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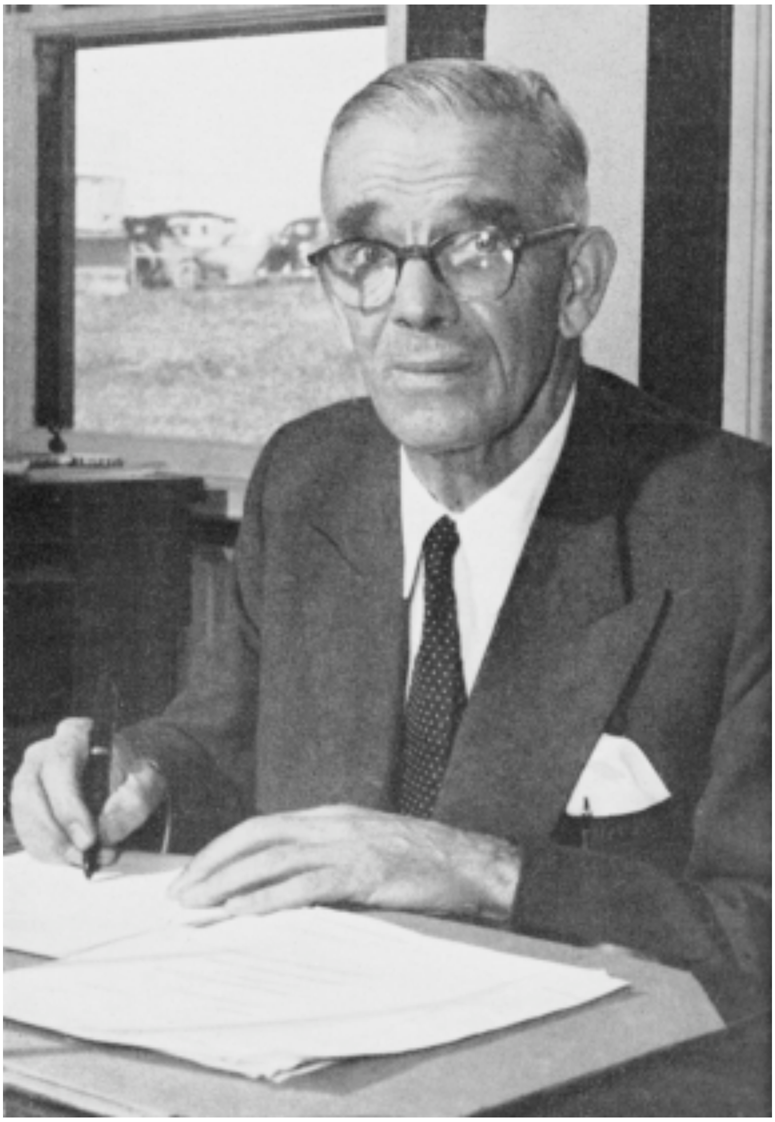
1931

THE PRODUCTION OF ZINC BY ELECTROLYSIS OF ZINC SULPHATE SOLUTIONS

HARRY HEY

The Royal Society of New South Wales



Harry Hey

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Liversidge Lecturer No. 1, 1931

HARRY HEY 1892–1960

Harry Hey was born on 20 June 1892 at Horbury, Yorkshire, England. His early education was at Dewsbury Technical College, Yorkshire (1905-1908). He then went to New Zealand where he attended the Petone (N.Z.) Technical School (1908-1910), and from 1910-1914 he attended lectures on chemistry and physics at Victoria College (University of New Zealand), Wellington. He did not sit for examinations there, but did one year of research with Professor T.H. Easterfield on the constitution of some fatty acids. In 1913-1914 he was lecturer on chemistry at Petone (N.Z.) Technical School, and for the period 1914-1915 he was chemist at the N.Z. Packing Company (Matangi, New Zealand), manufacturers of condensed milk and various other milk products. Hey then moved to Australia, initially employed as a chemist by Godfrey Hirst & Co., woollen manufacturers at Geelong near Melbourne; he had several publications and patents arising from this work (see publications list in the Appendix).

In 1917 Hey joined the Electrolytic Zinc Co. Australasia Ltd. as a research chemist at Risdon, Tasmania. He became officer-in-charge of development of autogenous roasting of zinc concentrate and the production of sulfuric acid by both the contact and chamber processes at Risdon, Cockle Creek in N.S.W., and various centres in South Australia. He became metallurgical assistant to the General Manager of the Electrolytic Zinc Co., and in 1927 was made chief metallurgist, with supervisory control of all chemical and metallurgical operations at Risdon and Rosebery, and of roasting and acid plants on the Australian mainland: in the same year he was an expert witness in the USA on a patent action on the electrolytic production of zinc. It was during this phase of his career that Hey was selected as the first Liversidge Lecturer by the Council of the Royal Society of New South Wales.

In 1935 Hey took on the added responsibility of consulting metallurgist to Gold Mines of Australia and associated companies, and he was responsible for the development of processes and designs of plants for the treatment of gold ore at Triton Gold Mines, N.L. at Reedy, Western Australia, Cox's Find, Erlistoun, W.A., Central Norseman Gold N.L., Norseman, W.A., Bendigo Mines, and Gold Mines of Kalgoorlie.

In 1934 he became involved with the general direction of work done by Dr Ian W. Wark on flotation processes at the University of Melbourne; Hey's participation in the flotation studies was acknowledged by Wark in his monograph 'Principles of Flotation'. Hey also stimulated and aided research carried out at the University of Melbourne under Professor Sir David Masson on the electrochemical characteristics of aqueous solutions of zinc sulfate.

Hey's rise through the ranks at E.Z. Industries was rapid: he became technical superintendent in 1943, he was made a director of the Company in 1944, general manager in 1945, managing director in 1947, and in 1952 he succeeded Sir Walter Massy Green as Chairman of the Company. He was also a Director of Imperial Chemical Industries Australia and New Zealand (ICIANZ), the Associated Pulp and Paper Mills, the Atlas Insurance Co. Ltd, and Australian Fertilizers Ltd. In 1953 he was Deputy President of the highly successful Fifth Empire Mining and Metallurgical Congress. He chaired the Commonwealth Government's Explosives and Chemicals Industry Advisory Committee, and he was a member of the Atomic Energy Commission's business advisory group. Harry Hey was three times president of the Australasian Institute of Mining and Metallurgy.

Due to the early leadership and expertise of Herbert W. Gepp (later Sir Herbert), and then the research skills and leadership of Hey, the metallurgical achievements of the Electrolytic Zinc Co. earned an international reputation. Hey was also well liked at the Company, and there was general sadness when he died in office in 1960, while still Chairman of the Company.

Honours and Awards

1931 Liversidge Research Lecture, Royal Society of N.S.W.

1938 Fellow Australian Chemical Institute (FACI)

1943, 1944, 1949 President, Australian Institute of Mining and Metallurgy

1951 Gold Medal of the Australasian Institute of Mining and Metallurgy for research into means of using sulfur.

1955 Life membership of the Australasian Institute of Mining and Metallurgy

1955 Kernot Memorial Medal for Engineering Achievement, University of Melbourne.

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Liversidge Research Lecture No. 1, 1931

THE PRODUCTION OF ZINC BY ELECTROLYSIS OF ZINC SULPHATE SOLUTIONS*

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With five text figures and one plate

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The public opening of the Faraday Exhibition in London less than 24 hours ago reminds us that it is but 100 years since Michael Faraday made the discovery in which lies the origin of the dynamo, and thus laid the foundation for the development of electrical machinery, which is the basic requirement for any electro-chemical industry. The first commercial "dynamo electric machine" was produced by Siemens in 1867 and from then onwards chemists, physicists, engineers and others have given a great deal of attention to applied electrochemistry, of which the electrolytic zinc industry is an important branch.

The world's production of zinc during 1930 by all processes totalled approximately 1,400,000 tons, and the present annual capacity of plants using the electrolytic process aggregates approximately 550,000 tons. Australia's share is 55,000 tons, increasing to 70,000 tons when the Risdon extensions are completed. The power required for depositing zinc in the world's electrolytic zinc plants when on full production amounts to a continuous load of 270,000 H.P., D.C.

As recently as 1914 there was no electrolytic zinc industry. Its development has been truly remarkable. Its position to-day is an outstanding example of the application of rigid chemical control to large scale operations. The electrolytic zinc plant is really a laboratory on a large scale in which thousands of gallons, instead of litres, of solution are handled in tanks and pumps instead of beakers and pipettes. The removal of some impurities is carried to a degree farther than was previously necessary for the analytical determination of these same substances; new standards of analysis were necessary and new methods have been devised.

History

Australia - especially the State of New South Wales - was particularly concerned with the early attempts to develop the electrolytic zinc process. A large quantity of zinc-bearing by-product had accumulated at Broken Hill, and it was thought to be suitable for treatment by some such process.

Prior to 1913 literally hundreds of experimenters attempted to recover zinc by hydrometallurgical processes which, in many cases, involved the electrolysis of a solution

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*First Liversidge research lecture delivered on 24th Sept., 1931, at Science House, Sydney, arranged by the Royal Society of New South Wales under the terms of the Liversidge bequest. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1931, **65**, M1-M48.

of either zinc sulphate or zinc chloride. Accounts of their experiments are distributed throughout the literature of many countries, more especially in patent records, but it was not until 1914 that the modern electrolytic zinc process or, indeed, any commercial process involving the electrolysis of zinc sulphate solutions, can be said to have been established. Small plants were operating earlier in Germany and in England, using a zinc chloride electrolyte, but these plants have been closed and the chloride process abandoned. Unless otherwise specified any further reference will be confined to the sulphate process.

