TRANSPORT OF LEAD INTO CATHODE ZINC

by

Gordon Thomas

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PREFACE

Electrodeposition of metals may be divided into four categories. In electroplating, articles are coated with a layer of metal for the purpose of ornament or protection. The physical form of the deposit is of prime importance since upon it depend such properties as lustre, hardness and ductility. Good adherence of the deposit to the plated article is also a requisite. The process of electroforming is the production or reproduction of articles by electrodeposition. Reproduction of printing plates and phonograph matrices are common examples of electroforming.

In electrorefining, the anodes consist principally of the metal to be refined. The purpose is to convert an impure into a pure metal as, for example, with copper. Except for marked roughness which may cause short circuits and thus lower current efficiency the structure and physical properties of deposits are of minor importance.

The process of electrowinning employs insoluble anodes in a solution derived by leaching ores. The purpose is to recover a pure metal from a solution which usually contains other metals. As in electrorefining, the physical structure of the deposit is of small importance since the metal in both cases is usually re-cast from a melt before use. Also, since the deposit is stripped from the cathode starting sheet, the adhesion in both cases must be of a limited degree.

Electrowinning of metals includes processes of great commercial importance, not the least of which is the electrowinning of zinc by which zinc of 99.9+% purity is now produced. The most important problem relating to the preparation of high purity zinc is probably the prevention of contamination by lead originating at the lead anodes used in the electrowinning process. It is with this problem that the present thesis is concerned. In its broadest aspects, the solution of such a problem encounters many aspects of physicochemical theory and practice, and it is virtually impossible to review at all adequately the literature concerned with all these aspects. For example, the present problem has as one of its major considerations the factors responsible for passivity in metals. As early as 1916 (1), the literature treating of this subject encompassed papers numbering in the hundreds. The introductory remarks to follow have therefore been written with a view almost solely to bring before the reader the directly relevant information required to orient the problem as it existed when the present study began, and to make possible a discussion of the results obtained.

INTRODUCTION

The electrowinning of zinc embodies two main steps: preparation of a zinc solution, and deposition of zinc from that solution. Zinc ores are roasted to decompose zinc sulphide into zinc sulphate and zinc oxide, which are soluble in water and sulphuric acid respectively, and to oxidize the associated sulphides. The roasted ore is leached with spent electrolyte containing sulphuric acid. The solution containing dissolved zinc is separated from insoluble materials and purified prior to use in electolytic cells. The impurities present in the electrolyte depend upon the source of the zinc ore and govern to a greater or less degree the preliminary treatment of the electrolyte.

Impurities in general may be classified as harmless, detrimental, or beneficial (2-7). In moderate amounts, sodium, potassium, calcium, magnesium and aluminium may be considered harmless in electrolysis. The status of manganese is not clear; it has been reported to be harmless in small amounts but larger amounts cause formation of holes in the zinc deposit and also necessitate frequent cleaning of cells owing to MnO_2 formation. On the other hand, it has also been reported to lower the lead content of cathode zinc.

Arsenic, antimony, copper, germanium, tellurium, cobalt, nickel, vanadium and uranium are considered harmful. Certain of these impurities lower hydrogen overvoltage and cause loss of current efficiency, while others lower current efficiency by re-solution of the zinc deposit following its deposition on the cathode. Still others cause tree formation on the cathode, which results in short circuits in the cells. The deleterious effects of tellurium are pronounced even at concentrations as low as 1 mgm. per liter. The presence of iron above 20 mgm. per liter lowers current efficiency by alternate oxidation of ferrous and reduction of ferric ions. Cadmium and lead cause no loss of current efficiency but lower the grade of zinc. Chlorine, fluorine and nitrate cause corrosion of anodes, sticking of the zinc to the cathode, or corrosion of the aluminium cathode.

Cobalt in excessive amounts causes serious loss in current efficiency but in smaller amounts reduces both corrosion of anodes and lead content of cathode zinc.

The extent to which impurities may be present in purified solutions entering the electrolytic cells is indicated by the following typical analysis (2) in which concentrations are expressed in milligrams per litre: $MgSO_4$ 7000, $CaSO_4$ 1900, Mn 560, SiO_2 133, Cl total 113, Cl chloride 30, F 23, Fe^{++} 16, Al 12, Cd 4.5, Co 3.7, Fe^{+++} 3, Cu 0.11, As + Sb 0.08, Pb trace.

In principle, the electrowinning of zinc involves electrolysis of the acid zinc sulphate electrolyte using an inert anode (lead is generally used) and a cathode from which the zinc deposit may be readily stripped (aluminium has been found to serve the purpose well). Wide variations in cell operation are found between different electrolytic zinc plants (2,4,8-16). The concentration of zinc entering the cells varies from 110 to 215 grams per liter while the sulphuric acid content of electrolyte leaving the cells varies from 100 to 200 grams per liter. Electrolyte temperature may be as low as 23°C at one plant, while at another it is as high as 40°C, and the current densities used in various plants may range from 30 to 100 amperes per square foot. The large electrolytic cells or tanks contain from 12 to 45 anodes. In most plants the number of anodes per cell is one greater than the number of cathodes but some plants use twice as many anodes as cathodes.

In spite of the great differences in operating conditions mentioned above and the different sources of ores, the electrolytic zinc from all plants is of very high purity. As an example may be considered the plant at Trail, B.C. (2) which produces "A" grade zinc of directly melted cathodes and die-casting grade zinc from specially selected cathodes. A representative analysis of "A" grade zinc in 1935 showed its composition to be approximately 99.9683% zinc with Pb, Cd, Fe and Cu to the extents of 0.024, 0.005, 0.0017 and 0.0010% respectively; the corresponding values for die-casting zinc are of the order 99.9930% zinc with 0.0035, 0.002, 0.0007 and 0.0008% of the other metals mentioned. In more recent years, the purity of electrolytic zinc has been somewhat improved over the above figures. The main impurities of zinc are seen to be lead, cadmium, iron and copper, and impurities other than these four may be considered as negligible.

The major contaminant of electrolytic zinc is lead. That a certain amount of lead appears in the deposit is to be expected since lead or lead alloy anodes are used in the deposition of zinc. It is not surprising therefore that many investigations have been made with a view to reducing contamination from this source.

Two reactions at anodes may be of particular interest. The first is the possible combination of anions of the electrolyte with the metal anode, while the second is the discharge of anions with the formation of oxygen. With soluble anodes, the first reaction takes place almost exclusively. When both reactions are present, dissolution of the anode does not occur in accordance with Faraday's law.

Most metals dissolve as anodes when the potential is slightly more positive than the reversible value in the particular electrolyte. Anodes of iron, cobalt and nickel (17) at low current densities dissolve quantitatively according to Faraday's law. If current density is increased however the anode potential rises sharply while dissolution of the anode practically ceases and the current decreases. The anode is then said to be in the passive state although its appearance is unchanged. With further increase in current density the potential becomes more anodic until a new process, generally oxygen evolution, commences after which considerable current flows with little further change in anode potential. The passive anode may be returned to the active state by reversing the current through the cell. On open circuit, the active state may be restored on standing, or more quickly by scratching the surface or touching it with a less noble metal under the surface of the electrolyte. Chemical passivity of iron was observed at the end of the 18th century (18) on placing iron with a fresh metallic surface in concentrated nitric acid. Similarities in a metal rendered passive by chemical and electrochemical means indicate that the fundamental cause is the same for both.

One of the earliest theories put forward to explain passivity was that of Faraday (19) in 1836. He considered that the passive metal was covered by an oxide film. The apparently unchanged appearance of the metal in its active and passive state was believed due to the protective film being in some cases so thin as to be invisible.

Faraday's views were upheld for many years but later their validity was questioned. Critics were of the opinion that his film was not only invisible but also imaginary.

However, in more recent years the belief that very thin films are present on passive metals has been defended (20).

Glasstone (17) relates that while the supposed identity in light-reflecting powers of active and passive metals disparages Faraday's views, it has been shown that a difference exists in the reflection of plane polarized light from the two surfaces. In addition, photoelectric emission from passive iron is less than from the active metal, indicating the presence of a film. Indeed Evans (21) succeeded in isolating from passive iron a thin non-magnetic skin of Fe_2O_3 by gentle anodic action or by means of iodine. The thin, colourless, transparent film so isolated was quite invisible when attached to the passive metal.

On investigating the passivity of metals, Müller (22-25) found that increasing current density or previously saturating the electolyte with the corresponding salt of the anode metal shortened the time required to produce passivity. The inference was that the anode metal dissolved until the solution became saturated, followed by separation of the solid and its deposition on the anode. This "layer polarization" was followed by passivation, consisting either in evolution of oxygen or dissolution of the anode metal at a higher valency. Using various metals as anodes, Müller derived relations between current density and electrode potential with the time required for passivation.

The reactions occurring at lead anodes in the electrowinning of zinc using acid zinc sulphate electrolyte produces a visible layer of lead peroxide. The resulting "mechanical passivity" is probably fundamentally the same as the electrochemical passivity mentioned above. In accordance with the mechanism outlined by Glasstone (17) and Hickling (26) for passivity of anodes in general, lead anodes may first dissolve under the influence of an applied electromotive force with the formation of plumbous ions which then form a layer of insoluble lead sulphate over the anode. The resulting increased current density at the uncovered portions of the anode causes the potential to rise until hydroxyl ion discharge occurs. The discharged ions react with the lead to form a layer of lead peroxide which is however, neither entirely adherent nor protective so that it increases in thickness. Although the main reactions following the above are those leading to oxygen evolution, a certain amount of anode corrosion continues.

As a result of small but continued corrosion of lead anodes, electrolyte becomes contaminated with corrosion products including not only lead ions but also $PbSO_4$ and PbO_2 ranging from molecular size to coarse particles. This anode corrosion not only shortens the useful life of the anodes and necessitates periodic cleaning of the anode surfaces, but transport of corrosion products to the cathode decreases the purity of the deposit. It is little wonder then that much investigation has been directed toward increasing the passivity of anodes.

For many years pure lead was used as anode material. There was a belief that the greater the purity of the lead, the smaller was the corrosion of the anode. More recently however there has been a tendency to alloy the lead with one or more other metals, not only to decrease corrosion but also to lower the anode potential. Notable advances have been made by groups headed by Fink, Tainton and Hanley.

Fink and Eldridge (27) investigated the behaviour of thallium-lead anodes in acid copper sulphate electrolyte, the choice of thallium being made on the assumption that thallium as anode material might form the higher oxide due to reaction with anions at the electrode and then break down to form the more stable lower oxide and liberate oxygen more freely than possible with other metals. The corrosion rate curve for lead alloy anodes with increasing thallium content showed a rapid decrease with up to 2% thallium, a rather flat minimum from about 20 to 60% thallium and a sharp increase with more than 70% thallium. Binary lead alloy anodes containing bismuth or tin were inferior to those with thallium. The most satisfactory lead alloy anode was one containing 10% thallium and 20% tin which, in comparison with pure lead anodes, brought about a fifty fold decrease in corrosion rate, largely due to a very adherent film formed during electrolysis.

Using a 5% brine solution as electrolyte, Fink and Pan (28) found that the corrodibility of lead or silver decreased very rapidly upon the addition of small percentages of the second metal. The anode corrosion rate curve and cell voltage curve obtained by plotting these values against the silver content of the lead alloy anodes were very similar, both curves showing sharp breaks at about 2% silver. The breaks in these curves closely corresponded to the eutectic point in the melting point curve of the Ag-Pb system. Alloys containing from 60 to 80% silver by weight showed the least corrosion. Decreased anode corrosion was considered to be due to an anode film consisting of an inner layer of PbO_2 and AgCl and an outer layer of PbO_2 and Ag_2O; the AgCl served as a binder or filler to plug up the pores of the lead peroxide. Oxygen was believed to be discharged on silver-rich crystals and to attack the adjacent lead forming lead peroxide until a bridge of lead peroxide joined the various silver-rich crystals. Within certain ranges of silver concentration, differences in the bridging distances and the size and adherence of the lead peroxide particles caused changes in the passivity of the anodes.

