Lennings Holdings Limited.

Leslie G.M. Limited.

Libanon G.M. Co. Limited.

Lonrho S.A. Limited.

Loraine Gold Mines Limited.

Marievale Consolidated Mines Limited

Matte Smelters (Pty) Limited.

Natal Cambrian Collieries Limited.

Northern Lime Co. Limited.

O'okiep Copper Company Limited.

Otjihase Mining Co. (Pty) Limited.

Palabora Mining Co. Limited.

Photometric Sorters.

Placer Development S.A. (Pty) Ltd.

President Steyn G.M. Co. Limited.

Pretoria Portland Cement Co. Limited.

Prieska Copper Mines (Pty) Limited.

Rand Mines Limited.

R. J. Spargo Limited

Rooiberg Minerals Development Co. Limited.

Rustenburg Platinum Mines Limited (Union Section).

Rustenburg Platinum Mines Limited (Rustenburg Section).

St. Helena Gold Mines Limited.

Shaft Sinkers (Pty) Limited.

S.A. Land Exploration Co. Limited.

Stilfontein G.M. Co. Limited.

The Griqualand Exploration and Finance Co. Limited.

The Messina (Transvaal) Development Co. Limited.

The Randfontein Estates Gold Mining Co. Witwatersrand Ltd.

The Robbins Co. (Africa) (Pty) Ltd.

The Steel Engineering Co. Ltd.

Trans-Natal Coal Corporation Limited.

Tvl Cons. Land & Exploration Co.

Tsumeb Corporation Limited.

Union Corporation Limited.

Vaal Reefs Exploration & Mining Co. Limited.

Venterspost G.M. Co. Limited.

Vergenoeg Mining Co. (Pty) Limited.

Vlaktfontein G.M. Co. Limited.

Welkom Gold Mining Co. Limited.

West Driefontein G.M. Co. Limited.

Western Areas Gold Mining Co. Ltd.

Western Deep Levels Limited.

Western Holdings Limited.

Winkelhaak Mines Limited.