It is instructive to review the outstanding early attempts to produce electrolytic zinc. In 1881 Letrange obtained patents(a) for producing zinc by electrolysing zinc sulphate solutions. His process included roasting, leaching and electrolysis. He used sheet zinc cathodes and carbon anodes, but he did not succeed in producing zinc on a commercial scale. His work is of interest, chiefly because he used insoluble anodes; cells without diaphragms and an electrolyte containing free acid. It has been claimed by Ralston(b) that Letrange practically anticipated modern practice, but as far as can be determined at this date the only feature in common with present practice is the use of sulphate solutions containing free acid.

About 1891 Sherard Cowper Cowles (the inventor of the Sherardising process) was experimenting with the electrogalvanising of iron and steel articles, using zinc sulphate solutions, and some three or four years later he erected an experimental plant in Cornwall for recovering electrolytic zinc from the Broken Hill material already mentioned.(c) He removed copper and cadmium from the impure zinc sulphate solution (obtained by roasting and leaching) with scrap zinc or zinc dust, and he sometimes found it necessary to remove manganese. The solution purified in this way contained approximately 100 grams of zinc as sulphate per litre. He electrolysed with lead anodes and aluminium cathodes and he apparently also recognised that free sulphuric acid in the electrolyte improved the character of the deposited zinc. As far as the author knows, Cowper Cowles was the first experimenter to use aluminium cathodes, and it is likely that he also recognised the need for careful purification of the solution. He did not succeed in establishing the process on a commercial basis.

Probably the most ambitious unsuccessful attempt to produce electrolytic zinc commercially was made by Ashcroft at Cockle Creek, near Newcastle, in New South Wales, in 1897, following upon experiments carried out by him in Broken Hill and in England.(d) It is said that £250,000 was spent on this venture. His original intention was to electrolise [sic] zinc chloride solutions, and, in fact, his plant was designed for and operated with such solution for most of its life, but for some weeks the electrolyte was zinc sulphate. He used diaphragm cells fitted with iron or zinc cathodes and lead and carbon anodes.

Ashcroft recognised that copper, iron, arsenic, antimony, etc., were harmful, and he also states that he had considerable trouble with manganese. However, subsequent work with Broken Hill ores has shown that Ashcroft's troubles were due mainly to cobalt, which he unknowingly precipitated when removing manganese from solution.

Early in the twentieth century, Englehart, Huth and Laszczynski, of the Siemens Halske organisation, made notable advances in the subject, particularly in respect of purification of solutions. They recognised that it was necessary to convert iron to the ferric state before it could be satisfactorily precipitated, and, in fact, patented a process involving the use of manganese dioxide for this purpose. Lime or zinc oxide was then added for precipitating the iron and with it certain other impurities, particularly arsenic and antimony, together with silicic acid. The staff of this organisation also proposed the use of moulded manganese dioxide anodes, but this type of anode has not been adopted in any commercial plant.

About 1910 the General Electric Company of America developed a sulphate process, the original basic feature of which was the maintenance of a neutral electrolyte by feeding zinc oxide directly to the cells. Under these conditions the zinc deposit was spongy. Some years later an electrolyte containing free acid was investigated and Hansen, of this organisation, collected much instructive data respecting roasting, leaching, purification and electrolysis.(e)

All this preliminary work - some of it expensive - had failed to establish the process on a commercial scale, but it had served a very definite and useful purpose by indicating some of the pitfalls and had shown that the removal of certain impurities from the solution was essential for successful electrolysis. It is perhaps unfortunate that there was a mistaken idea that the electrolytic zinc process could only be justified for the treatment of those complex ores which could not be economically treated by the older distillation process. These ores contained many interfering substances (some of which consumed acid), and others were very definitely toxic, in that their presence in the electrolyte, in many cases even in minute quantities, prevented the satisfactory deposition of zinc. Most of the ores also contained excessive silicious material which formed soluble silicates during roasting.

The successful commercial production of electrolytic zinc was established with the completion of the plants erected in 1915 at Great Falls, Montana, U.S.A., by the Anaconda Copper Company, and simultaneously at Trail, British Columbia, Canada, by the Consolidated Mining & Smelting Company. These plants were erected primarily to satisfy the urgent demand for pure zinc for use in the manufacture of high grade brass, etc., required for munitions. Their construction followed an extensive series of investigations, not only connected with the process reactions, but concerning the equally important development of the most suitable equipment, and it is to the credit of the organisations responsible that the modern equipment, and, in essentials, the process, is but little changed from the plants erected in 1915 and the practice followed there. The Tainton process, referred to later, is an exception to this generalisation.(f)

Interest in the process was rekindled in Australia in 1916, when attempts were made to treat Broken Hill concentrates at Bully Hill, California, and at Broken Hill. Preliminary work showed that electrolytic zinc could be satisfactorily produced, but only after the recognition that cobalt was present in the Broken Hill concentrates and that it was a toxic impurity. In 1917, the first small scale plant was erected at Risdon, producing a few pounds of zinc per day; this was followed by a somewhat bigger plant, and this again by another which had an ultimate output of 25 tons per day. The latter plant was used for providing data on which to design the present plant which has an output of approximately 150 tons slab zinc per day.

Since 1917, many refinements have been introduced at all the plants, but the main principles of the process remain unaltered. There have certainly been many changes in practice which have enabled the recovery of zinc to be increased and/or costs to be reduced. This is the natural result of continued extensive research, both pure and applied, and to-day electrolytic zinc containing more than 99.9% zinc can be produced as cheaply as, if not more cheaply than, retort spelter of considerably lower grade produced by the old-established method of distillation from a mixture of zinc oxide bearing material and carbon.

Outline of Present Practice

The three major objectives of the electrolytic zinc metallurgist are: -

(a) Recovery of the maximum amount of zinc as zinc sulphate in solution from a given raw material;

(b) Removal of dissolved impurities to the required degree as cheaply as possible and with the minimum loss of zinc; and

(c) The deposition of zinc of maximum purity and satisfactory physical condition from the purified solution with the minimum power consumption.

These objectives are all inter-related, and to attain them the various operations, comprising the electrolytic zinc process in toto, have necessarily to be carried out under carefully controlled conditions.

The process is a cyclic one and the sequence of steps is:-

(1) Roasting the raw zinc sulphide material under such conditions that the zinc sulphide is converted to zinc oxide and a controlled amount of zinc sulphate.

(2) Leaching, or dissolving the zinc oxide from the calcines produced in step (1), using spent electrolyte produced in step (4).

(3) Purification, or removal of those impurities which either interfere with the electrodeposition of zinc or contaminate the deposit.

(4) Electrolysis of the purified solution whereby it is depleted of portion of its zinc with the regeneration of equivalent sulphuric acid for re-use in the leaching step.

(5) Melting the cathode zinc produced in step (4) and casting the molten metal into ingots for sale, and

(6) Treatment of these residues or precipitates which contain substances having some value.

Nature of Zinc Bearing Material Treated

Most of the raw material is obtained from mixed lead-zinc ores, which are treated by the flotation process for the production of lead and zinc concentrates. The former contains the bulk of the lead sulphide and the latter consists mainly of zinc sulphide contaminated with iron and other sulphides. The iron may be present as pyrrhotite or pyrite. Sometimes the former is free; sometimes it is in solid solution in the zinc sulphide mineral.

In addition, practically every zinc concentrate contains some siliceous gangue and traces of other impurities which, whilst small in amount, have a significant effect on the subsequent treatment of the concentrates and/or products obtained therefrom.

The zinc concentrates supplied to electrolytic zinc extraction plants contain 45-60 % zinc, 4-12 % iron and some lead and silver - all as sulphides.

Impure zinc oxide produced from lead blast furnace slag is also used at two plants.

Roasting

The primary object of roasting is to convert the various sulphides to oxides. When a mixture of the sulphides of zinc and iron is heated under oxidising conditions such as apply during commercial roasting, some of the iron oxide combines with zinc oxide to produce zinc ferrite ($ZnO.Fe_2O_3$). As this substance is relatively insoluble in dilute sulphuric acid, any zinc oxide so fixed is not recovered during leaching. The amount of ferrite formed depends on the grain size of the iron oxide and zinc oxide and also upon the temperature at which the two oxides are in contact.

When the zinc mineral contains iron sulphide in solid solution the two oxides are formed in molecular contact, and under these conditions the whole of the iron oxide will combine with equivalent zinc oxide irrespective of roasting temperature. On the other hand, where the zinc sulphide and iron sulphide are in separate minerals, combination between the oxides can be minimised by controlling roasting temperature; for example, if a mixture of zinc oxide and ferric oxide in the ratio of 2 ZnO to 1 Fe_2O_3 be heated at 700°C for 4 hours, 36% of the iron oxide is converted to ferrite. At 1000°C the conversion is 87% in the same period.(g)

Practically all the iron sulphide in the Broken Hill zinc concentrates is in solid solution in the zinc mineral, and consequently temperature control during roasting is not important, excepting in-so-far as it affects the output of any given furnace. The other notable Australian zinc-bearing ore - the Rosebery-Hercules ore of Western Tasmania - contains a small amount of iron in the zinc mineral and, in addition, much free pyrite, some of which is recovered in and contaminates the zinc concentrate. In this case roasting temperatures therefore affect the amount of zinc ferrite formed.

The silica contained in zinc concentrates is important because some of it always combines with the oxides of zinc and lead during roasting, and the amount increases with increasing temperature. The resulting silicates are soluble during leaching.

The figures of Table I represent the effect of roasting temperature on the solubility of the various impurities in dilute sulphuric acid. The amount of each inipurity is relative to 100 grams of zinc.

TABLE I.

Relationship between Roasting Temperatures and Solubility of varlous impurities in Calcines produced from Broken Hill concentrates containing 49% Zinc.