Lower corrosion loss of silver-lead anodes containing

50 to 60% silver in brine solution was found possible by Fink and Pan (29) by saturating the electrolyte with $PbCl_2$. Apparently the $PbCl_2$ formed insoluble PbO_2 which separated out on the surface of the anode and strongly adhered to it. In a pure brine electrolyte, rate of corrosion of lead anodes containing 2.25% Ag increased as electrolysis was continued. Introduction of a third metal such as manganese or mercury was detrimental to the protective film.

The use of anodes containing 60% silver and 40% lead for electrolysis of brine solutions has also been investigated in the Ukraine. Measurements of current-voltage curves (30) indicated that $PbCl_2$, AgCl, PbO_2 and Ag_2O were formed at the anodes with the chlorides initially formed converted later to the oxides.

Tainton (31,32) obtained patents for the use of lead anodes containing a small proportion of silver for electrolysis of zinc sulphate solutions containing manganese sulphate. The alloy anode was claimed to produce a deposit substantially free of lead and of the formation of "trees" while the manganese precipitated as MnO_2 at the anode was also practically free of lead. In a later paper, Tainton et al (33) found that on using silver-lead anodes containing free silver, i.e. above the eutectic of 2.6% silver, re-solution of the zinc deposit occurred to a considerable extent as a result of free silver dissolving from the anode and depositing on the cathode. Even with anodes containing 1% silver, re-solution of zinc was also encountered to a certain extent.

During plant operation, Tainton et al (33) showed that on changing from pure lead anodes to lead anodes containing 1% silver, in acid zinc sulphate electrolyte with addition agents such as glue, silicic acid or gum arabic, the lead content of cathode zinc decreased from approximately 0.07% to a value of 0.0015%. With glue as addition agent, the zinc deposit with silver-lead anodes had a rough, cratered appearance in contrast with smooth zinc deposits with pure lead anodes. However, exceptionally smooth bright zinc deposits were possible with silver-lead anodes if silicic acid were used as addition agent in place of glue.

In their experience (33), silver-lead anodes in general proved superior to lead alloy anodes containing such metals as As, Sb, Ba, Bi, Ca, Ce, Cu, Hg, Tl and Sn. Among a number of ternary alloys containing lead and silver, some advantage was found in Pb-Ag-As and Pb-Ag-Sn combinations. The Pb-Ag-Sn anodes gave exceptionally smooth deposits, while the Pb-Ag-As anodes put very little lead in the zinc or in MnO_2 when manganese was present in the electrolyte.

The influence of binary and ternary lead alloys on anode polarization and lead content of cathode zinc was studied by Hanley et al (6,35) in electrolyte free of addition agents. The alloying elements were Ag, As, Al, Ba, Bi, Ca, Cd, Hg, Mg and Tl. In comparison with pure lead, the effect on anode polarization and lead content of the zinc deposit on addition of calcium and/or silver was as follows: 2.3% calcium decreased anode polarization by 45% while the lead content decreased only slightly; 1% silver decreased the anode potential slightly but decreased the lead content six-fold; 2.3% calcium + 1% silver decreased anode polarization by 45% and lead content decreased approximately six-fold. Thallium or calcium when present in small amounts increased the lead content of cathode zinc, but in larger amounts they decreased the lead in the zinc deposit. Remarkable passivity was exhibited by lead anodes containing over 4% thallium but there was little lowering of the anode potential. Pb-Sn anodes were more passive than pure lead while Pb-Sn-Ca anodes corroded more readily than pure lead. The lead content of zinc deposits was decreased the greatest amount by the use of alloy anodes containing 0.1% calcium, 4% thallium and the remainder lead.

The behaviour of lead anodes in sulphate electrolyte with particular reference to the influence of cobalt salts was investigated by Rey et al (35). Electrolyte filtered after use with pure lead anodes contained between 7 and 8 mgm. per liter of lead while unfiltered electrolyte contained approximately three times that amount due to suspended lead peroxide particles. The filtered electrolyte was apparently oversaturated since agitation with lead sulphate reduced the lead content to between 3.5 and 4 mgm. per liter. With lead anodes containing 1% silver, the lead content of the solution did not exceed 4 mgm. per liter while no lead peroxide appeared in the electrolyte, even after 18 hours. The presence of 7.5 mgm. per liter of cobalt as sulphate in the electrolyte decreased the electrochemical attack of metallic lead underlying the lead peroxide film and retarded the formation of lead peroxide in suspension in the electrolyte.

Rey et al (35) determined the rate of precipitation of lead at a cathode from an acid zinc sulphate electrolyte containing 7 mgm. per liter of lead and concluded that lead in very dilute solutions is deposited at the cathode at a much slower rate than the introduction of lead into solution from a lead anode. The deposited zinc showed a lead content of 0.045%. The amount of lead going into solution as a result of chemical attack of PbO_2 or discharge of the lead-lead peroxide couple was considered to be small. Electrochemical attack of metallic lead through the pores of the lead peroxide film was of first importance as far as the entrance of lead in solution was concerned and appeared to be the only cause for the production of lead peroxide in suspension.

These same authors found that if lead anodes were used in acid zinc sulphate, then immersed in a cobalt solution, washed in water and replaced in cobalt-free electrolyte, no lead peroxide contamination of the electrolyte occurred for several hours, following which the lead peroxide suddenly appeared. These authors also showed that on placing cobalt in the electrolyte, the anode potential of a pure lead anode was decreased. One explanation of the effect of cobalt was that the discharge of sulphate ion was facilitated by the presence of the cobalt (probably Co_2O_3 precipitated on the anode) acting as an oxygen carrier. Another interpretation was the formation of an impermeable film on the anode protecting the metallic lead from electrochemical attack.

Koenig, MacEwan and Larsen (36) investigated the behaviour of pure lead and binary lead alloy anodes during electrodeposition of zinc to observe the effect produced on anode potential and lead content of the cathode zinc by the variables anode composition, current density, sulphuric acid concentration and metal ion impurities in the electrolyte. The anode potential of a new anode was found to decrease very rapidly during the first six hours of operation (from more than 2.93 to approximately 2.88 volts), but after ten hours the change was very slight. The anode potential was also shown to increase with increasing acid concentration of the electrolyte.

Koenig et al showed that with increased concentrations of cobalt or iron in the electrolyte, both anode potential and lead content of the zinc deposit were progressively decreased, the changes being greater with cobalt than with iron. When the concentration of cobalt reached 20 mgm. per liter, the anode potential was less noble by 117 mv. while the lead content was decreased from 0.029% to 0.002%. Iron at a concentration of 100 mgm. per liter reduced the anode potential by 65 mv. and the lead content to 0.010%. With chromium present, similar but smaller changes were observed, the corresponding values for a concentration of 50 mgm. per liter being a 16 mv. change and a 0.028% lead content. Manganese, which irreversibly oxidized to $MnO_2.H_2O$, and nickel were without effect on the anode potential. Sodium and magnesium, exhibiting but one valence, were not oxidized at the anode and exerted no apparent influence on the anode potential. While no values were given for the influence of manganese, the lead content of the zinc deposit was but slightly changed by the presence of nickel, sodium and magnesium.

These authors also showed that it was necessary to maintain the cobalt concentration in the electrolyte to keep the lowered potential and prevent the formation of lead peroxide. Occluded lead peroxide was considered primarily responsible for the lead in zinc deposits. By enclosing a pure lead anode in a canvas bag and electrolyzing for several hours, a considerable quantity of lead peroxide was found in the canvas bag while the amount of lead appearing in the electrodeposited zinc was too small to determine quantitatively. This appears to be the only reference to the use of filters to study the relative importance of lead in solution as compared with lead peroxide in suspension, in promoting lead contamination of cathode zinc.

On using binary alloy anodes of lead with Sn, Bi, Cd, Mg, As and Ag, Koenig et al (36) indicate that, all of the alloying elements dissolved from the anode to a certain extent during electrolysis. The potentials of all anodes investigated were less noble than that of pure lead, the decrease in potential being 38, 47, 50, 80, 91 and 116 mv. respectively for the above mentioned alloys.

The same authors found no relation between anode potential and the lead content of cathode zinc. In comparison with pure lead anodes, the Pb-Bi anodes lowered the potential and raised the lead content almost three-fold. Pb-Mg, Pb-Ag and Pb-Sn anodes containing small amounts of tin lowered both the anode potential and the lead content. The Pb-Sn anodes, with increasing proportions of tin, continued to decrease the anode potential but raised the lead content of the zinc deposit. A simple relation was found to exist between the current and the anode potential.

Surface characteristics of the anodes are also of importance in the passivity of anodes, in certain electrolytes. In two patents, the purity of zinc deposited from anodes was claimed to be improved if the surface of the anodes were worked so as to increase the active surface (37) or if the anodes were immersed in a reducing bath such as acid $FeSO_4$ solution (38). Pletenev and Soboleva (39) found that the best materials for use as insoluble anodes in the electrodeposition of zinc were lead alloyed with 1% silver, and lead electrolytically plated with lead from a fluosilicic acid bath. However, in brine electrolyte it was found (40) that the structure of the anode as influenced by the temperature, conditions of its preparation and the degree of smoothness of its surface did not influence the velocity of corrosion.

Conditions of electrolysis (41) did not appear to have much effect on the rate of corrosion of lead anodes containing 3 to 5% silver. Snow (10) states that the amount of lead in zinc deposits may not necessarily be proportional to the rate of corrosion of the anode, but may be more a function of anode potential as effected by electrolyte composition and anode current density.

The presence of cobalt sulphate lowers the lead content of cathode zinc but at the same time lowers the current efficiency. The decreased current efficiency is considered

(42) to be due to the re-solution of zinc deposits; deposition of cobalt forms a cobalt-zinc couple in which the zinc dissolves anodically. The permissible amount of cobalt in electrolytes for deposition of zinc varies over a wide range depending on operating conditions. As little as 0.15 mgm. per liter of cobalt has been reported (5) to be fatal for electrodeposition of zinc, whereas a current efficiency of 92% has been obtained (43) with electrolytes containing as much as 200 mgm. per liter of cobalt.

The effect of cobalt (42-44) is much less pronounced with high current density, with low acidity, or with electrolytes containing gelatin or other colloids or ammonium sulphate. In plant practice it has been found (2) that the permissible amount of cobalt depends on what other impurities are present from the leached ore. At the Trail, B.C. plant, cobalt concentration is maintained between 3 and 4 mgm. per liter at which concentration it gives lead control with no loss of current efficiency. Control of cobalt concentration may be obtained (2,10,45,46) by an inorganic method using alpha nitroso beta naphthol or by inorganic methods involving precipitation with zinc dust after preliminary addition of proper amounts of salts of copper, arsenic and antimony.

Addition agents, which are usually colloidal and present in small concentrations in the electrolyte, have been defined

(47) as substances which have marked influence upon the character of deposits without materially changing the physical properties of the solution. Smoother, brighter deposits in place of roughness or trees result from the presence of addition agents which decrease the size of crystals and crystal aggregates in the deposit. Certain addition agents also increase polarization or overvoltage for hydrogen discharge thereby increasing current efficiency for electrodeposition (47).

Most research on addition agents has concerned itself with colloidal materials and their effect at the cathode. However, metallic ions in concentrations much lower than those usually employed with addition agents have been found to exert considerable influence on cathode reactions. For example, cobalt and germanium in small concentrations cause considerable re-solution of zinc deposits on cathode (4). Anodic reactions are also considerably influenced by electrolytes containing only trace amounts of metallic ions, as in the case of cobalt which increases the passivity of lead anodes.

It will be evident from the foregoing survey that the transport of lead into cathode zinc, the problem with which the present thesis is concerned, has received relatively limited attention as revealed by available literature. In considering various approaches that might be made to a solution of the problem, it seemed of paramount importance to determine as unequivocally as possible the extents to which contamination of the cathode zinc was derived from lead in the form of ions in the solution as compared with lead carried mechanically to the cathode and adsorbed there as an insoluble oxidation product of the anode material. This information appeared to be essential to an understanding of the mechanism by which the extent of contamination is reduced by the presence of certain known substances (e.g. traces of cobalt), since only with such information is it possible to determine whether the problem lies within the scope of corrosion by oxidative attack or corrosion by a process of solution. For this reason, considerable effort was devoted to filtration studies under various conditions, in extension of the work of Koenig et al (36). It then became possible to focus attention on other aspects of the system which gave promise of indicating the mechanism of the passivity promoted at the anodes under certain conditions.

