

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

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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 m³ 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 m³ each, in series, and coarse material is drained into a third agitator (of 20 m³ 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.

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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/m². A slight decrease in the lead content of the deposited zinc was observed, as reported by Martin and his co-workers¹.

TABLE I

LIMITS OF CONTAMINANTS IN ZINC ELECTROLYSIS²

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 Winterhager² have summarized the findings of various authors, which are listed in Table I.

Bratt's results³ are given in Table II, and those of Ault and his co-authors⁴ in Table III.

TABLE II

EFFECT OF IMPURITIES ON CURRENT EFFICIENCY³

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 Δ C.E.	Max. Δ C.E.	Min. Δ 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 ₂	160	40	-1,00	-1,30	-0,79
NH ₃	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.

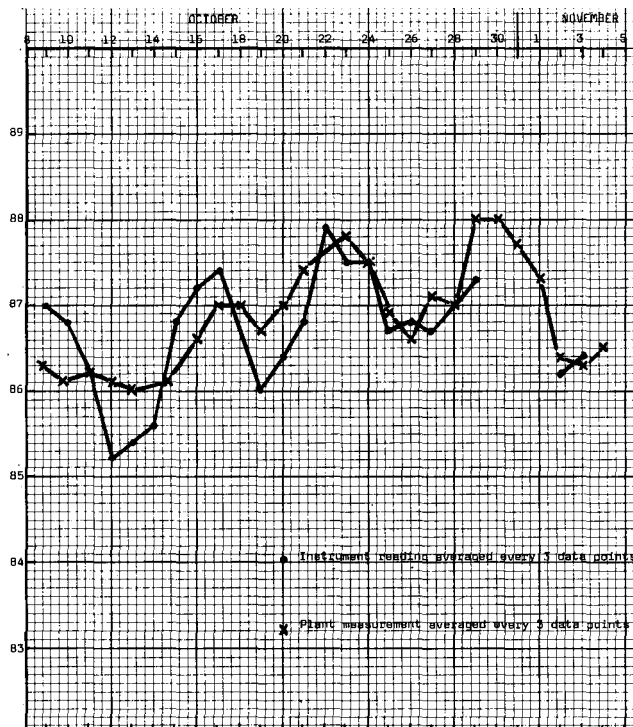


Fig. 1—Correlation between current efficiency and quality of electrolyte on the plant

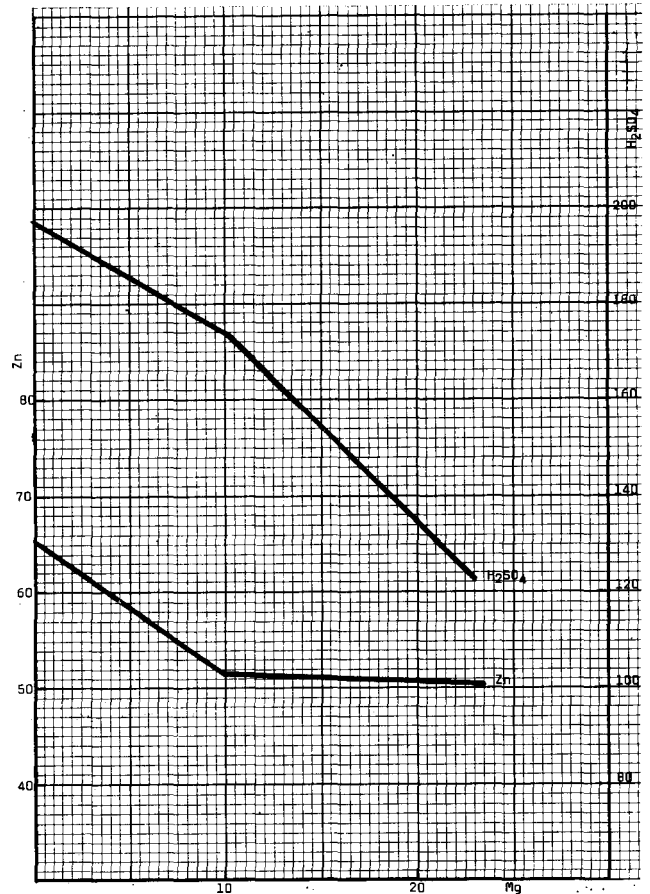


Fig. 2—Composition, in grams per litre, of the cell feed when the manganese concentration in the electrolyte is less than 5,5 g/l

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