Roasting Temperature			700°C	800°C	900°C
Zinc	dissolved,	Grams	100	100	100
Mn	"	"	0.90	1.10	1.58
Total Fe	"	"	0.70	0.55	0.71
Fe (ous)	"	"	None	None	None
SiO_2	"	"	1.29	2.97	3.85
Cu	"	"	0.38	0.25	0.26
Cd	"	"	0.45	0.40	0.25
Ag	"	mgs.	30	56	75
Sb	"	"	3.2	1.4	0.9
Co	"	"	12.9	12.9	13.3
C1	"	"	Trace	Trace	Trace

With increasing temperature the amounts of soluble manganese and silver increase, but less copper, cadmium and antimony dissolve.

As the result of improvement in metallurgical practice in Broken Hill, the zinc concentrates now produced there contain 52.5 % zinc, less silica and less copper than formerly.

Roasting is usually carried out in multiple hearth furnaces, and at most plants it is done in one operation. In Australia roasting is done in two stages. The first stage is carried out on the mainland at locations adjacent to superphosphate plants. The sulphur is reduced from 30% to 6%, of which 1.5 to 2% is sulphur remaining as sulphates of lead, calcium and zinc. Sulphuric acid is produced from the sulphur dioxide contained in the roaster gases. Both the chamber and contact methods of making sulphuric acid are used.

The normal annual output of the Australian acid plants utilising zinc concentrate gases is equivalent to 70,000 tons of 100% acid when on full production. From this 215,000 tons of superphosphate are manufactured.

Considerable research was necessary before the manufacture of contact acid from zinc concentrate roaster gas became an established process, because the roaster gases contain interfering amounts of arsenic and chlorine compounds in addition to lead sulphate and calcine dust. Some of these impurities settle in dust chambers, but final purification is effected by saturating the gases with water and passing them through an electrostatic precipitator. The removal of lead sulphate, arsenic and chlorine compounds during this treatment is 100%, 99% and 92% of the respective amounts of these impurities entering the electrostatic precipitator.

The gases are subsequently washed to remove the remaining chlorine compounds, are dried and are passed through a platinum contact mass. This mass has now been in use for over four years without regeneration.

The roasted concentrates or pre-roast calcines produced at the various mainland roasting plants are forwarded to Risdon, and are subjected to the second or re-roasting stage, in which sulphide sulphur is reduced from 4.5 to 0.5%, and the sulphate sulphur increased to whatever is necessary to replenish any mechanical or chemical losses of sulphuric acid or zinc sulphate during leaching. This at Risdon is equivalent to 3% sulphate sulphur in the calcines leached.

Another important function of the re-roasting operation is the elimination of chlorides which contaminate the partly roasted calcines. These are introduced at the various roasting plants in the water used for wetting these calcines to minimise dusting during shipment to Risdon.

Chrome steel has replaced the cast iron and cast steel previously used for roasting furnace rabble arms. The Australian furnaces used in the first stage have been fitted since 1920 with rabbles of alloy steel containing 27% chromium. This steel will withstand a temperature of 900˚C continuously for 12 months or more without serious oxidation or failure from other causes. Other alloys containing chromium, nickel and tungsten or silicon are giving encouraging results at Risdon.

Leaching

The spent electrolyte returned to the leaching plant from the electrolytic cells is of varying sulphuric acid concentration. The concentration is fairly regular from day to day at any one plant. Only portion of the zinc is removed during electrolysis; therefore all these solutions contain zinc sulphate.

Three distinct methods of leaching are practised at various plants. These are:

(1) Batch leaching, where the roasted zinc concentrate, usually referred to as calcines, is added to a given volume of leach solution. It is usual to add the calcines in more than one stage and to continue this addition until the acidity of the solution has been reduced to a predetermined figure. The solution obtained is subsequently treated for the removal of iron, arsenic, antimony and silver, which is referred to later.

(2) Two-stage continuous counter-current leaching, the equipment for which consists of two series of leaching vessels, four or more in each series, together with settling or thickening equipment. Partially leached calcines and spent electrolyte are fed continuously into the first vessel of one or "acid" series. During its passage through the series the zinc oxide is completely dissolved. The mixture overflows the last vessel of the series and is settled and filtered. The residues are discarded. The solution which still contains acid is mixed with new calcines and fed through the second or "neutral" series of leaching vessels in which the acid is completely neutralised, but only portion of the zinc oxide is dissolved from the new calcines. There thus remains free zinc oxide, some of which reacts with and precipitates the iron, arsenic, antimony, silica and some of the copper which had dissolved during the other leaching stage. The mixture is settled and the solution overflowing the settlers or thickeners is sent forward to the purification section. The settled solids are mixed with spent electrolyte and the mixture is sent on to the first leaching stage.

At some plants the spent electrolyte is divided over both stages, but in all cases the solution overflowing the "acid" leaching series contains free acid and the overflow from the "neutral" series is neutral or basic.

(3) For this method of leaching the calcine is separated into two products - a magnetic portion, which contains the bulk of the zinc ferrite, and the non-magnetic portion, which is said to contain the free zinc oxide and any gangue material. As ferrite is soluble in sulphuric acid of moderate strength at relatively high temperatures, the magnetic portion is first leached with the spent electrolyte, and after most of the ferrite is dissolved, the non-magnetic portion is added to the partially neutralised solution which, incidentally, contains ferric sulphate equivalent to the zinc ferrite dissolved. The iron is precipitated as basic sulphate along with silica, and these remain with the insoluble portion of the residues after settlement and filtration.

This method, (3), which can be operated either continuously or intermittently, is usually only applied where high acid spent electrolyte is available. Filtration which is difficult enough with a saturated solution of zinc sulphate is made more difficult by the presence of much basic sulphate of iron. The method was developed in conjunction with the Tainton process which operates under high acid electrolysis conditions.

The batch method (1) was the procedure originally followed at the Trail and Anaconda, plants, and, after leaching, a small amount of lime or limestone was added to the mixture of residue and solution to precipitate iron, silica, arsenic and antimony. Since 1920, however, the second method has been applied at these plants and it has become the general practice at most of the more recent plants.

The advantages of the second method are:-

(a) The solution, immediately prior to leaving the leaching circuit, is in contact with zinc oxide, thus ensuring nearly complete precipitation of iron, arsenic and antimony, and

(b) The residues are discarded from an acid pulp; the maximum amount of zinc oxide is thus recovered.

Its disadvantages are:-

(c) The residues are thickened twice, and

(d) The discarded residue contains the precipitated silicic acid and basic iron salts which make filtration difficult.

A modification of the batch leaching as described under (1) is used at Risdon and leaching is continued until the acidity is reduced to two grams sulphuric acid per litre. When separated from the solution, the residues, which are practically free from precipitated iron or silica, are in a satisfactory physical condition for subsequent treatment for recovery of lead and silver.

The residues from the leaching stage contain zinc ferrite and zinc sulphide which was not oxidised during the roasting of the zinc concentrates, and some undissolved zinc oxide, together with insoluble gangue material. The zinc sulphide and zinc oxide are contained in the coarser particles, and at Risdon this coarse material is separated from the finer residues and is subjected to further treatment which comprises, firstly, fine grinding and leaching with spent electrolyte, and, secondly, treatment in flotation machines for the recovery of the zinc sulphide as a concentrate which is roasted and leached. The residues from the flotation machine join the fine residues from the major leaching operation and the mixture is settled in thickeners. The settled solids are then filtered.

The filtered residue contains most of the lead and silver originally in the concentrates and is shipped to Port Pirie for treatment.

Purification of the Solution

Removal of Iron, Silica, Arsenic and Antimony. The zinc sulphate solution obtained by applying the two-stage continuous counter-current leaching method (2) is practically free from iron, arsenic and antimony, and the silica, which dissolved has been precipitated. These impurities have been discarded in the leach residues. The solution still contains copper, cadmium and manganese, and in some cases cobalt. On the other hand, the solution obtained at Risdon by the single stage batch process contains all the impurities dissolved during leaching in addition to 2 grams free sulphuric acid per litre. Neutralisation of the acid and precipitation of the iron, silica, antimony and arsenic is effected by treatment with finely ground limestone and the precipitate - which is composed mainly of gypsum, basic ferric sulphate and hydrated silica - is coagulated by prolonged agitation. For rapid filtration it is essential that there be sufficient gypsum crystals in the precipitate to provide a support for the gelatinous iron and silica precipitates. The presence of ferric iron is necessary for the removal of arsenic and antimony.

The modus operandi at Risdon is the result of considerable investigation and, so far as the author knows, it is the only plant where this procedure is followed. The precipitate contains a small amount of coagulated silver chloride, which is removed by washing the filtered precipitate with sodium thiosulphate. The wash water goes forward with the main solution.

With any method of leaching it is necessary to convert any dissolved ferrous sulphate to the ferric condition. Agitation with air during leaching usually does this but it is necessary to add manganese dioxide when much ferrous iron is present.

The recovery of zinc from the calcines is determined largely by the thoroughness with which the residues and, at Risdon, the limestone precipitate, are washed. Because of the cyclic nature of the process, the permissible amount of wash water is definitely limited to the amount of the solution discarded with the residues and the water lost by evaporation, due to circulation of the solution. Water was originally added to the calcines at Risdon to minimise dusting during the handling of this material between the reroasting furnaces and the leaching section. In recent years, however, zinc sulphate circuit solution has been substituted, and thus no new water goes into the circuit at any point other than as wash water through the residues or limestone and other precipitates.

The circuit solution is cooled at Risdon by running it down towers under conditions whereby cooling of the solution is brought about by evaporation of water. Water equivalent to that evaporated is available for use as wash water.

Removal of Copper and Cadmium. The next stage in the preparation of the solution is the removal of copper and cadmium. Hydrogen sulphide and various sulphides have from time to time been proposed for this purpose, but zinc dust is in universal use. Nearly complete removal of copper can be effected by agitating the solution with equivalent zinc dust, but the precipitation of cadmium requires excess over that theoretically necessary. Most of the antimony and arsenic which has escaped precipitation during the preceding step is removed with the copper and cadmium.