EXPERIMENTAL

THE POLAROGRAPH

To study the transport of lead into cathode zinc, many determinations of the lead content of zinc were required. Of the various procedures available for lead determination, the polarographic and spectrographic methods appeared preferable to others. Since a spectrograph was not available for routine analysis, the polarographic method was selected. The polarograph allowed precise determinations of trace amounts of lead in the presence of small amounts of other impurities occurring in the deposited zinc.

Although a commercial recording polarograph has certain advantages, the present study was made with a simple manual polarograph assembled from equipment available in the laboratory. It must be admitted that the choice of a "breadboard" model was considerably prejudiced by discussions with several individuals who had used both recording and manually operated instruments; without exception, they assented that the possible vagaries of polarography could be best eliminated with the simpler instrument. Details for the construction of a polarograph have been given frequently in the literature (48-52) and from which a suitable design was obtained for routine lead analysis.

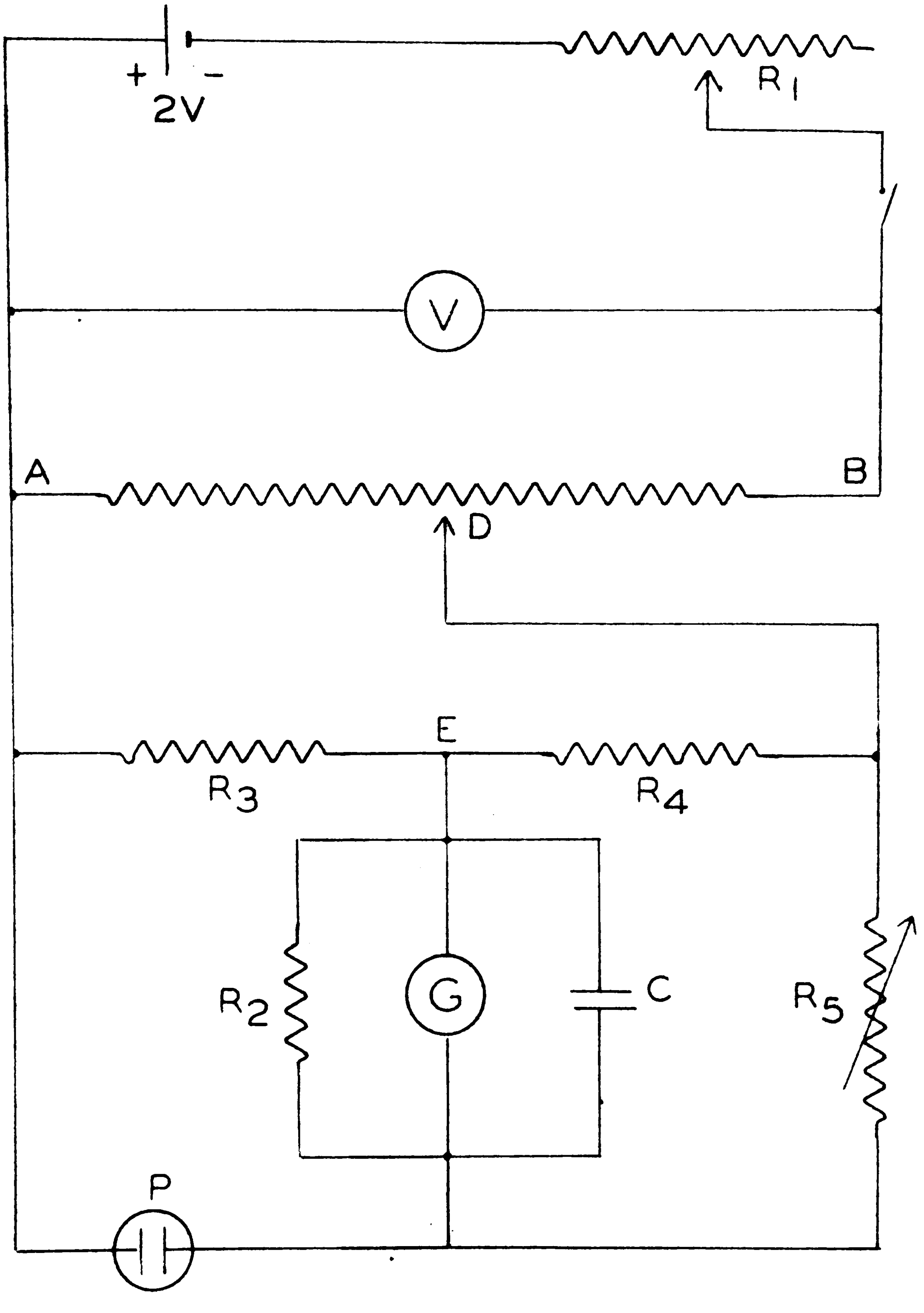
The electrical circuit of the polarograph used is shown in Fig. 1. The 2 volt battery consisted of three storage

Figure 1

Electric circuit of polarograph

Legend

R_1	Variable 80 ohm resistor.
V	Voltmeter.
A-B	Calbrated slide wire.
D	Sliding contact.
R_2	Ayrton shunt.
R_3	Fixed 1000 ohm resistor.
R_4	Fixed 10 ohm resistor.
R_5	Variable 100,000 ohm resistor.
G	Galvanometer.
C	10,000 mfd. condenser.
P	Polarographic cell


+
-
2V
R1
V
A
B
D
E
R3
R4
R2
G
C
R5
P

cells in parallel. The voltage drop across AB, as measured by the voltmeter V, was set to the desired value by the 80 ohm variable resistor R1. The resistance AB was a Leeds and Northrup calibrated slide wire, of which the sliding contact D allowed the potential applied to the polarographic cell P to be varied.

The moving coil mirror galvanometer was a Leeds and Northrup model having a sensitivity of 0.36 μv/mm., a critical damping resistance of 53 ohms and a period of 5.4 seconds. A 50 cm. frosted glass scale was placed 3 yards in front of the galvanometer for use with this instrument. An Ayrton shunt R2 allowed the sensitivity of the galvanometer to be varied without changing its damping resistance. The 10,000 mfd. dry electrolytic condenser C served to reduce the galvanometer oscillations. The components mentioned above comprised, when assembled, a simple polarograph, which did not contain resistances R3, R4 and R5, and in which the sliding contact D was connected to point E of the circuit.

A compensating circuit (53) consisting of the above three resistors was included in the circuit. The fixed resistors R3 and R4 were 1000 ohms and 10 ohms respectively, while R5 was a variable 100,000 ohm resistor. By a suitable adjustment of R5, the residual current flowing from A through the polarograph cell, the galvanometer and R4 to D could be balanced out by an equal current flowing from A through R3, the galvanometer and R5 to D. Consequently the slope of polarographic curves between steps was made nearly horizontal. This enabled the step height due to the presence of a substance at low concentration to be more readily detected and measured.

The resistance of the polarographic circuit in parallel with the slide wire AB was considerably greater than the resistance of the slide wire and the polarographic cell itself had a high resistance. Consequently the potential applied to the polarographic cell for any setting of the potentiometer was given, with only small error, by the fraction AD/AB of the value recorded by the voltmeter. This method of measuring the potential applied to the cell was found adequate for the present investigation.

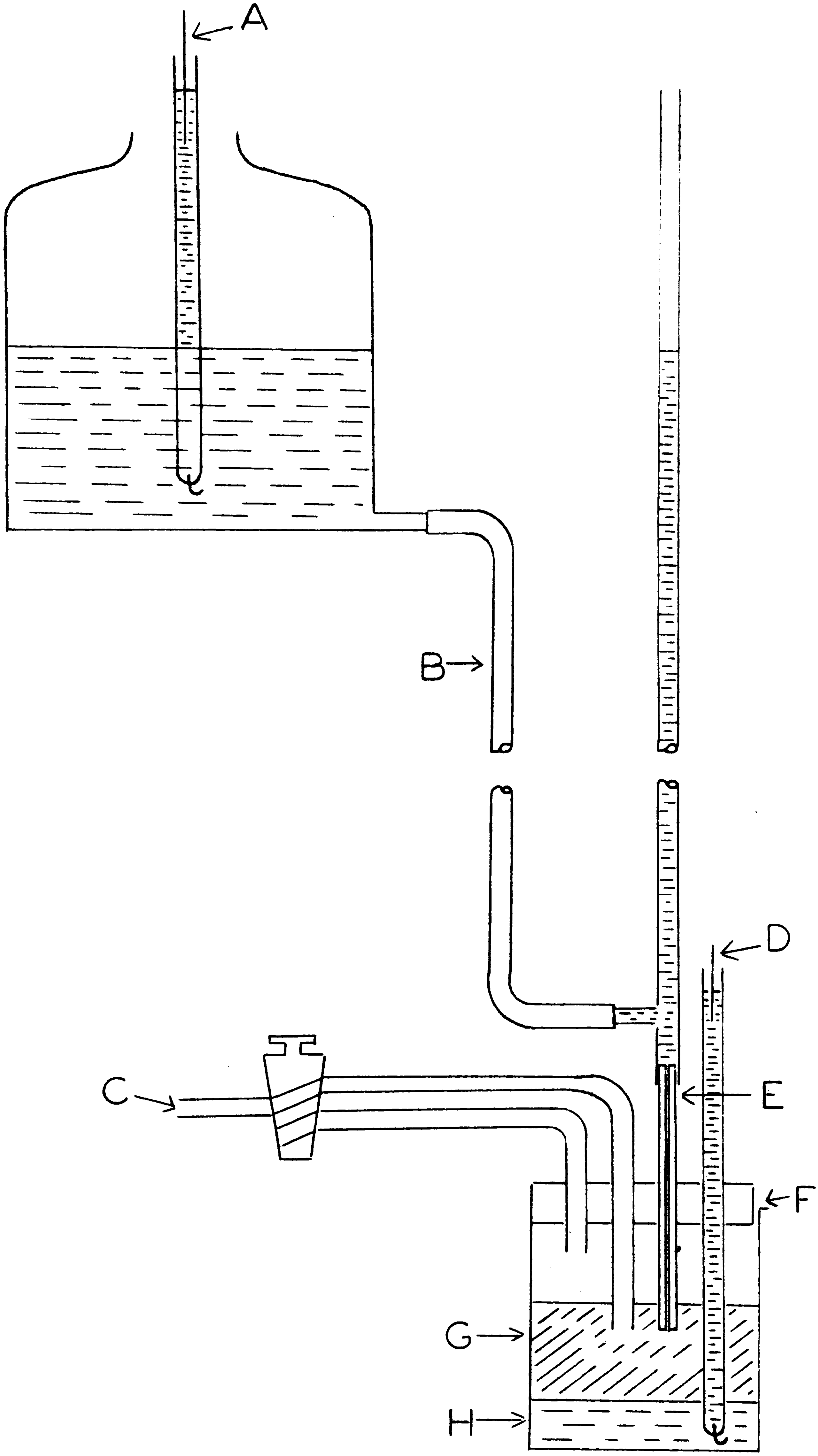
The dropping mercury electrode assembly is shown in Fig.2. It consisted of a mercury reservoir connected to a 75 cm. length of glass tube by a flexible rubber tube, which enabled a constant pressure to be maintained on the dropping mercury. In practice, air was found to diffuse through the rubber tube and form air bubbles in the mercury column and thus interrupt the electrical connection. Neoprene tubing was subsequently used in place of the rubber tubing. Before use the flexible tubing was soaked in sodium hydroxide solution, rinsed carefully in distilled water to remove surface impurities and then dried.

Figure 2

Polarographic cell assembly

Legend

A	Negative terminal.
B	Flexible neoprene tubing.
C	Nitrogen inlet.
D	Positive terminal.
E	Capillary tube.
F	Nitrogen outlet.
G	Polarographic solution.
H	Mercury pool


A
B
C
D
E
F
G
H

The vertical glass tube was connected by a short neoprene tube to a glass capillary. Initially, ordinary glass capillary tubing was drawn down to such a fine diameter as to allow mercury to drop in 3 to 6 second intervals under a pressure of approximately 50 cm. of mercury when the tip was immersed in N KCl. Suitable tips were difficult to prepare and did not give satisfactory continuous performance. Hand fabricated tips were replaced by special marine barometer tubing of 0.05 mm. uniform bore from Corning Glass Works, Corning, N.Y. An 8 cm. length of this tubing provided a uniform drop rate for mercury under the above conditions. Occasionally the tip became contaminated and gave erratic results. Placing the tip for a few minutes in concentrated nitric acid, with the mercury dropping, remedied this situation.