In the original Anaconda plant, the mixture of zinc dust and solution was agitated by using compressed air, and this practice was followed until recent years. The trend at Risdon has been to take extreme precautions against introducing air into the purification tanks; in fact, the purification section was remodelled some time ago in order to prevent ingress of air through the glands of the pumps handling the mixture of precipitated copper and cadmium and solution between the tanks and the filter presses.

The solutions at Risdon prior to zinc dust purification contain approximately 250 mgs. of cadmium and 200 mgs. of copper per litre, but the amounts vary over a fairly wide range from day to day. In order therefore to confine the consumption of zinc dust within the lowest possible limit, it is an advantage to know the actual concentration of copper and cadmium in the solution going to the purification tanks. Within the last year a method has been developed at Risdon for the quick electrolytic estimation of copper and cadmium, using a mercury cathode. Analyses obtained in this way are used as the basis for calculating the amount of zinc dust to be added.

At the present time the precipitation of the two impurities is done in batches. An ingenious continuous process has been developed, but for economic reasons it has not been adopted.

At most of the electrolytic zinc plants, the solution is suitable for electrolysis after treatment with zinc dust. It is true that many of the zinc concentrates treated in these plants contain some cobalt, but usually in insufficient amounts to cause trouble during electrolysis. It accumulates in the circuit solutions until the concentration is such that the amount of solution discarded from the plant in the various residues contains as much cobalt as is introduced each cycle. For example, if one-tenth of a milligram of cobalt per litre were introduced during each leaching cycle, and if 1% of the circuit solution were discarded as indicated, the amount of cobalt discarded would be equivalent to the amount introduced when the concentration in the circuit solution reached approximately 10 mgs. per litre.

Removal of Cobalt.- At Risdon appreciable amounts of cobalt dissolve from the Broken Hill concentrates, and the amount dissolved in each cycle must be removed. Because of this the Risdon practice from this stage onwards differs from most of the other plants. Zinc dust will precipitate cobalt frorn a water solution of its sulphate, but has very little effect in the presence of a large amount of zinc sulphate; consequently, the removal of cobalt during zinc dust treatment is negligible.

Many reagents oxidise cobalt if manganese is also present, and in this condition it is easily precipitated. The permanganates, lead peroxide and calcium plumbate, have been used for this purpose. With solutions containing much manganese, as is the case at Risdon, the cost of these reagents is excessive because it is necessary to oxidise all the manganese before the cobalt can be precipitated. Methods based on the use of the reagents mentioned have been investigated at Risdon, but only two methods which are of a different type have been used on a plant scale. These are:-

(1) The so-called "arsenic purification" method, in which cobalt is co-precipitated with arsenic and copper by the addition of zinc dust. In practice, sodium arsenite and copper sulphate are added to the solution, which is heated and then treated with zinc dust. The cobalt, arsenic and copper are precipitated together. It is an expensive method, because zinc dust consumption is high and it is necessary to heat the solution.

(2) The precipitation of cobalt by nitroso beta-naphthol from the cold copper and cadmium-free solution. This was suggested in 1917, but has only been applied regularly on a commercial basis during recent years. In practice the calculated amount of sodium beta-naphtholate is added to the solution, then sufficient sodium nitrite and finally sulphuric acid to form the nitroso salt in the solution. The cobalt is precipitated as the characteristic red cobalt-nitroso beta-naphtholate, and the mixture of the precipitate and solution is neutralised with sodium carbonate. About 9.5 lbs. [pounds weight] of beta-naphthol and equivalent sodium nitrite are required for precipitating 1 lb. [pound weight] of cobalt.

The latter method has entirely superseded the "arsenic-purification" process, and is one of the major developments which has rendered possible the change in electrolytic procedure which is referred to later.

The cobalt in the solution feeding the electrolytic cells at Risdon is maintained at about 10 mgs./litre. The spent electrolyte contains a similar amount. Approximately 10 mgs. are introduced into the solution, each leaching cycle, and thus the solution after leaching contains 20 mgs./litre. It is therefore necessary to remove cobalt from 50% of the solution each cycle to maintain the required concentration in the feed to the cells. About 60 lbs. [pounds weight] of cobalt are removed from the solution daily. Until two years ago the Risdon electrolyte contained 70-80 mgs. cobalt per litre, and the removal of cobalt from a much smaller volume of the solution was sufficient to maintain the cobalt concentration constant.

Removal of Chlorides.- The other purification stage concerns the removal of chlorides. The electrolyte is maintained at about 75 mgs. chlorine as chlorides per litre, and it is necessary to purify sufficient solution to take care of any chlorides introduced during leaching. The precipitation is effected by silver sulphate; the silver chloride produced is separated by filtration and is reconverted to silver sulphate by treatment with zinc dust and heating with sulphuric acid, when hydrochloric acid is volatilised to waste.

Those portions of the solution treated for removal of cobalt and/or chlorine join the main copper and cadmium-free solution. The combined solution after addition of glue is in suitable condition for electrolysis.

At Risdon the daily volumes of solution treated in leaching and the various purification stages are:-

During leaching	600,000 galls. - 16,000 gallon batches
For removal of iron, arsenic, etc	600,000 galls. - continuously

For removal of copper and cadmium	600,000 galls. - 14,000 gallon batches
For removal of cobalt	300,000 galls. - 14,000 gallon batches

Portion of the solution is treated intermittently as required for removal of chlorine.

In some stages the circuit solution is very corrosive, as it contains ferric and copper sulphate and free acid. There have been many corrosion problems in connection with pumps, filters, launders and tanks. It has been found that celery top pine grown in Tasmania resists the action of acid zinc sulphate solution better than does any other timber yet experimented with at Risdon. Acid-resisting bronze and Staybrite are used for some metal parts, but wherever possible the flow sheet of the plant is arranged so that corrosive solution flows by gravity through lead pipes.

Over 100 tons of leach residues and 30 tons of limestone precipitate are filtered from the solution each day. Filtration problems arise and they are investigated, with the result that the filtration technique has gradually improved over a period of years.

The partial analysis of the solution after purification is given in Table II.

TABLE II

Analysis of Risdon Cell Feed Solution.

Zinc	114.9 g/l	Total Nitrogen	245 mgs/l
Manganese	13.1	Ammonia Nitrogen	215 mgs/l
Magnesium	1.75		
Sodium	9.16	Nitrite	9
Potassium	1.71	Calcium	440
Sulphate (SO_4)	222.22	Phosphate (PO_4)	2.1
Cobalt..........	10.0 mgs/l	Aluminium	0.5
Copper..........	0.6	Lead	0.025
Cadmium	6.4	Bismuth	Nil
Silica	80.0	Nickel	Nil
Chlorine	75.0	Selenium	Nil
Iron	1.55	Tellurium	Nil
Arsenic	< 0.1	Tin	Nil
Antimony	0.11	Glue	27 mgs/1

The Specific Gravity is 1.334.

The solution is analysed daily for zinc, cobalt, antimony, copper, cadmium and chlorides. Rigid control during purification and accurate analysis enable the concentration of impurities in the cell feed solution to be maintained within very narrow limits.

Electrodeposition

All zinc sulphate solutions are electrolysed under the general conditions of the two following processes:

(1) The so-called low acid, low current density process where the feed solution contains 100 to 150 grams of zinc per litre. The sulphuric acid concentration during electrolysis is 90 to 140 grams per litre, and the current density varies between 25 and 45 amperes per square foot at various plants. The zinc and acid concentration and current density are maintained at fairly constant figures at any one plant.

(2) The Tainton high acid, high current density process operating with feed solution containing 215 grms./litre zinc. The acidity of electrolyte is maintained at 280 grms./litre sulphuric acid, and the current density is 100 amperes per square foot.

The end products of electrolysis are zinc, sulphuric acid equivalent to the zinc, manganese dioxide, oxygen and some hydrogen. Portion of the hydrogen is produced by the direct electrolysis of water, but some results from the re-solution of zinc already deposited.

The so-called low acid, low current density process is applied at Anaconda, Trail, Risdon and other plants, and in fact, about 95% of the world's output of electrolytic zinc is produced by this process. Certain advantages have been claimed for the Tainton high acid process, principally in connection with the capital cost of plant because of the smaller volume of solution to be treated for a given output of zinc, and because of the heavier deposit of zinc per unit of cathode area. Another claim is that the high current density counteracts the effect of impurities in the electrolyte. Actually, there is little, if any, saving in capital costs after providing the more elaborate plant necessary to treat a hot, practically saturated, solution of zinc sulphate and to withstand the more corrosive high acid solution. Furthermore, electrolysis is conducted at a very high acidity in order to keep power consumption within reasonable limits, and thus most of the benefit expected from using a high current density is not realised in practice.

In the plants using the low acid, low current density process the cells are rectangular boxes constructed either of timber, lead lined, or of concrete, lined with a mixture of sulphur and sand. They are in series, usually six in number, and are so arranged that the spent electrolyte overflows the first cell of the series, into the second and so on through the whole series.

The cathodes at all plants are aluminium sheets, 1/8 in. to 3/16 in. thick, from 2ft. to 3ft. long by 2ft. wide. The sheet aluminium is riveted to a copper head-bar which rests on the busbar. The anodes are cast lead, 3/16 in. or more thick, and are usually somewhat smaller than the cathode in area. Each anode is cast around a copper head-bar, which rests on the appropriate busbar. The anodes quickly become coated with lead peroxide or manganese dioxide or a mixture of the two, and these oxides form the actual anode surface.

The number of cathodes in each cell varies at different plants. They are connected in parallel to the cathode busbar, and the anodes are hung between cathodes and are also connected in parallel to their busbar. The space between the surfaces of the cathode and anode varies from 1.5 in. to 2.25 in. at different plants.