The polarographic cell, Fig.2, consisted of a 30 ml. pyrex beaker into which a #8 rubber stopper fitted snugly except for the small opening near the pouring lip. This opening served as an exit for nitrogen gas. This type of cell was easily cleaned between experiments and thus very satisfactory when numerous analyses had to be performed. For each experiment, 10 ml. of purified mercury and 7 ml. of the solution to be analysed were placed in the beaker. Through the rubber stopper passed the fine capillary tube for the dropping mercury cathode and a second tube for making electrical contact with the mercury pool anode at the bottom of the beaker. Nitrogen gas was passed through the solution prior to an experiment and over the solution during the experiment. Air-free conditions were thus readily obtained. During analysis, the beaker was partially immersed in a water bath maintained at 25°C.

Great care was exercised in the purification of the mercury for the dropping mercury reservoir. This was necessary to prevent complete blocking of, or erratic drop rate from, the fine marine barometer tubing. Pure mercury was also required for the mercury pool of the polarographic cell to prevent contamination of the solution being analysed. In the purification, concentrated sulphuric acid was placed over the mercury and air bubbled through it for one day. The mercury was then allowed to fall in the form of a fine spray several times through long columns of solutions of sodium hydroxide, nitric acid and distilled water in that order. The final stage in the purification of the mercury consisted of vacuum distillation.

Nitrogen purifier

The gas stream from a commercial nitrogen tank was used to circulate an ammoniacal solution of cuprous ammonium ions over a bed of copper ribbon (54). During the circulation oxygen was absorbed from the gas stream and the resulting cupric ammonium ions were reduced again to the cuprous state during passage of the solution over the copper metal. The oxygen-free nitrogen was drawn off from above the cuprous ammonium solution and scrubbed in successive towers containing sulphuric acid and water. The purified nitrogen was used to de-aerate solutions for polarographic analysis.

Preparation of solutions for analysis

A number of methods for the polarographic analysis of lead and other metallic impurities of commercial zinc are available in the literature (55-60). These methods vary in several respects. The zinc may be dissolved in hydrochloric or nitric acid and the acidity of the resulting solution then adjusted to a suitable value by addition of sodium or ammonium hydroxide. Oxidizing or reducing agents may also be added to bring certain impurities into solution. In certain instances, the proper oxidation state is required, either to analyse for these impurities or to prevent the interference of these impurities with the analysis of the other constituents.

For the routine analysis of lead in zinc, the procedure (59) recommended by British Standards publication 1225 appeared to be the most suitable. The procedure as stated in this publication consists of the following:-

(1) Dissolve 5 g. of zinc in 20 ml. of concentrated hydrochloric acid with gentle heating.

(2) Add a few drops of saturated potassium chlorate solution, then boil for 5 min. to remove excess.

(3) Cool and make the volume to 20 ml.

(4) To 5 ml. add one drop of 0.01 percent aqueous solution of methyl violet and ammonia (sp. gr. 0.88) drop by drop until the colour just changes to violet, and make to 7 ml.

(5) De-aerate solution by passing hydrogen for 10 min.

(6) Polarograph solution for lead.

It will be noted that the above procedure requires the solution to be heated and also brought to a definite volume. For this purpose, long necked 20 ml. pyrex volumetric flasks were used, the calibration mark being located just above the bulb of the flask. This type of flask allowed for expansion of the liquid while the zinc was being dissolved with evolution of gas and during the boiling of the potassium chlorate solution. The volume of the solution could also be brought to exactly 20 ml. in this same flask.

Constant attention was required during boiling to prevent bumping and consequent loss of solution. Consequently, instead of boiling the solution after addition of potassium chlorate, the flasks were simply placed in a hot water bath and allowed to remain there for several hours. A second modification of the procedure involved the use of nitrogen (56,57,61) for de-aeration of the solution.

In all polarographic work in this investigation using metallic zinc samples the entire procedure outlined above was required for each sample. When certain zinc salt solutions were to be analyzed for lead, the solutions were polarographed starting at stage (4) of the procedure.

Operation of the polarograph

Since the study involved many analyses for lead in zinc, the characteristics and capabilities of the polarograph were first investigated. In these experiments, 7 ml. of the solution to be analyzed was placed in the 30 ml. beaker along with 10 ml. of mercury. Commercial nitrogen, directly from the tank, was bubbled through the solution for 15 min. Then, by means of a three way stopcock, the nitrogen was allowed to pass over the solution during analysis. The potential applied to the polarographic cell was increased by stages from 0 to 1 volt, using the slide wire. At each setting of the slide wire the current through the cell was measured by the galvanometer.

For a given potential applied to the cell, the current varied with the size of the mercury droplet at the cathode. The current increased with increasing size of the droplet and then fell immediately to zero at the instant the mercury droplet left the capillary tip. The galvanometer, in attempting to follow these variations, oscillated between maximum and minimum values, the dry electrolytic condenser across the galvanometer serving to decrease somewhat the extent of these oscillations. An average of the maximum and minimum value may be used as a measure of the current through the circuit for each given applied potential or the maximum value only, as recorded by the galvanometer, may be used with the same precision (51). Since maximum values only were more convenient with the manual polarograph, these values were used throughout this research.

Owing to the fluctuating nature of the electric current, no attempt was made to obtain absolute values for the current. Furthermore, for polarographic analysis, only the relative increases in current are of importance. Consequently the following procedure was employed during analysis.

With an applied potential across the polarographic cell somewhat less than the decomposition potential of the solution under investigation, the suspension of the mirror galvanometer was arbitrarily adjusted so that the hair-line in the spot of light from the mirror appeared at a suitable position on the 50 cm. frosted glass scale. The maximum deflection of the galvanometer, as indicated by the hair-line, was then recorded. The potential applied to the cell was increased by degrees and the maximum deflection of the galvanometer recorded for each potential.

In preparing graphs from the data so obtained, changes in galvanometer deflection from the arbitrarily assigned initial deflection were plotted against the potential applied to the cell. This method proved to be perfectly adequate and satisfactory. However, the arbitrary initial setting of the galvanometer must be kept in mind when comparing several curves plotted in the same figure. Only the step heights in each curve are of significance, not their position relative to one another.

Use of compensation circuit

High purity zinc was dissolved in conc. hydrochloric acid to give a concentration of dissolved zinc of 250 g. per liter. This solution was then polarographed beginning at stage (4) of the standard procedure. The simple polarograph, not containing the compensation circuit, was employed to give the polarogram shown as curve (a), Fig.3, plotted from the data of Table 1.

The compensation device for the residual current shown in Fig.1 was now connected into the circuit. The same solution as that used in the previous experiment was again employed. With the variable resistor R5 set at 30,000 ohms, the polarogram shown as curve (b) Fig.3 was obtained.

In each of these curves, there are two waves or steps. The mid-points of these waves occur when the e.m.f.'s across the cell are approximately 0.48 volts and 0.66 volts. The potential of the dropping mercury electrode at these points

Table I

Use of compensation circuit

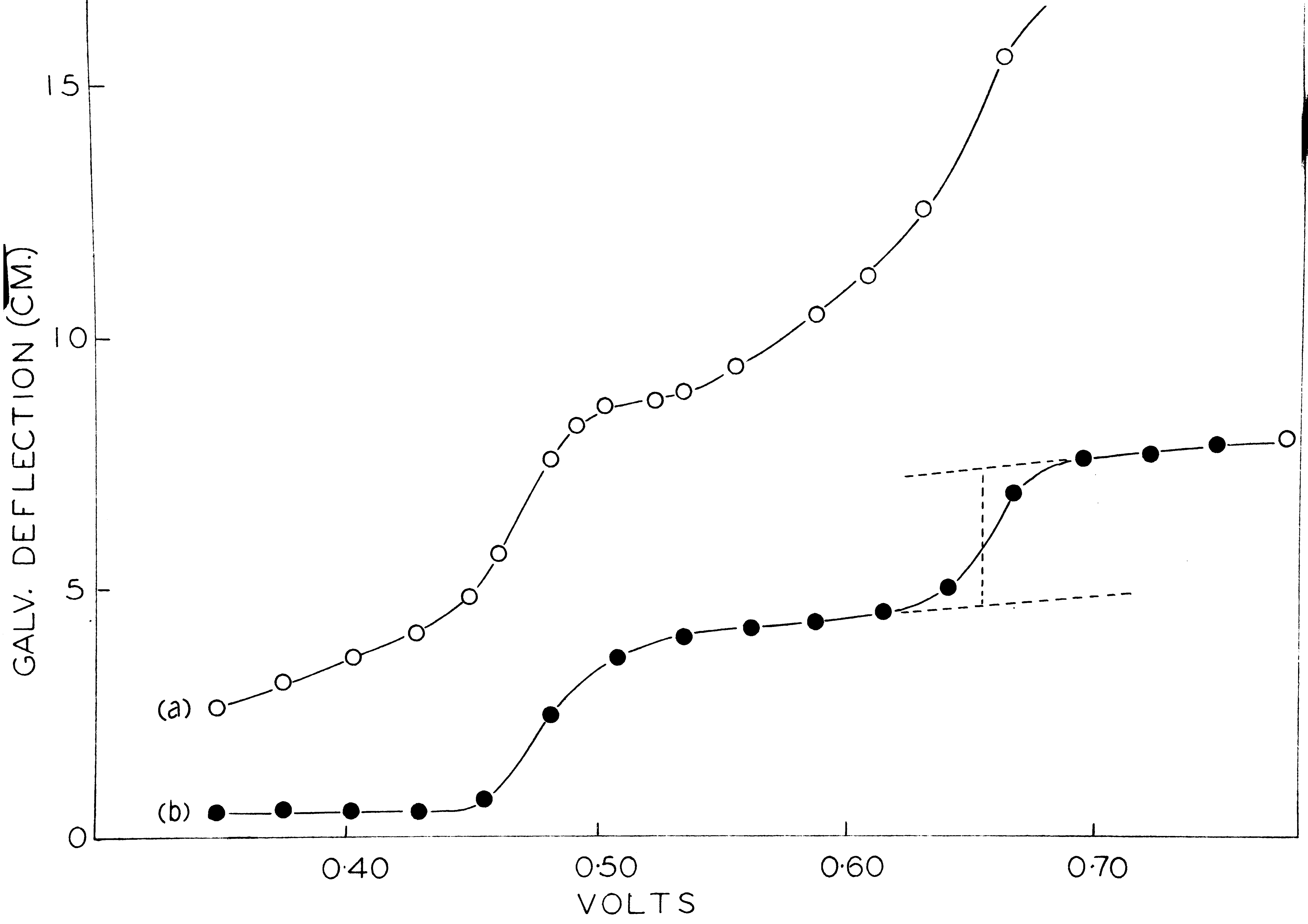
Applied potential (volts)	Galvanometer deflection (cm.)	
	(a) Simple polarograph	(b) R5 at 30,000 ohms.
0.35	2.6	0.5
0.37	3.1	0.5
0.40	3.6	0.5
0.43	4.1	0.5
0.45	4.8	0.7
0.46	5.7	-
0.48	7.6	2.4
0.49	8.3	-
0.50	8.7	-
0.51	-	3.6
0.52	8.8	-
0.54	9.0	4.0
0.56	9.5	4.2
0.59	10.5	4.3
0.61	11.3	-
0.62	-	4.5
0.63	12.6	-
0.64	-	5.0
0.66	15.6	-
0.67	-	6.9
0.70	17.3	7.6
0.72	17.8	7.7
0.75	-	7.9
0.78	-	8.0

Figure 3

Effect of compensation circuit on polarogram

(a) Polarogram obtained without compensation circuit.

(b) Polarogram obtained with compensation circuit.


GALV. DEFLECTION (CM.)
15
10
5
0
(a)
(b)
0·40
0·50
0·60
0·70
VOLTS

against some standard such as the saturated calomel half-cell is spoken of as the half wave potential.

The method of measuring the step height (61) is also shown on curve (b) of Fig.3. Lines are drawn along the flat portion of the curve preceding and following the step to be measured. The height between these lines is then measured along the vertical line drawn through the mid-point of the step. The step height of this particular wave corresponds to an increase of galvanometer deflection of 2.8 cm. This step was shown later to be due to the presence of cadmium in solution since subsequent addition of cadmium to the solution resulted in an increase in the step height at this potential. Similarly, the preceding step was shown to be due to lead.

With the compensation device included in the circuit, adjustment was possible so that the flat portions of the polarograms between the steps were nearly horizontal. The step heights were then more readily and accurately measured. Consequently, the polarograph with the included compensation device was used for all subsequent measurements.

Reproducibility of the polarograph

Although the removal of oxygen from solutions is necessary, the importance of removing the last traces of oxygen is not stressed in most procedure dealing with the polarographic analysis of lead in zinc. Perhaps this is due to the use in many cases of recording instruments in which only a very short period of time is required to complete an analysis. However, it was found that practically complete removal of oxygen from solutions was necessary for an analysis using a manually operated polarograph. This point is brought out in the following experiments.

Commercial nitrogen directly from a tank was bubbled through a zinc chloride solution for 15 minutes and over the solution during the remainder of the operations. The applied potential across the polarographic cell was fixed at 0.3 volts and the current through the circuit was noted from time to time. Increase in current, as observed by the position of the hair-line on the galvanometer scale varied from 0.8 to 2.6 cm. during five minute intervals, while the total increase over a one hour period amounted to 18 cm. Similar results were obtained for other applied potentials across the polarographic cell. Increasing the bubbling period up to one hour prior to taking current measurements showed comparable results.

The above experiment was now repeated using the apparatus referred to previously (54) for reducing the oxygen content of nitrogen to a negligible amount. In this experiment the maximum galvanometer deflection over 5 minute periods amounted to only 0.1 cm. for a given applied potential across the polarographic cell circuit.

The interference of oxygen as indicated above was also evident in polarograms obtained using commercial nitrogen directly from the tank. In these instances, no satisfactory determination of lead in zinc was found possible. However, excellent reproducibility of results was obtained using nitrogen, rendered free of oxygen as shown by the following experiment. A polarographic solution was prepared from five ml. of a zinc chloride solution containing 100 grams of zinc per liter. Three polarograms were recorded with this solution, with the results shown in Table II and the curves of Fig.4. The step heights for lead obtained from curves a, b and c are 3.1, 3.0 and 3.0 cm. respectively. The agreement between the various experiments as shown by these curves, where oxygen-free nitrogen was used, indicates the reliability of the polarograph used.

Table II

Reproducibility of results with polarograph

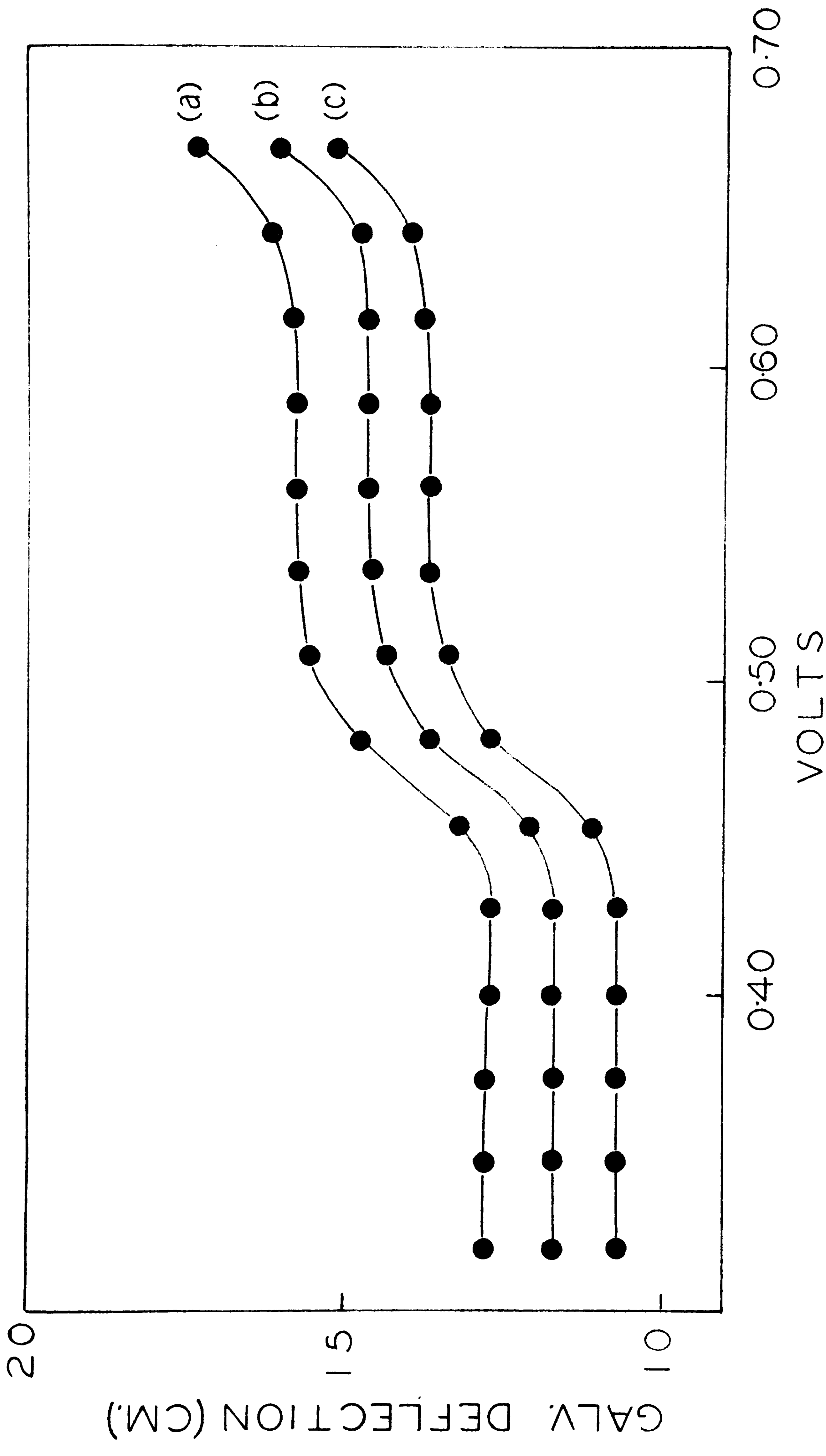
Applied potential (volts)	Galvanometer deflection (cm.)		
	(a)	(b)	(c)
0.32	12.8	11.7	10.7
0.35	12.8	11.7	10.7
0.37	12.8	11.7	10.7
0.40	12.7	11.7	10.7
0.43	12.7	11.7	10.7
0.45	13.2	12.1	11.1
0.48	14.8	13.7	12.7
0.51	15.6	14.4	13.4
0.54	15.8	14.6	13.7
0.56	15.8	14.7	13.7
0.59	15.8	14.7	13.7
0.62	15.9	14.7	13.8
0.64	16.2	14.8	14.0
0.67	17.4	16.1	15.2

Figure 4

Reproducibility of Polarograph

Legend

(a), (b) and (c) Consecutive polarograms


GALV. DEFLECTION (CM.)
20
15
10
VOLTS
0·40
0·50
0·60
0·70
(a)
(b)
(c)

Calibration of the polarograph

A 100 gram sample of Tadanac zinc was dissolved in 400 ml. of concentrated hydrochloric acid, cooled, and the volume made up to 390 ml. To four separate 39 ml. portions of this solution was added respectively 1 ml. of a 0.1% lead solution (B), 1 ml. of a 0.2% lead solution (C), 1 ml. of a 0.3% lead solution (D), and 1 ml. of a 0.4% lead solution (E). To the remaining 234 ml. was added 6 ml. of distilled water making a total of 240 ml. (A). Solutions (B), (C), (D), (E) represent concentrations of 0.01, 0.02, 0.03 and 0.04% lead with respect to the high purity zinc.

Polarographic solutions were then prepared from these standard solutions by addition of ammonium hydroxide, methyl violet and water. The step height for lead was obtained from the polarograms, recorded in triplicate, of these solutions. For any one determination of the lead step height, the deviation was found to be less than 2% of the average value in the lower concentration range and less than 0.5% in the higher concentration range.

In Table III are given the lead step heights for the five standard solutions as well as for solutions containing various proportions of (A) and (B). Calculations from the step heights of these solutions showed that the high purity zinc contained 0.0036% lead. The corrected values of the lead content of the other standard solutions are also given.

Table III

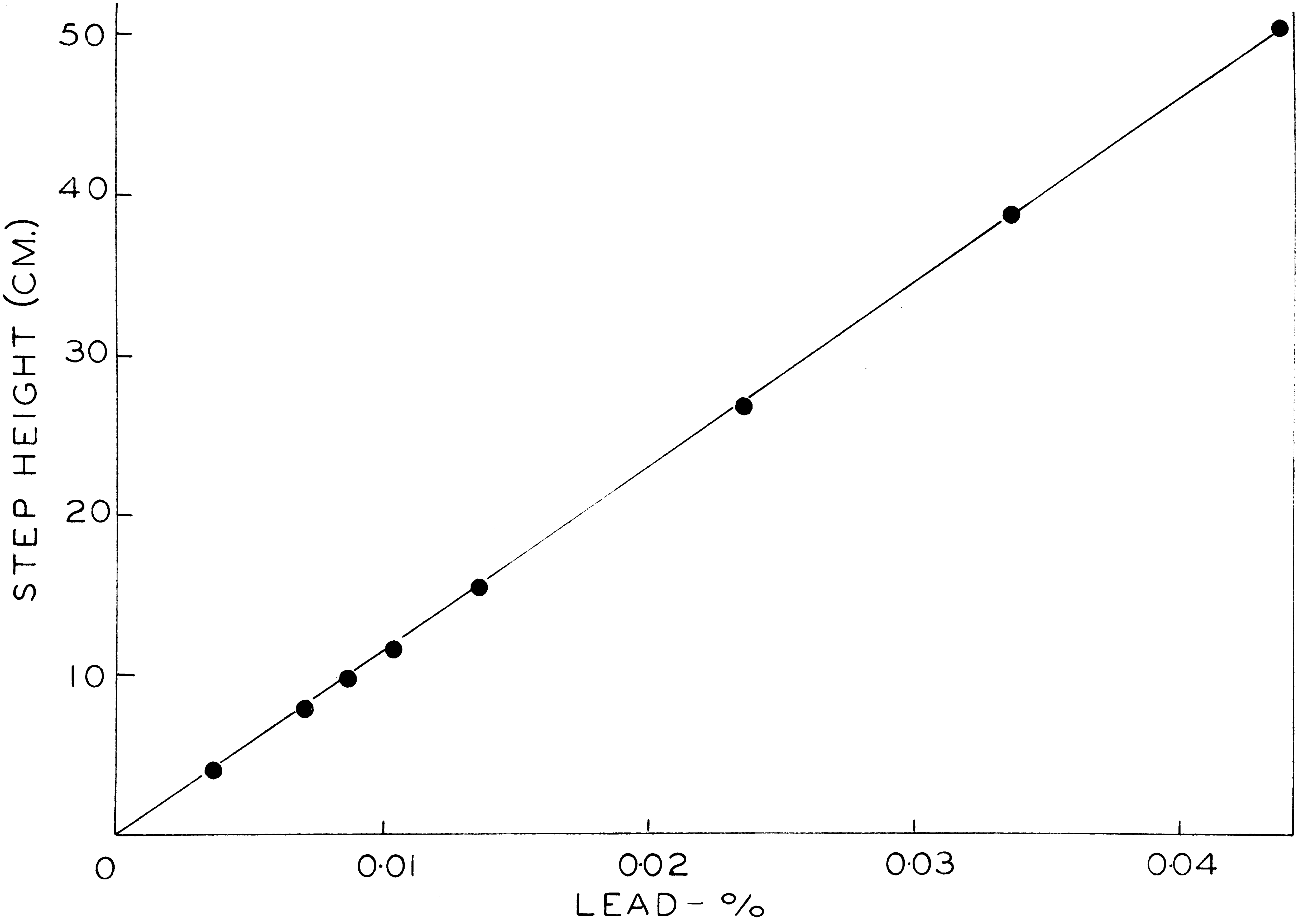
Calibration of polarograph

Solution	Step height	% Lead
A	4.1	0.0036
2A:1B	7.9	0.0070
1A:1B	9.8	0.0086
1A:2B	11.6	0.0103
B	15.6	0.0136
C	27.0	0.0236
D	38.9	0.0336
E	50.6	0.0436

The step height of lead was then plotted against the percentage lead content of zinc in the standard solutions and shown in Fig.5. As shown by the graph, a linear relation was obtained. This linear relation, together with an accuracy of at least 2% obtainable from a single polarogram, showed the polarograph to be admirably suited for the determination of small amounts of lead.