The neutral purified solution is usually fed in parallel and in equal amounts to all the cells in one series, or else to all cells excepting the last in the series. Thus the acidity in each of the cells to which feed solution is added is identical.

There are 504 cells at Risdon arranged in three large units of 144 cells each and 1 small unit. Each cell contains 33 cathodes and 34 anodes. The submerged area of both sides of each cathode is 13.0 sq. ft. and the corresponding area of the anode is 11.15 sq. ft. There are approximately 16,000 cathodes in constant use with an aggregate area of more than 200,000 sq. ft.

The electrical circuit in each 144 cell unit is approximately 12,000 amperes at 520 volts, which is equivalent to 3.61 volts per cell.

Each cell is provided with cooling coils, through which cooled water is circulated in amount sufficient to maintain the temperature of the electrolyte within the prescribed limits.

Diaphragms are not used in any modern zinc cell.

The objective during electrolysis is the maximum economic yield of zinc from the available power. It is possible by costly purification and extra cell-room supervision coupled with the removal of the deposited zinc at more frequent intervals to appreciably increase the yield per unit of power beyond that attained in practice, but the electrolytic zinc industry is like every other industry in that any increase in technical efficiency must always be compared with the cost of obtaining it.

In the literature concerning zinc electrolysis, frequent reference is made to "Current Efficiency," "Cell Voltage"or "E.M.F" and "Yield of Zinc per Unit Power." A definition of each of these terms follows:-

Curent or Ampere Efficiency is the yield of cathode zinc expressed as a percentage of that theoretically possible from the current employed in the cell. The theoretical yield is 1.219 grms. of zinc per ampere hour.

The Cell Voltage or E.M.F. is the drop in potential across the cell between the terminals of the anode and the cathode, and is the sum of the anode potential, cathode potential and the volt drop due to the resistance of the electrolyte. The anode potential may be defined as the difference in potential between the anode and the solution immediately in contact with the anode. The cathode potential may be similarly defined as the difference in potential between the cathode and the solution in contact therewith. It is obvious that with a given current efficiency, the energy consumption in the cell is directly proportional to the cell voltage.

The Yield of Zinc per H.P. Day or Kw. Hour, D.C. is a function of the current efficiency and cell voltage.

The current efficiency is used as a measure of the electrolytic efficiency from day to day with an electrolyte of a given composition and system of electrolysis, and ranges between 90% and 93% at various plants. It varies with minor fluctuations in the purity of the solution, and generally it can be stated that it is a measure of the efficiency of the purification stage of the process and also of the care with which electrolysis is conducted.

Cell voltage, on the other hand, which should be nearly constant from day to day in any given plant, varies between different plants.

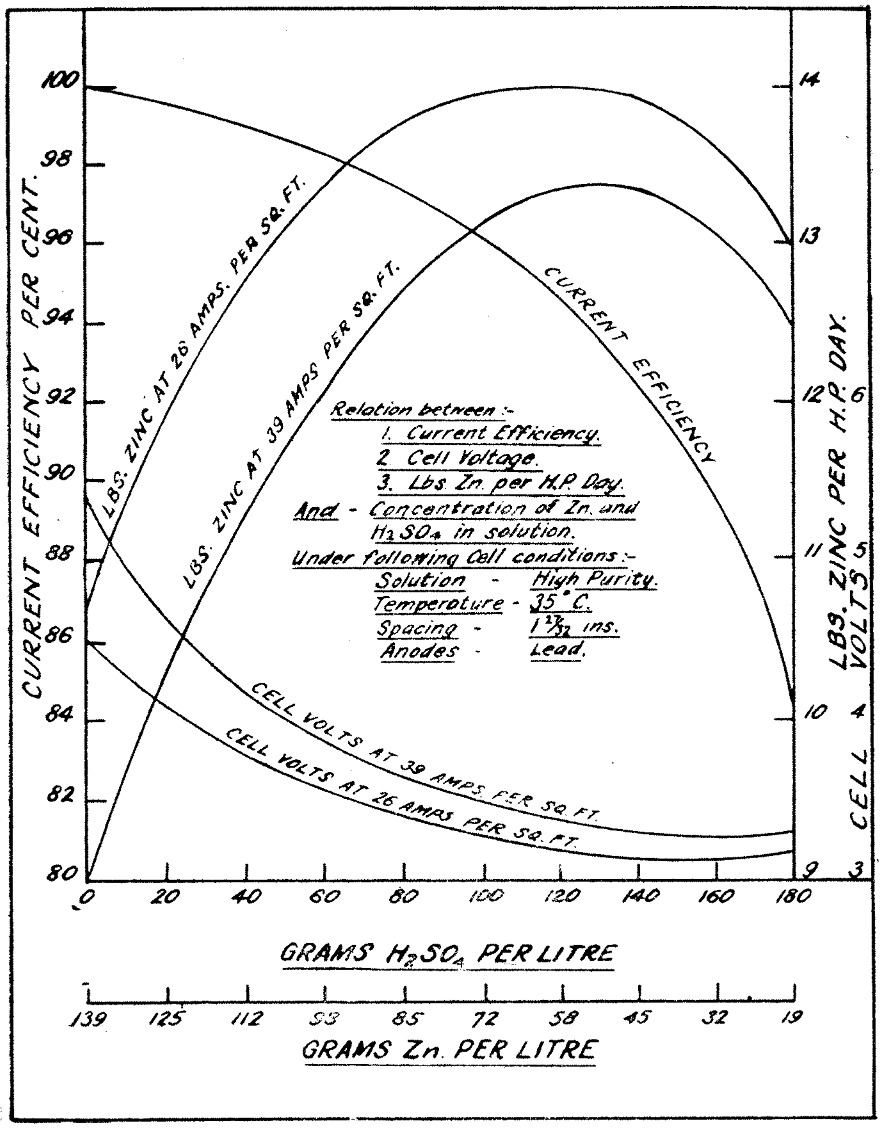


FIG. 1

The inter-relation between current efficiency, cell voltage and yield of zinc at varying acidity is expressed in Figure 1, in which is correlated the data obtained from the laboratory electrolysis of a highly purified solution originally containing 139 grams of zinc per litre. The solution used was the purest it has been possible to prepare at Risdon from the purest available materials. It was electrolysed at the temperature and electrode spacing mentioned. It is not directly comparable with the figures obtained on a Works scale, but any plant solution can be examined in much the same way as the pure solution referred to in the curves, if due allowance is made for deposition time. With pure solutions the time effect is not nearly so marked as when impurities are present.

The variables which affect current efficiency or cell voltage or both, and which therefore must be considered in determining the optimum conditions for the electrolysis, of any given solution are:-

(1) *Current Density.* This has little effect on current efficiency unless toxic impurities are present, but the cell voltage increases with increasing current density. It is obvious that whilst a decrease in cell voltage is desirable, a decrease in current efficiency is not.

(2) *Acidity.* An increase in acidity generally reduces cell voltage, but adversely affects current efficiency. The optimum acidity varies according to the amount and nature of the impurities in the solution.

(3) *Zinc Concentration.* This is usually increased when operating with higher acid because C.E. increases, with an increase in the $ZnSO_4/H_2SO_4$ ratio.

(4) *Anode Material.* Although lead is used as the original anode, the actual anode surface is usually a mixture of the peroxides of lead and manganese. The presence of certain other oxides derived from impurities in the electrolyte sometimes affects the anode potential and therefore the overall cell voltage.

(5) *Temperature.* Cell voltage and current efficiency both decrease with increasing temperatures with most plant solutions.

(6) *Length of Deposition Period.* Overall current efficiency decreases rapidly with time once cathode corrosion has started.

(7) *Spacing between Electrodes.* The smaller the gap the lower the cell voltage. This benefit is to some extent offset by the greater danger of shorting and consequent reduction in current efficiency.

(8) *Addition Agents.* Substances, such as glue, silicic acid, various gums, etc., are usually added to counteract the effect of impurities.

(9) *Impurities in the Electrolyte,* either dissolved or suspended.

The conditions under which electrolysis is carried out are governed largely by the nature and amount of impurities present in the solution after standard purification; the effect on labour costs, and on the life of the lead and aluminium electrodes.

The more important data respecting the electrolytic practice at Anaconda, Trail and Risdon are:-

	Anaconda	Trail	Risdon	
			Present	2 yrs. ago
Zinc concentration of feed solution gm/l	110	150	115	113
Acid in Cell Discharge gm/1 H_2SO_4	105	135	90	65
Current Density amp/sq.ft. Cathode	30	30-45	27.5	28
Temperature of electrolyte °C	35-45	30-40	34-37	34-37
Deposition period, hours	24	24	72	72

The change from 65 to 90 grams acid at Risdon has appreciably increased power efficiency and was made possible by the substitution of the "beta-naphthol" method for the "arsenic method" for removing cobalt. It is now economically possible to operate with an electrolyte containing 10 mgs. instead of 70 mgs. cobalt. Before making the change, 2 years intensive research on electrolysis was necessary and some hundreds of tests were made.

The most notable difference between practice at the three plants mentioned is that of the deposition period, which is three times as long at Risdon as at the other plants. Despite this, the Risdon current efficiency is between 91-92%. For some months, when cathodes were stripped every 48 hours, the current efficiency was approximately 1% higher, and daily stripping gives a still higher figure. The advantages of a 72 hour over 24 hour deposition period are, firstly, low labour charge per unit weight of zinc produced because the cathodes are stripped less often, and, secondly, the cathode zinc is three times as thick and thus gives a higher yield during melting. The penalties are that the yield of zinc per unit power is somewhat lower, and greater control is necessary in respect of condition of the solution. The balance between the advantages and penalties is dependent largely on the selling price of zinc and on local conditions.

With 24 hour deposition, the Risdon cell acidity could, if desired, be increased to the Anaconda figure and, with increased zinc concentration as well, to that of Trail.