Figure 5

Calibration chart for polarograph



50
40
30
20
10
STEP HEIGHT (CM.)
0
0·01
0·02
0·03
0·04
LEAD - %

ELECTROLYTIC APPARATUS

Electrolytic cells

Glass battery jars 9.5 x 9.5 x 19 cm. were selected for electrolytic cells. Into one side of each jar, 2.5 cm. from the top was drilled a small hole into which was sealed a short length of glass tube which served as an overflow pipe. This tube allowed a constant level of solution to be maintained in the cell when a continuous flow of electrolyte was used. The dropwise inflow of fresh feed electrolyte from a 20 liter aspirator bottle was regulated by a hosecock clamp and glass stopcock.

In certain experiments, the cathode was enclosed in various diaphragms. In these cases, the electrodes were placed in plain battery jars and a siphon from the cathode compartment led to a battery jar containing an overflow pipe. By this method, catholyte overflow was obtained and the solution in the electrolytic cell maintained at a constant level with a constant flowing electrolyte.

The above cells were employed when the stirring of the electrolyte was obtained by the evolution of gas at the electrodes. When an electric motor was used to give additional stirring, an oblong glass battery jar was employed. This jar measured 9.8 cm. x 22.5 cm. x 18.5 cm. high and contained an overflow pipe as above.

The electrolyte was prepared by addition of excess grade

"A" zinc to dilute C.P. sulphuric acid, containing some copper sulphate to hasten solution, in 20 liter carboys. The solution was stirred at intervals and allowed to stand until the sulphuric acid had all reacted. The presence of excess zinc, with its high position in the e.m.f. series of elements, removed the copper from solution together with lead, cadmium and other impurities initially present in the zinc. The resulting filtered solution containing approximately 150 gm. per liter of zinc was titrated with standardized potassium ferrocyanide. From this zinc sulphate solution was prepared both the cell electrolyte and the feed electrolyte.

The standard cell electrolyte was made up to contain 57 gm. per liter of zinc as sulphate and 105 gm. per liter of free sulphuric acid. The standard feed electrolyte contained 127 gm. per liter of zinc as sulphate and was thus equivalent to the cell electrolyte in sulphate ion. With these solutions, it was then possible to adjust the rate of inflow, during electrolysis, so that the reduction of zinc content of the added solution from 127 to 57 gm. per liter of zinc was equal to the weight of the zinc deposited. This decrease in zinc content generated free sulphuric acid equal to 105 gm. per liter so that all tests were made in a bath of constant composition in respect of zinc and sulphuric acid.

Electrodes

Each electrode was T-shaped so that lugs at the top rested on the top edges of the electrolytic cell. Electrical connection to the electrodes was made at the ends of these lugs, removed from any corrosive spray from the cell electrolyte. Each cell contained one cathode midway between two anodes, with a three inch spacing between anode faces obtained by two pieces of slotted lucite placed above and resting on the electrodes.

Cathodes were 20 gauge aluminium sheets, each 9 cm. wide at the level of the solution and submerged to a depth of 10.5 cm. A small bore, thin walled rubber tube, slit lengthwise, fitted snugly around the edge of the cathode so that during electrolysis, zinc deposited only on the faces of the cathode and not along its edges, thus facilitating removal of the zinc deposit. A short interval of immersion of the cathode in electrolyte (2) before making electrical contact was also found to make the deposit strip from the cathode more readily.

The T-shaped lead anodes were 7.6 cm. wide at the level of the solution and submerged to a depth of 9.4 cm.

Four types of anodes were used. One of these consisted of pure lead foil. The remaining three types were prepared from rolled lead sheet 0.5 cm. thick, and were of pure lead, lead containing 0.7% silver, and lead containing 0.7% silver and a trace amount of radium D. The rolled lead anodes were obtained from the Consolidated Mining and Smelting Company of Canada.

Power to the electrodes was from the 110 volt d-c. mains. The cells were connected in series with an ammeter, a 10 ohm fixed resistor and a 7 ohm variable resistor. This circuit enabled regulation of the cathode current density to 40 amp. per sq. ft. when the anodes were placed three inches apart.

RADIOACTIVITY

Measuring Instruments

When anodes contained radioactive lead, the zinc deposit became radioactive due to transported lead. A counting device was required to measure the radioactivity of the deposit. A model 161 Scaling Unit from the Instrument Development Laboratories was employed in conjunction with two types of counter tubes. A mica window counter tube from the National Research Council Laboratories, Atomic Energy Project, Chalk River, was used for samples of metallic zinc containing radioactive lead. For solutions of zinc, a dip type G.M. counter tube from Herbach and Rademan Inc. was connected to the scaling unit. The dipping Geiger tube was sealed to a ground glass joint fitting into an outer glass vessel which contained a measured volume of radioactive solution. This arrangement provided a constant depth of immersion of the dipping Geiger tube in the solution.

Preparation of radioactive lead anodes

It was hoped to follow the transport of lead by the use of radioactive lead anodes as well as by polarographic analysis. For this purpose, a vial containing two millicuries of radium D in the form of the nitrate was procured from the Eldorado Mining and Refining Limited. It was the intention to incorporate the microscopic amount of radioactive salt obtained into a cathode by electrodeposition from a solution containing the radioactive material in the presence of a larger concentration of inactive lead. The cathode deposit containing both active and inactive lead could then be mixed uniformly with sufficient molten lead to form suitable radioactive anodes.

Since nitric acid was required to dissolve and remove the radium D nitrate from its original container, preliminary experiments were made to determine the effect on a lead deposit with nitric acid in the electrolyte. Tree-like deposits were to be avoided since this might give rise to loss of radium D due to mechanical breakage or subsequent oxidation of these projections.

An electrolyte for deposition of lead (62) was prepared containing 150 g. per liter of basic lead carbonate, 240 g. per liter of 40% hydrofluoric acid, 106 g. per liter of boric acid and 0.2 g. per liter of gelatin. Cylindrical electrodes 15 cm. in length and 1 cm. in diameter were cast from Grade A lead. A hard rubber battery jar served for the electrolytic cell.

With a cathode current density of 11.5 amp. per sq. ft., it was found that needle-like crystals were produced on the cathode when as little as 0.65 ml. of concentrated nitric acid was present per liter of electrolyte. When the amount of nitric acid in the electrolyte was reduced to four drops per liter, a smooth lead deposit was obtained.

With the information from the above experiments, the following procedure was adopted. To the vial containing the almost invisible amount of radium D nitrate was added three drops of warm concentrated nitric acid to dissolve the crystals. The vial was carefully rotated to bring the acid into contact with its entire inner surface, and the contents removed to a beaker by repeated washing with distilled water. The washing was continued until the Geiger counter showed that the vial no longer contained a significant amount of radium D nitrate.

The fluoborate electrolyte was prepared using the wash water containing the radium D nitrate. Lead electrodes were inserted and the cell operated at an initial cathode current density of 11.5 amps. per sq. ft. Owing to the increasing size of the cathode during deposition, the cathode current density decreased with time. A drop of cell electrolyte was removed periodically, placed on a filter paper, and its radioactivity measured by a Geiger counter. Electrodeposition of lead was continued until the electrolyte had lost its radioactivity, i.e. until the radium D nitrate in solution had been deposited on the cathode as lead.

The lead cathode was dissolved in molten lead to distribute the radioactive lead evenly throughout the entire mass. This lead was sent to the Consolidated Mining and Smelting Company of Canada, Limited for incorporation of 0.72% silver and fabrication into rolled lead anodes for subsequent work at this laboratory.

RESULTS

RADIOACTIVITY OF ZINC DEPOSITS

Measurements of radioactivity

A series of electrodepositions were made using the radioactive lead anodes. The square type of electrolytic cell was initially filled with standard electrolyte. An aluminium cathode was brushed with steel wool, and rinsed off in distilled water before use in each experiment. The cathode current density was maintained at 40 amps. per sq. ft. Standard feed electrolyte was added during electrolysis and convection currents due to evolution of gas at the electrodes served to stir the electrolyte. Electrolysis was carried on for periods of time ranging from 1 1/2 to 3 hours.

At the conclusion of each electrolysis, the cathode was immediately removed, washed in distilled water and dried. The zinc deposit on each side of the cathode was readily removed. From the top, centre, or bottom portions of the deposit were obtained 5.00 gram samples of zinc which were dissolved in hydrochloric acid, as well as circular zinc discs of 27 mm. diameter. The 20 ml. of zinc chloride solution obtained from each 5.00 gram sample provided sufficient volume of solution for analysis both by the polarograph and the dipping type Geiger tube. The circular zinc discs punched from the deposit were used with the mica window Geiger tube.

The various experiments involved electrodeposition at intervals over a period of two weeks. Between experiments, the radioactive lead anodes remained in position in the cell electrolyte. During this time, since a fresh solution was not used for each experiment, the cell electrolyte became saturated or nearly so with lead.

Initial radioactivity measurements were made using a dipping Geiger tube. By employing a solution, a perfectly uniform sample could be obtained, with no variations between samples due to possible differences in extent of surface oxidation or in crystal structure such as might occur with solid samples. A 5.0 ml. sample of solution was placed in an outer glass tube, into which was fitted the dipping Geiger tube.

When counts were taken on the solution for ten minute periods, the dipping Geiger tube appeared satisfactory. However, owing to the low radioactive lead concentration of the solution, a counting period of at least one hour was found to be necessary. When this period of time was used, the dipping Geiger tube gave quite erratic results. Subsequent information obtained from other research investigators revealed a lack of consistent results with dipping Geiger tubes, and the use of this type of tube was discontinued.

The circular discs obtained from the electrodeposited zinc were placed at a fixed distance and directly under a mica window Geiger tube connected to a scaling unit which recorded the radioactivity of the disc. The 5.00 gram samples of zinc for polarographic analysis were obtained from portions of the deposit immediately surrounding the disc. Polarograms were recorded for each sample, and the percentage lead content of the deposit obtained by reference to the calibration curve. A comparison of the percentage lead content of the zinc and the radioactivity of the deposit is given in Table IV.

Since the radioactivity of a sample changed with time, as will subsequently be shown, the number of days that had elapsed between electrodeposition and the measurement of radioactivity of the sample is also given in Table IV. From the table, it is seen that for the various samples the ratio of the counts per minute to the percentage lead content, although always of the same order of magnitude, is not constant. Furthermore, for a given number of days between deposition and counting, the variations in the value of this ratio were of considerable magnitude, so that a single measurement of the radioactivity could not be taken as a measure of the lead content of a sample.

Table IV

Radioactivity of samples compared with lead content

Percent lead	Days between deposition and counting	Counts per minute	$\frac{\text{Counts per min.}}{\text{Percent lead}}$
0.008	7	15	1.8×10^3
0.008	7	11	1.3×10^3
0.024	7	54	2.3×10^3
0.034	7	77	2.2×10^3
0.017	3	78	4.6×10^3
0.017	3	79	4.6×10^3
0.028	2	96	3.4×10^3
0.019	2	40	2.1×10^3
0.037	2	93	2.5×10^3
0.030	2	46	1.5×10^3
0.018	3	44	2.5×10^3
0.016	3	30	1.9×10^3
0.018	3	32	1.8×10^3
0.016	3	45	2.8×10^3

The amount of radioactive material going into the deposit was greater at the beginning of electrodeposition than at later stages of deposition. This was readily shown by comparing the radioactivity of both sides of a circular disc taken from the deposit. When the surface of the disc adjacent to the cathode face during electrodeposition was exposed to the counter tube, a certain count was obtained. When the outer or opposite surface of the same disc was exposed to the counter tube, a lower count always resulted. A few typical values for three separate discs are shown in Table V. Another generality brought out by this Table and particularly by Table VI that the ratio of the radioactivity of the inner to outer sides of a sample was decreased by increasing the interval of time between deposition and radioactivity measurements.

Table VI shows a typical example of the change in radioactivity with time elapsed between electrodeposition and counting. The radioactivity was found to decrease rapidly at first and then approach a steady value. This trend was observed when either the inner or outer surface of the disc was exposed to the counter tube.

Table V

Comparison of radioactivity of two surfaces of zinc deposits

Days between deposition and counting	8	30	35
Inner surface; Counts per minute	314	30	45
Outer surface; Counts per minute	61	23	27

Table VI

Change of radioactivity of a sample disc with time

Time in days between plating and counting	2	8	9	25	28
Inner surface; Counts per minute	-	314	284	109	102
Outer surface; Counts per minute	96	61	58	-	29

Comments on measurements of radioactivity

Radium D, an isotope of lead, with a half-life of 22 years and energies of radiation of 0.026 and 0.047 Mev respectively for its β^- particles and γ rays, changes into radium E which has a half-life of 5 days and an energy of radiation of 1.17 Mev for its β^- particles and changes into radium F. Radium F, with a half-life of 136 days, emits α particles and weak γ rays to decompose into stable lead.

Of the above radioactive series, only the radium E emits radiation of sufficient energy to penetrate the window of the Geiger tube and permit counting. Hence, starting with a pure sample of radium D, the radioactivity as measured by the counter, would increase as radium E was being formed. The measured radioactivity would not however increase indefinitely. Instead, since the radium E being formed decomposes into radium F, an equilibrium value for the radioactivity is obtained.

The number of atoms N_2 of radium E, with a disintegration constant λ_2, formed in time t from the number of atoms N_1 of radium D, the long lived parent element, with a disintegration constant λ_1, is given by the equation:

$$N_2 = N_1 \frac{\lambda_1}{\lambda_2} \left(1 - e^{-\lambda_2 t}\right) \qquad (1)$$

while the relation between the amounts of radium D and radium E present at equilibrium is given by the equation:

$$N_2 = N_1 \frac{\lambda_1}{\lambda_2} \qquad (2)$$

The latter equation shows that at equilibrium the radioactivity of a sample of the zinc deposit should be proportional to the amount of radioactive lead and consequently proportional to the total lead present in the deposit.

Table VII

Establishment of radioactive equilibrium from initially pure radium D

% of equilibrium value	0	50	80	90	99	99.9
Time in days	0	5	11.5	16.5	33.1	49.7

In Table VII several values are given calculated from equation (I) to show how equilibrium is attained with time. Thus, starting with a given amount of pure radium D, a time interval of 33.1 days is required for 99% of the equilibrium value for the radium D-radium E mixture be established.

The radioactive anodes containing radium D were fabricated two months prior to use in electrolysis so that the radium D-radium E equilibrium may be considered established as indicated by Table VII. The half-life of radium D being 22 years assures practically constant radioactivity of the anodes during the time in which the experiments were made. On electrolysis, besides the ordinary lead of the anode, small amounts of radium D and radium E may be expected to be transported to the cathode. In addition, it is reasonable to suppose that the proportion of radium D (the isotope of lead) in the transported lead is the same as the proportion of radium D in the anode.

When only radium D, is transported with ordinary lead to the cathode, the Geiger counter (which responded only to radium E) would indicate increasing radioactivity with time until equilibrium between radium D and radium E is established, as given by equation 1 and table VII. Conversely, if only radium E and no radium D were carried to the cathode, the radioactivity would decrease by one half every 5 days until practically no radioactivity remained. The experimental results show that neither of the above conditions were fulfilled.

If radium D and radium E are transported to the cathode in amounts corresponding to their equilibrium concentrations, the radioactivity of the zinc deposit, as measured by the Geiger counter, would remain practically constant for a considerable period of time. Moreover, the extent of this radioactivity would be a measure of the lead content of the zinc sample. Had such conditions prevailed during electrolysis, this method would have provided a very simple and rapid means of analyzing the zinc samples for their lead content. Since the radioactivity of the samples did not remain constant, it is clear that radium D and radium E were not transported in amounts proportional to their equilibrium concentrations.

If, now, both radium D and radium E were transported during electrolysis, but the ratio of radium E to radium D transported to the cathode were greater than that corresponding to equilibrium in the anode, the radioactivity of zinc samples, as determined with the Geiger counter, would initially decrease and finally reach some steady value. The above conditions were obviously those that actually existed during electrolysis. Such being the case, the shape of curves for the radioactivity of zinc samples with time would be dependent upon the ratio of the amounts of radium D and radium E carried to the deposit. The radioactivity of the sample after equilibrium had been reached however would be a measure of the radium D and hence of total lead carried to the deposit. Unfortunately, the time required to reach equilibrium made radioactivity measurements unsuitable for routine analysis of lead in the samples of zinc.

Some interesting points have, however, been revealed by the Geiger counter experiments. Radium E or bismuth is transported more readily from the anode to cathode than radium D or lead. Also the radioactivity of samples depends upon which surface of the deposit is exposed to the counter tube, and not upon the average lead content of the sample. Since there was greater radioactivity on the inner surface of the deposit, lead appears to have been deposited initially at a greater rate than at the end of the electrolysis period. This observation could be used if desired to record changes in the rate of lead deposition on the cathode during short periods of electrolysis.

EFFECT OF FILTERS ON LEAD CONTENT OF CATHODE ZINC

Silver-lead anodes

Several series of experiments were made to determine the effect of filters on the lead content of electrodeposited zinc. In the second series were studied the effects caused by contamination of the electrolyte, by mechanical agitation, by changes in catholyte volume and by changes in the type of anode.

In the previous experiments with radioactive silver-lead anodes, considerable variations in the lead content were obtained as shown in Table IV. This was believed due in part to differences in the extent to which the peroxide coating became detached from the anodes while immersed in the cell electrolyte between experiments. Consequently, in all following experiments, except where specifically noted, the silver-lead anodes were brushed with steel wool or emery paper and then rinsed off by a jet of water just prior to their use in each experiment.

In the first series of experiments, with the use of filters, the cathodes were enclosed in small bags of either light vinyon #2 or heavy vinyon #17 fabric. Electrolysis was carried on for periods ranging from 1 1/4 to 3 hours to give deposits which were readily removed from the cathode. Both the anodes and the cathode were removed from the cell after each experiment while the electrolyte remaining in the cell was used for subsequent experiments. The 5.00 gram samples were taken from the central part of the deposits, generally 2.50 grams from each side, and their lead content was determined polarographically. The results are given in Table VIII.

From Table VIII it is evident that by the use of filters, the lead content of the zinc was reduced by approximately one third regardless of whether the light vinyon #2 or the heavy vinyon #17 fabric was used.

These results also show that the use of filters decreased the current efficiency, the effect being much more marked with the heavier filter. During electrolysis, the concentration of the zinc was in the catholyte decreased owing to electrodeposition of zinc, since the fabric, in addition to its filter effect, also prevented the free flow of cell electrolyte to the immediate vicinity of the cathode. This decrease in the zinc concentration of the catholyte was undoubtedly responsible for the decreased plating efficiency.

Table VIII

Effect of cathode filters on lead content of cathode zinc

	Current efficiency %	Lead content %
(a) No filter	93	0.021
	88	0.017
	84	0.025
		0.016
	85	0.018
Av.	87	0.019
(b) Vinyon #2		0.014
		0.021
	84	0.010
		0.010
	81	0.013
		0.009
Av.	83	0.013
(c) Vinyon #17		0.013
	48	0.011
	40	0.013
		0.014
Av.	44	0.013

Such behaviour obviously has an important bearing on the interpretation of the results obtained, since if free exchange of zinc ions between the inside and outside of the filter cannot occur, so also must the corresponding exchange of lead ions be hindered. Hence, it is not possible to infer the extent to which contamination of the deposit would occur under normal conditions of unhindered access of these ions to the cathode.

With a view to determining the effectiveness of the filter in reducing the lead content of the deposit under more nearly normal operating conditions, an attempt was made to maintain the catholyte zinc concentration by vigorous agitation with an electric stirrer. To provide sufficient space for the electric stirrer the larger oblong type of electrolytic cell was employed. Three different cathodes were used in the experiment, one of which was not surrounded by a filter bag, while the other two were enclosed in vinyon #2 and Vinyon #17 filter bags respectively. The filter bags were made to confine a smaller volume of electrolyte than in the previous experiment. The cathodes were connected in rotation into the electrical circuit between two silver-lead anodes for approximately fifteen minute periods, the procedure being repeated until a sufficiently large deposit of zinc for analysis was obtained. The two cathodes not in use at any time were suspended in the electrolyte at the opposite end of the cell to which the cathode in use was placed. Polarograms were obtained from the various 5.00 gram samples obtained from the central part of the deposit from each cathode face with the results shown in Table IX.

Table IX

Effect of vinyon filters and mechanical agitation

Type of filter around cathode	Current efficiency %	Lead content of cathode %	Average lead content of cathode %
No filter	85	0.0320 0.0362	0.034
Vinyon #2	54	0.0308 0.0214	0.026
Vinyon #17	25	0.0152 0.0131	0.014

Apparently, mechanical agitation of the electrolyte was inadequate to maintain high current efficiency when filters were used, but did promote a higher lead content in the zinc deposit. It is also apparent that, with vigorous agitation, the coarse filter was less effective than the fine filter in reducing the lead content of the zinc. On the other hand, the effectiveness of the fine filter was essentially independent of the conditions of agitation.

The marked increase in lead content of the unprotected cathode and of the cathode surrounded by the coarse (#2) filter, with increased vigour of agitation, would result directly from the larger amount of anode coating material kept in suspension under such conditions. The unprotected cathode would be subject to contamination by particles of all sizes in the suspension, the coarser of which separated out under normal conditions of operation, i.e. with agitation due to gas evolution only. With the coarse filter, exclusion of the coarser material from the cathode would reduce the contamination as observed, but penetration of finer particles which normally were not in suspension apparently occurred to increase the lead content above that observed with milder agitation. The fact that no significant increase in lead content of the deposit occurred with vigorous agitation when the cathode was surrounded by the fine filter (#17) would seem to imply that the contamination in this case was due to particles too small to settle out even in the mildly agitated electrolyte and small enough to pass through the tightly woven #17 filter, together with colloidal material and ions.

If the amount of lead in the zinc deposited on the unprotected cathode is taken as reference, then about 25% of this amount was due to particles too large to pass through the vinyon #2 filter, 35% due to particles small enough to pass through the vinyon #2 but not the vinyon #17, while the remaining 40% was due to still smaller particles, i.e. colloids or ions

In a further attempt to increase the current efficiency when filters were used, an increase in catholyte volume was sought by enclosing the anodes rather than the cathodes in filter bags. In this way the catholyte volume was retained at almost the total volume of the cell used (9.5 cm. x 9.5 cm. x 19 cm.).

For each experiment there was used fresh cell electrolyte, the circulation of which was maintained by evolution of gases at the electrodes. In these three hour experiments the feed electrolyte was dropped on the surface of the anolyte within the filter bag so that the arrangement provided anolyte feed and catholyte overflow. In one series of experiments however, cellophane filters were used and feed electrolyte was added to the catholyte. Three thicknesses of cellophane were required since a single layer tended to disintegrate. In Table X are presented the percentage lead contents of these deposits, along with current efficiencies.

The results in Table X show that the high current efficiency obtained when no filters were used was somewhat reduced when the anode was enclosed in vinyon filters with

Table X

Lead content of cathode zinc using anode filters

Type of anode filter	Current efficiency %	Lead content %
No filter	93	0.0086 ; 0.0099
		0.0089 ; 0.0104
	91	0.0109 ; 0.0108
		0.0123 ; 0.0106
Av.	92	0.0103
Vinyon #2	82	0.0063 ; 0.0080
		0.0066 ; 0.0086
	81	0.0046 ; 0.0073
		0.0052 ; 0.0080
Av.	82	0.0068
Vinyon #17	77	0.0050 ; 0.0056
	80	0.0049 ; 0.0059
		0.0046
Av.	79	0.0052
Cellophane	87	0.0032 ; 0.0038
		0.0030 ; 0.0034
	89	0.0033 ; 0.0046
		0.0030 ; 0.0036
Av.	88	0.0035

anolyte feed. However, the much greater catholyte volume in these experiments prevented the drastic decrease in current efficiency observed in previous experiments. As indicated by the results with the cellophane filters, the decrease in current efficiency can be further minimized, apparently, by adding the feed electrolyte to the surface of the catholyte, in a manner similar to that when no filters were used.