Effect of Impurities on Electrolysis

All commercial zinc sulphate electrolytes contain impurities, some of which are harmless, some are deposited with the zinc, and others, even when present in small amounts, have a profound effect on electrolysis. The latter are usually referred to as toxic impurities, which include amongst others antimony, cobalt, arsenic, nickel, copper and germanium.

Some impurities which have no deleterious effect when present alone in small amounts sometimes accentuate the toxic effect of others. On the other hand, there is very definite evidence that one, at least, which is generally recognised as toxic has a beneficial effect when used in homeopathic doses under certain conditions. The fact that the joint behaviour of two impurities frequently differs greatly from that expected from their individual effect, undoubtedly explains why there is so much difference of opinion respecting this general question. The effects of the more important impurities have been studied, some in great detail, but in a lecture of this type, generalizations only can be made, because variations in acidity, etc., have an important bearing on results, and to properly survey the effect of even one impurity would entail a study of a large amount of elaborate data.

Manganese. Of the heavy metals, manganese is by far the most common impurity in the electrolyte; indeed, it is doubtful whether any electrolyte obtained from flotation zinc concentrates is entirely free from it. It accumulates in the circuit until it reaches the concentration at which the rate of deposition as manganese dioxide at the anode balances the amount of manganese sulphate introduced during leaching. The rate of deposition as the dioxide varies with the acidity of the electrolyte, the condition of the anode surface, the nature of other impurities present and the addition agents used. Under present Risdon conditions the equilibrium manganese concentration is approximately 13 grams per litre.

Manganese has little effect on current efficiency under normal conditions, but it does reduce the conductivity of the electrolyte and therefore increases cell voltage. The removal of manganese dioxide which precipitates at the anodes and collects in the lower part of the cell, entails some labour charge. Unfortunately this product always contains lead peroxide and lead sulphate, and thus has little commercial value.

Sodium, Potassium and Manganese Sulphates. These sulphates are all present in the electrolyte and usually have little effect, excepting again on the conductivity of the solution. Some zinc concentrates contain so much magnesium that it is necessary to discard spent electrolyte to maintain a reasonable magnesium concentration in the circuit.

Cadmium. Any cadmium present in the electrolyte is deposited with the zinc and reduces its grade. Apart from this, it has little effect.

Lead. Lead is present in all cathode zinc and most of it originates from the anode. The condition of the anode surface largely determines the amount deposited with the zinc, and it may be reduced by using a diaphragm between the anode and cathode, which prevents migration of lead. This, however, is not practicable.

Toxic Impurities and Addition Agents. Before discussing the effect of toxic impurities, it is necessary to comment on the use of addition agents which are used during electrolysis to counteract or control the effect of such impurities. Various substances have been suggested, including a number of gums and silicic acid, but glue is the universal reagent, particularly for electrolytes containing cobalt, and its use gives most remarkable results. Most operators use some glue, but because of the relatively large amount of cobalt in Broken Hill concentrates the electrolytic procedure at Risdon has been moulded around its use, and it is probably the most important factor contributing to the successful electrolytic treatment of these concentrates.

The mechanism of the action of glue is as yet somewhat of a mystery. Its effects, however, are most striking. Cathode zinc contains nitrogen, whether as glue or one of the decomposition products is not known. It has been suggested that glue migrates to the cathode and forms a film through which zinc ions can pass, but which resists, for example, cobalt ions. The alternative suggestion is that it forms a complex with cobalt and thus interferes with its deposition. Whilst little is known of the way glue functions, we are grateful for its effect.

The most prevalent toxic impurities present in zinc sulphate electrolytes are cobalt and antimony, but there are usually also traces of copper and arsenic and sometimes nickel.

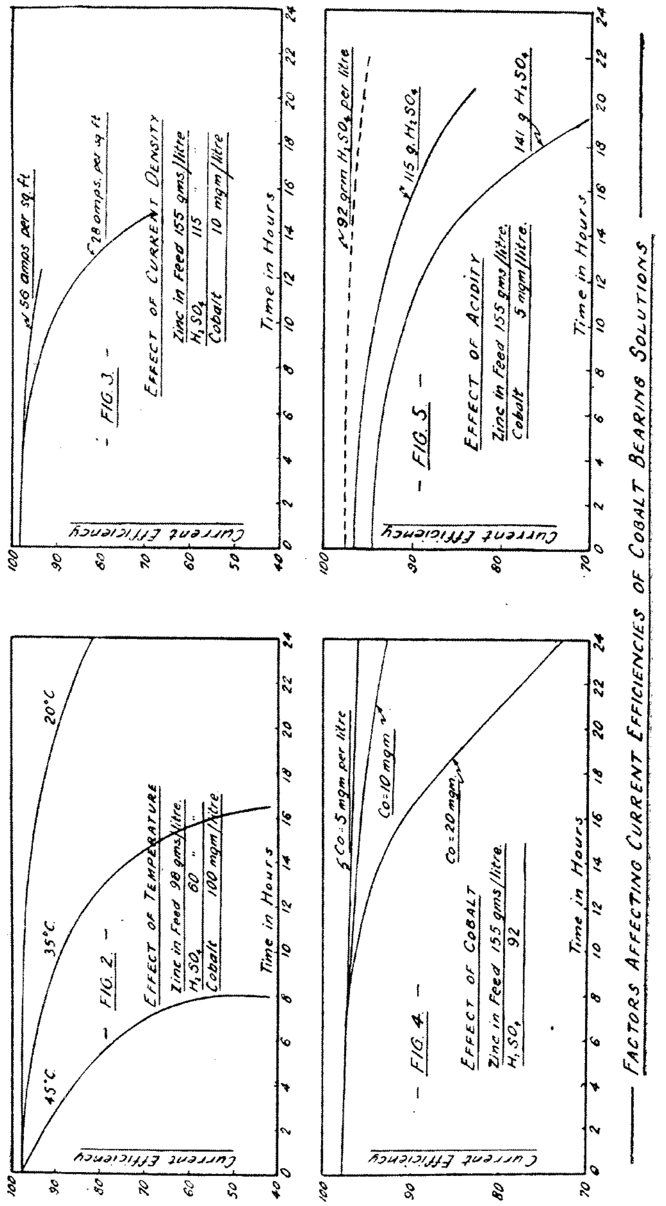
Various investigators have attempted to determine the effect of both cobalt and antimony, but it is difficult to obtain agreement between the results of the different observers, for the reason already stated that traces of some impurities have a profound effect on the behaviour of others.

The toxic effect of most impurities which reduce current efficiency, is accentuated by increase in time of deposition, concentration of the impurity, temperature of electrolyte, acidity of electrolyte and also by decrease in current density.

Cobalt. The toxicity of cobalt was first recognised during the experimental treatment of Broken Hill concentrates in 1916, and about that time it was discovered that its ill effect could be controlled by addition of glue. The early discovery of the effect of glue enabled the Australian industry to be established on a commercial footing, but despite this, the removal of cobalt or its control during electrolysis has continuously occupied the attention of the Risdon technical staff.

Laboratory studies have been made of zinc sulphate solutions containing cobalt as the only impurity, and of the Risdon plant solutions. Figures 2 to 5 show the effect of temperature, acidity and current density when electrolysing solution (otherwise highly purified) to which various amounts of cobalt have been added. The concentration of zinc, acid and cobalt are stated on each graph. They are not identical in each case, and the ones used were chosen to emphasize the effect of the variable being investigated. Cobalt was the only impurity in the solution other than traces of silicic acid.

Tests with high cobalt Risdon plant circuit showed that a solution containing as much as 70 mgs. of cobalt per litre, can be electrolysed at 20 grams acid per litre, and 30 amperes / sq. foot to give a current efficiency of 96% during 48 hours deposition without glue. The same solution electrolysed at 55 grams per litre, and with the other conditions unchanged, gave extremely poor cathodes after only 19 hours deposition. No attempt was made to determine current efficiency, as zinc was dissolving from the cathode after 12 hours only, and from then onward current efficiency was nil or thereabout. A similar test was made, simultaneously, using glue as an addition agent, and a most excellent deposit was obtained. The solution containing glue could have been electrolysed for 72 hours with good current efficiencies. These two cathodes (a) without glue, and (b) with glue (conditions otherwise similar), obtained after 19 hours deposition are shown in Figure 6, Plate I. The photograph shows the zinc deposits on the aluminium cathodes.



FACTORS AFFECTING CURRENT EFFICIENCIES OF COBALT BEARING SOLUTIONS

Cobalt has a beneficial effect on the anode potential, and therefore on the cell voltage. With a current density of 30 amps. the anode potential at a lead anode is lowered by 0.15 volts when the electrolyte contains 100 mgs. of cobalt per litre. Assuming an overall cell voltage of 3.65, the reduction is equivalent to 4%, which has a marked beneficial effect on power consumption. Furthermore, the presence of cobalt in an electrolyte restrains the migration of lead from the anode to the cathode, and therefore, improves the grade of the zinc deposit.

A considerable amount of data has been accumulated in relation to the effect of cobalt. It is, however, a subject which is intensely interesting and will well repay further study.

For some years the Risdon plant operated on a solution containing 70 mgs. or more of cobalt per litre, and electrolysis was conducted on a 72 hour deposition period with a spent electrolyte containing 65 grams per litre acid, and using, 5 to 3 lbs. [pounds weight] of glue per ton of cathode zinc deposited. Two years ago the procedure was modified, and the electrolyte now contains only 10 mgs. of cobalt per litre and electrolysis is conducted at 90 grams acid per litre using approximately 1 lb. [pound weight] of glue per ton of zinc deposited. This change, coupled with a reduction in electrode spacing, has enabled the Risdon zinc output to be increased by nearly 10% and, in addition, the structure of the cathode zinc has improved. It is emphasized, however, that the optimum amount of glue addition is dependent on the composition of the electrolyte, and it by no means follows that the conditions found best at Risdon will be applicable to every other solution.

Nickel. Some zinc concentrates contain nickel, which dissolves during the leaching of the calcine. It is toxic even in the absence of cobalt, but more so if cobalt be present. Up to 25 mgs/litre of nickel can be tolerated with little effect on current efficiency, provided cobalt and antimony are low and glue is used. With a solution containing 70 mgs. of cobalt, which, without nickel but with glue yields excellent current efficiencies, 5 mgs. of nickel will cause a drop in efficiency. The amount of nickel in Broken Hill concentrates is insignificant.

Antimony. This impurity shares with cobalt the responsibility for the failure of the early efforts to establish the electrolytic zinc process on a commercial basis, and even since 1914 it has been subjected to considerable verbal and literary abuse, some of which it undoubtedly deserves. Under certain conditions, however, it has beneficial properties, and for some time antimony was deliberately used at Risdon as an addition agent to maintain the amount of antimony in the electrolyte between 0.2 and 0.3 mgs. per litre.

Zinc deposited from electrolyte containing antimony is rough in structure, and the extent of roughness increases with increasing antimony content. This roughness is particularly in evidence with cobalt-bearing solutions using glue as an addition agent. Figure 7 illustrates the effect of antimony on the structure of cathode zinc. The bulk solution used when producing each of these cathodes was high cobalt Risdon Works solution, from which antimony, arsenic and copper had been removed, and a pure antimony salt then added as required in each case. It contained 80 mgs. cobalt and 100 mgs. glue. The deposition period was 72 hours at 30 amperes/sq. ft., and the temperature was 35°C.

The overall current efficiency when operating with a six-cell series, with 55 grams acid in the first five cells and 65 in the last, would be approximately:-

With less than 0.1 mg. antimony	88% to 90%
With 0.3 mg. antimony	93%
With 0.5 mg. antimony	94%

A variation in the nature and amount of the other impurities would naturally affect the electrolytic behaviour of the solution.

A higher antimony concentration reduces current efficiency, and with the cobalt and glue concentration specified, the optimum amount of antimony is between 0.2 and 0.3 mgs/litre, because with higher amounts the reduction in melting efficiency offsets the gain in current efficiency.

The relationship between cobalt, antimony and glue is obscure, and it is a subject which justifies further investigation.

In a solution free from cobalt or containing a small amount only, antimony has an effect on the structure of the zinc, and it lowers current efficiencies when present in appreciable amounts. The maximum permissible amount varies according to the nature and quantity of other impurities present.

Arsenic. In solutions practically free from cobalt and antimony, arsenic is not very troublesome, but with solutions containing 70-80 mgs. of cobalt per litre and some antimony, less than 1.0 mg. per litre of arsenic has a disastrous effect.

Figure 8a illustrates the cathode zinc produced from a solution free from cobalt and antimony, but containing 5 mgs. arsenic / litre. The current efficiency was over 92% after 72 hours deposition at 100 grams acid / litre.

Figure 8b is a photograph of a zinc deposit produced from solution containing 70 mgs. cobalt and 1 mg. arsenic per litre. The holes are characteristic of arsenic and cobalt together. Despite the presence of glue, the current efficiency was very low after 72 hours at 65 grams acid. The same solution, without arsenic, would have yielded a current efficiency of 88% or better.

In a series of tests using glue and the standard 72-hour deposition period with acidity of 55 and 65 grams per litre, the following efficiencies were obtained:-

No arsenic	90%
0.25 mgs. per litre arsenic	81%
0.5 " " "	73%
1 mg. " " "	66%

Copper. Copper is easily removed during treatment of the solution with zinc dust, and a very small amount only is usually present in most commercial electrolytes. With 70-80 mgs. of cobalt, 0.5 mgs. of copper is harmful under some conditions, particularly with increasing acidity of electrolyte and age of deposit. With 10 mgs. cobalt, this amount has little or no effect.

Germanium. Germanium has recently been found in the electrolyte in some of the American plants.(f) This impurity is normally removed during the co-precipitation of the antimony, arsenic and iron. In the absence of sufficient iron, removal of germanium is incomplete, and electrolytic troubles arise. According to Tainton, 0.1 mg. per litre seriously reduces current efficiency. It is possible that antimony has hitherto been blamed for some of the electrolytic effects of germanium.

Other elements have some effect and selenium is notable in that whilst it reduces current efficiency, the zinc produced in its presence is bright and silvery in appearance.

Electrodes

The condition of the electrodes is important, and one of the major items of expenditure in connection with the electro-deposition of zinc is the cost of replacing anodes and cathodes.

Anodes. Pure lead is used in most plants for anodes, but lead containing 1% silver, and in some cases a little arsenic, is used in the Tainton process. The anode potential is lower and the cathode zinc contains less lead when lead-silver anodes are used.

Lead containing various amounts of antimony was used in a few cells at Risdon some time ago, primarily as a means of maintaining the optimum amount of antimony in the electrolyte. The zinc produced in the cells using these anodes was rough in structure, and was characteristic of cathodes deposited in the presence of antimony. Despite considerable research by the Risdon staff, using various alloys containing lead as the major constituent, and also with other alloys, no anode material has been developed which is superior to lead.

All lead anodes become distorted during use, and it is a routine duty to keep them straight and spaced correctly. The attention required increases with age, but apart from this there is a relationship between anode age and current efficiency, and it is therefore usual to discard anodes before they are mechanically unsound. This relationship is probably due in some way yet undetermined to intercrystalline penetration by lead peroxide, and possibly other substances. The extent of this penetration is probably partly dependent on the composition of the electrolyte.

Hydrochloric acid in solution corrodes the anodes, and it is mainly on this account that its concentration is maintained at a low figure.

Under the old Risdon conditions the optimum life of anodes is about three years, but the corresponding figure with the Risdon low-cobalt solution has yet to be determined. Discarded anodes are re-melted, and the reclaimed lead, amounting to 60 to 70% of that originally in the anode, is utilised for new anodes.

Cathodes. Sheet aluminium is universally used as the base on which to deposit zinc, although attempts have been made to use zinc sheets. Aluminium-silicon alloy sheets have also been investigated at Risdon. Corrosion of the aluminium above the solution line largely determines the life of the cathode. There is always more or less spray immediately above the electrolyte, and some of this condenses on the unsubmerged portion of the cathode. Furthermore, the solution creeps up the surface, and as the cathode is warm, water is evaporated and acidity increases with consequent acceleration of the corrosion. At some plants the effective life of aluminium is little more than one year, when the cathodes are discarded and sold as scrap.

An investigation extending over several years has been conducted at Risdon to determine the most satisfactory way of counteracting corrosion, and for some time it has been the practice --

(1) To use sheets which are thicker in the unsubmerged portion, and

(2) To further protect this by coating it with a thin deposit of zinc to within an inch or so of the head bar by simply increasing the solution level above normal in a series of cells, in which all the cathodes are electroplated with zinc periodically.

As a result of this strengthening and protection, the cathode life at Risdon was 4 years, until the acidity of the electrolyte was increased two years ago, since when corrosion has been somewhat more marked. There has thus been a further incentive to prosecute the investigation with renewed vigour, and a large number of varnishes, including Bakelite, also rubber and gutta percha, have been applied in a number of different ways without a great deal of success. Covering with lead has been partially successful, but the most satisfactory method is to rivet an aluminium strip reclaimed from discarded cathodes over the unsubmerged portion of the cathodes in use. This procedure is still under test, but it appears likely that it will become standard practice, and the future life of the cathode will probably be determined by the corrosion of the submerged sheet, particularly the edges. This is equivalent to a life of approximately 7 years.

Melting and Casting

All cathode zinc contains oxygen, and some zinc oxide separates when the cathodes are melted, the amount depending on the structure of the deposited zinc and on the oxidation of zinc during melting.

Two products are recovered - molten zinc and dross - the latter being a mixture of metallic zinc, zinc oxide and coal ash. To facilitate the separation of dross from the molten zinc, it is customary to add a small amount of ammonium chloride. After removal from the melting furnace the dross, whilst still hot, is treated with more ammonium chloride, and most of the metallic zinc is liquidated or "sweated" away from the oxide. Finally, after the remaining metal in the dross has solidified, the dross at Risdon is given a light grind, is screened, and the oversize particles, which are mainly metallic zinc, are returned to the melting furnace. This final dross treatment stage yields 1 ton of metallic zinc per day.

The ammonium chloride used at Risdon totals 2 pounds / ton of cathode zinc melted.

The melting efficiency, which is the yield of zinc in ingot form expressed as a percentage of the cathodes melted, has now reached 96.6% at Risdon.

Treatment of Residues

Some of the residues obtained during leaching and purification contain valuable products. Such residues are:-

(1) The leach residues, which retain most of the lead, silver and some of the zinc originally in the roasted zinc concentrates.

(2) The precipitate obtained by treating the solution with zinc dust. This precipitate contains most of the copper and cadmium dissolved during leaching.

(3) The cobalt nitroso beta-naphthol precipitate obtained by treatment of that portion of the solution from which cobalt is removed. It is contaminated with zinc sulphate.

Leach Residues.

Various methods have been proposed for recovering zinc from the zinc ferrite in the leach plant residues. Amongst these are:-

(a) Prolonged leaching with hot 10% sulphuric acid.

(b) Treatment with concentrated sulphuric acid and roasting.

(c) Modification of (b) in which roaster gases containing sulphur dioxide are substituted for sulphuric acid, and

(d) Reduction of the ferrite with carbon at a high temperature, and volatilisation of the zinc.

During the leaching with sulphuric acid (Method (a)), the ferrite is decomposed with the formation of zinc sulphate and ferric sulphate, which dissolve. Zinc oxide (as calcines), is added to the solution, and the iron is precipitated as basic sulphate, which is difficult to filter and wash, and contains much adsorbed zinc sulphate.

Method (b) is based on the fact that the decomposition temperature of iron sulphate is lower than that of zinc suphate. In practice acid equivalent to the zinc contained in the ferrite is mixed with the residues, and approximately 40% of the ferrite is decomposed, forming sulphates of iron and zinc. The mixture is heated to a temperature between 650° and 700°C when the iron sulphate decomposes into ferric oxide, and a mixture of sulphur dioxide and trioxide which attacks further ferrite. This cycle is repeated until the whole of the ferrite is converted to zinc sulphate and ferric oxide. The zinc sulphate is dissolved and the solution is added to the main circuit.

In method (c), the hot gases containing sulphur dioxide produced during the roasting of zinc concentrates are passed through the residue maintained at 650-700°C. The end products are much the same as those obtained when roasting with sulphuric acid.

In both methods (b) and (c), zinc is introduced into the circuit as sulphate, and either the sulphate concentration or the volume of the solution increases, unless sulphuric acid in some form or other is discarded from the circuit.

Residues are being leached with sulphuric acid at one plant, and are roasted with acid at another. The fourth method has been proposed from time to time, but as far as the author knows, has not been used commercially for the treatment of leach plant residues. A modification of the process based on roasting the residue with sulphuric acid, has been developed for the treatment of Risdon residues, but whether it is used or not will depend largely on the future price of zinc.

Copper-Cadmium Residues.

The "zinc dust" precipitate contains copper and cadmium, zinc and some silver, and is usually treated for recovery of cadmium metal, zinc sulphate solution which is returned to the zinc plant circuit, and a concentrated copper residue containing silver.

The "zinc dust" precipitate produced at Risdon contains:-

Cadmium	11-16%
Copper	8-10%
Zinc	28-32%
Silver	20-50 ozs. [ounces]

The precipitate is leached in zinc plant electrolyte under conditions whereby most of the zinc and cadmium dissolve together with a small amount of copper. Most of the copper and silver remain in the residue which is filtered, washed, dried and sold.

The resultant solution is agitated with a controlled amount of zinc dust to precipitate cadmium and copper. After separating the solids, the solution is returned to the zinc plant circuit. The precipitate is partly oxidised by drying, and is leached with cadmium plant spent electrolyte. The resulting cadmium sulphate solution is purified and electrolysed. The cadmium cathodes are melted under a flux. The Risdon production of cadmium is 200 tons per annum.

Cobalt Precipitate.

Cobalt-nitroso beta-naphtholate has certain desirable properties as a paint pigment and it is likely that its use for this purpose will become established within the near future.

General

The industry owes much to research, which in its widest sense relates to electrical, mechanical and chemical engineering, in addition to pure chemistry and physics. In this connection, it is perhaps not generally appreciated how difficult it sometimes is to interpret the information obtained from laboratory experiments and to use it to improve an industrial process. The first stage in the development of a modification of process frequently involves a large number of experiments in the Work's laboratory, using Work's solution; next comes the development of the technique for maintaining in the plant the optimum conditions determined in the laboratory. An economic study of the laboratory results is then necessary, and in many cases, plant has to be provided, or else the existing plant modified.

The evolution of a process modification from laboratory results is frequently tedious and is a responsible duty. This is particularly true when an alteration of solution composition is under consideration. If done thoroughly, it is undoubtedly an essential part of the research, and without it technical progress would be impossible.

Brief reference has already been made to specific changes in practice developed from research work. The improvement in the Risdon results during the past five years, as shown by various key figures, illustrates the general benefits derived from research work, and from the very rigid control of plant operations to conform with the optimum found during such research work.

The figures for the year ended June, 1926, are compared below with those realised during the year ended June, 1931:-

	Year ended June, 1926.	Year ended June, 1931.
1. Current Efficiency	88.8%	91.6%
2. Yield of Zinc/H.P. Day D.C. in pounds	10.9	12.23
3. Zinc dust used for precipitation of copper and cadmium in pounds / ton cathode zinc	42	19
4. Melting efficiency	94.1	96.6%

The author desires to emphasize here that in the production of electrolytic zinc, and to a greater extent, perhaps, than in the production of any other metal, extraordinarily close control is essential for high efficiency. The process is continuous and operates through every hour of every day in the year. When one realises that small variations in the composition of the electrolyte can produce widely different results, it is evident that the maintenance of high efficiency calls for the closest attention on the part of metallurgists, chemists and operatives generally.

There is still a lot of work to be done before there is a complete understanding of all the reactions which occur during the conversion of zinc sulphide to electrolytic zinc. This is particularly true of the reactions occurring in the cell, and it would be useful to have precise information on the four following matters:-

(1) The reason for the observed effects of toxic impurities;

(2) The manner in which glue and other addition agents, restrain the toxicity of cobalt and similar impurities;

(3) The anode reactions, with particular reference to the effect thereon of impurities introduced in the cell feed, and,

(4) The reason why impurities - and antimony in particular - modify the structure of the deposited zinc.

All these matters have had attention at the various electrolytic zinc plants and in university laboratories - in many cases by the various zinc companies' own staffs working there. These reactions are still, however, somewhat imperfectly understood, and there is need for further work.

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Explanation of Plate

Fig. 6. Cathode zinc after 19 hours deposition from electrolyte containing 70 mgs. cobalt /litre, (a) without glue, (b) with glue. (x 1/6).

Fig. 7. Cathode zinc showing effect of antimony in electrolyte (a) Nil Sb, (b) 0.1 mgs. Sb / litre, (c) 0.3 mgs. Sb / litre, (d) 0.5 mgs. Sb / litre. (x 1/4).

Fig. 8. (a) Cathode zinc produced from solution free from cobalt and antimony but containing 5 mgs. arsenic / litre, (b) Cathode zinc produced from solution containing 70 mgs. cobalt and 1 mg. arsenic / litre. (x 1/4).

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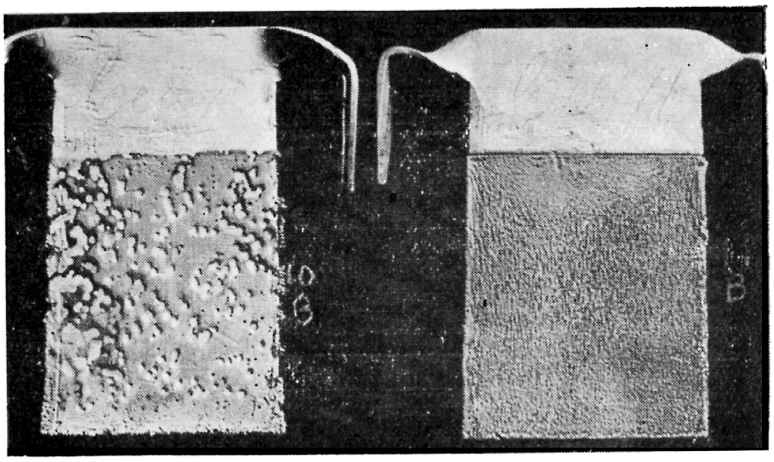
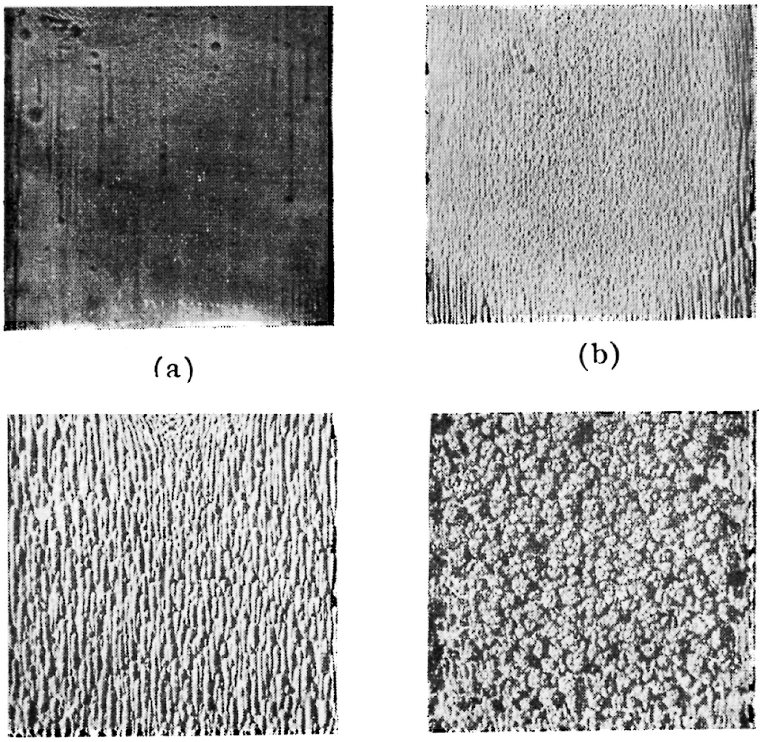
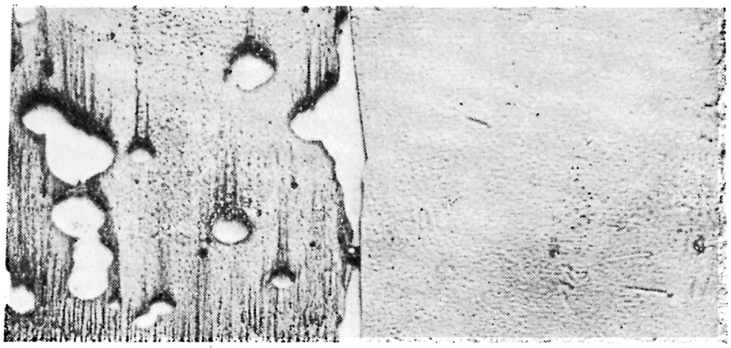


(a) Fig. 6. (b)



(a) (b)

(c) Fig. 7. (d)



(a) Fig. 8. (b)