The lead content of the electrodeposited zinc was decreased by the use of filters around the anodes in all the experiments. Approximately 35% of the total lead occurring in the deposit when no filters were used was due to lead in a form capable of passing through cellophane and presumably ions (this figure includes any lead initially in the cell electrolyte). An additional 15% was due to colloidal material or fine particles coming from the anode and capable of passing through the heavy vinyon #17 filter but not through cellophane while another 15% was due to somewhat larger particles which could pass through the vinyon #2 filter. The remaining 35% of the lead content consisted of still larger particles which could pass none of the filters.

Pure lead anodes

In previous experiments the anodes were a lead alloy containing 0.7% silver. The use of alloy anodes of similar composition in place of pure lead anodes has been reported in the literature (31-33,39) as an aid in reducing the lead content of electrodeposited zinc. It seemed of interest to repeat the previous experiments with lead anodes containing no silver, since by so doing it was not only possible that the effects of filtering might be accentuated, but it was hoped that some information might be obtained about the manner in which the presence of silver reduces contamination of the deposited zinc.

The rolled lead anodes employed in these experiments were similar to those previously used except for the absence of silver. Electrolysis, using different type of filters was carried on for 4 1/4 hours, the data from these experiments being tabulated in Table XI. With continued use of the heavy rolled pure lead anodes, the anode surface became quite uneven owing to different erosion rates from various parts of the surface during electrolysis. To obtain a reproducible anode surface and possibly more consistent values for lead content of the electrodeposited zinc, a number of anodes were prepared from a roll of gold assay lead foil, new anodes being used for each experiment. Table XII shows the data for experiments with these anodes with and without filters, the time of electrolysis in each case being 4 1/4 hours.

In a further attempt to obtain more reproducible results an experiment was made in duplicate using rolled lead anodes, with electrolysis continued for a total time of

Table XI

Effect of filters on lead content using rolled lead anodes

Type of anode filter	Lead content of zinc %	Average lead content of zinc %
No filter	0.0276	
	0.0155	
	0.0221	0.023
	0.0336	
	0.0142	
Vinyon #2	0.0167	0.017
	0.0169	
Cellophane	0.0059	0.005
	0.0046	

Table XII

Effect of filters on lead content using lead foil anodes

Type of anode filter	Lead content of zinc %	Average lead content of zinc %
No filter	0.0448	0.044
	0.0691	
	0.0198	
	0.0302	
Vinyon #17	0.0153	0.014
	0.0126	
	0.0135	
	0.0128	
	0.0156	
	0.0138	

Table XII

Progressive change in lead content of zinc from rolled lead anodes

Deposition time hr.	Total time hr.	Lead content of zinc - %	
		Cell A	Cell B
1.0	1.0	0.0253	0.0361
1.0	2.0	0.0388	
1.0	3.0	0.0473	
2.0	5.0	0.0351	0.0630
			0.0727
2.0	7.0	0.0289	0.0398
2.0	9.0	0.0319	0.0323
2.0	11.0	0.0445	0.0288
		0.0595	0.0558
2.0	13.0	0.0386	0.0399
		0.0854	
2.0	15.0	0.0480	0.0582
		0.0627	
2.0	17.0	0.0886	0.0809
		0.0425	0.0362

17 hours. It was considered that by this time behaviour of the anode would be stabilized and zinc deposits with uniform lead content might be obtained. The cathodes were removed

every two hours and replaced by fresh cathodes. The lead analyses of the zinc samples obtained during successive two hour deposition periods are shown in Table XIII.

It seems reasonable to assume that the experiments with cellophane filters show the amount of lead passing from the anode to the cathode in the form of ions. It is of interest that this was approximately the same whether pure lead or silver-lead anodes were used, while with coarser filters or no filters, the lead content of zinc samples obtained with pure lead anodes was much greater than with silver-lead anodes. This is understandable if the initial reactions in both cases is the formation of lead ions and $PbSO_4$, followed by formation of a PbO_2 coating on the surface. Since lead ions are formed in both cases, the amount of lead in the zinc due to ions should be similar with the two types of anodes while that due to peroxide particles should be less for the silver-lead anodes in which further corrosion is inhibited by the silver present.

It was possible to associate quite well the lead content of zinc deposits when pure lead anodes were used, as determined by polarographic analysis, with visual observations during the course of electrodeposition. On electrolysis, the pure lead anodes became covered with a comparatively thick coating of lead peroxide. About one hour after electrodeposition had begun, particles became detached from the anode coating and were seen to form a film over the bottom of the cell. As electrolysis continued the electrolyte became tinged a brown colour from the presence of suspended particles. In these and in certain subsequent experiments, it was found that whenever these visible signs of anode corrosion appeared, the zinc deposit always had a high lead content.

The incorporation of some of these particles from the lead anodes into the cathode deposit undoubtedly gave rise to the increased lead content of the zinc, while variations in the adherence, size and number of these particles was probably the cause of the observed variations in lead content of the zinc in the different experiments.

Graphite anodes

With pure lead anodes, the transport of lead from the anode to the cathode has been shown to be mainly due to the transport of particles rather than ions. Since no actual particles were observable on the washed cathode deposit, it seemed of interest to obtain, if possible, independent evidence for their transport. This was most readily done by substitution of graphite anodes for the lead anodes. Since graphite anodes undergo disintegration in acid sulphate electrolyte, particles of graphite might be expected to be transported to the cathode, where their presence should become immediately evident on dissolution of the zinc in acid.

Graphite blocks (Canadian National Carbon Co., Ltd. of Montreal) with an ash content of 1.5% were cut to regular anode size and placed in dilute hydrochloric acid for two days to leach out impurities. After washing with distilled water, they were placed in a cell and electrodeposition of zinc was continued for a period of three hours.

During electrolysis, the anodes discarded fine particles of graphite which mainly settled out to form a thin black sediment on the bottom of the electrolytic cell. On treating the samples of zinc with hydrochloric acid for polarographic analysis, fine particles of graphite remained undissolved in the reaction flask. This visible evidence that particles were transported from the anode to the cathode and incorporated into the deposit gives added weight to the previous assumption that high lead contents of zinc samples using lead anodes was due largely to the transport of lead peroxide particles.

Four samples of zinc obtained from the deposit were analyzed polarographically for lead content and gave values of 0.0008%, 0.0008%, 0.0012% and 0.0012%. The average value of 0.001% was of course due to lead initially present in the cell and feed electrolyte. From Table X and XI, lead contents of 0.0035% and 0.005% were obtained in zinc deposits when silver-lead and lead anodes respectively were used, enclosed in cellophane. Although the cellophane prevented free circulation between anolyte and catholyte, and hence ready transfer of ions between these, it may now be estimated that lead contents of at least 0.0025% and 0.004% appeared in the two deposits as a result of transport of lead in the form of ions. Similar comparisons may be made for other filters, e.g. from Table XI it appears that lead contents of at least 0.016% may be obtained from lead in the form of particles, colloids or ions capable of passing through a vinyon #2 filter.

Fine filters

In an attempt to distinguish the various size ranges of smaller particles involved in the transport of lead into cathode zinc, the following experiments were made using filters of finer pore sizes than vinyon. Although it is preferable to use anode filters and thus utilize a large catholyte volume to maintain current efficiency, this was not found possible with filter paper owing to its disintegration when placed too close to the anode. In place of anode filters, the cathode was placed within an open-faced lucite frame measuring 5 cm. x 8 cm. x 15 cm. to provide a substantial catholyte volume. The frame was then wrapped with cellophane, parchment paper, and #2 filter paper. Double layers of filter paper were used in two experiments to provide a greater filtering effect. Two new lead foil anodes were used for each experiment, the times of which were varied to determine the effect of time on electrodeposition. Anolyte feed and catholyte overflow was used for the filter paper experiments. The data for the various experiments are given in Table XIV.

Determination of the range of particle sizes of lead reaching the cathode through the various filters is difficult owing to differences in electrolyte circulation between anode and cathode compartments as indicated by the variations in current efficiency. A further difficulty arises from the number of layers of filter materials used in the various experiments. For example (c.f. Table XIV), the use of a double layer of filter paper resulted in a lower lead content of cathode zinc than when a single layer of filter paper was used. This is understandable since the anolyte agitated by oxygen evolution at the anode would facilitate transfer of particles through a single filter, while the relatively quiescent zone between the two filters would deter the transfer of particles through the second filter.

Nevertheless an approximate value for the proportion of lead in various particle sizes reaching the cathode may be obtained. From Table XIV the percentage lead contents of zinc samples obtained after a five hour deposition period were 0.0029, 0.0045 and 0.0055% when cellophane, parchment paper and filter paper respectively were used as filters. If it is considered that in 5 hours the electrolyte would

Table XIV

Lead content of zinc with fine filters

Type of filter	Time of deposition hr	Current Efficiency %	Lead content %	Average lead content %
Cellophane (3 layers)	5	55	0.0027; 0.0037 0.0026; 0.0037	0.0032
		62	0.0023; 0.0025 0.0027; 0.0030	0.0026
	6	48	0.0019; 0.0017 0.0019; 0.0018	0.0018
		50	0.0020; 0.0021 0.0023; 0.0022	0.0022
	12	10	0.0149	0.0149
		15	0.0109	0.0109
Parchment	5	64	0.0046; 0.0044	0.0045
Filter paper	1 1/2	89	0.0026	0.0026
		85	0.0029	0.0029
	4 1/2	86	0.0097; 0.0106	0.0101
		86	0.0097; 0.0095	0.0096
	5	88	0.0054; 0.0056	0.0055
Filter paper (2 layers)	1 1/2	88	0.0023	0.0023
		84	0.0029	0.0029
	4 1/2	82	0.0074; 0.0062	0.0068
		78	0.0063; 0.0068	0.0066

contribute a lead content of 0.001% to the cathode (c.f. experiment with graphite anode) the respective amounts due to that coming from the anodes were 0.0019, 0.0035 and 0.0045%. Of the total lead passing through a filter paper and being deposited on the cathode, at least 40% may be attributed to lead in the form of ions and at least 75% may be attributed to lead capable of passing through parchment paper.

Table XIV shows that the current efficiency using a single filter paper with anolyte feed and catholyte overflow was 88%, a value approximately the same as for previous experiments without the use of filters, which indicates good circulation of electrolyte. The lead content of the zinc deposit in this case was 0.0055% as compared with an average value of around 0.06% for pure lead anodes without filters. That is, the amount of lead transported to the cathode from a lead anode in the form of particles fine enough to pass through filter paper is but a small proportion of the total lead in the zinc deposit.

Table XIV shows that with cellophane filters, the lead content of cathode zinc changed from an average value of 0.002% to 0.013% when the time of electrolysis was extended from 6 to 12 hours. The corresponding current efficiencies (49% and 12%) indicate however the drastic changes in conditions of electrodeposition. The higher lead content on continued electrolysis might result either from a greater rate of deposition of lead relative to zinc or from greater re-solution of zinc in the electrolyte after deposition. The table also shows that the lead content of zinc deposits changed from the average values 0.0028% and 0.0026% to 0.0099% and 0.0067% respectively for experiments with single and double layers of filter paper when electrolysis was extended from 1 1/2 to 4 1/2 hours. This behaviour may be due in part to the factors considered above or, since the current efficiencies were but slightly changed with time, may be due to an increased number of particles produced by the pure lead anodes. The latter explanation appears justified since Table XIII indicates that in the first few hours, pure lead anodes gave higher lead contents to zinc deposits with increasing time.

EFFECT OF TIME ON LEAD CONTENT USING Ag-Pb ANODES

Normal electrolyte

Since the previous experiments with pure lead anodes indicated that the lead content of zinc deposits increased somewhat on continued electrolysis, it was of interest to determine whether silver-lead anodes behaved in a similar manner. An experiment was therefore made in duplicate using silver-lead anodes, the cathode and its zinc deposit being removed and replaced with a new aluminium cathode every hour. Electrodeposition with two cells connected in series, electrically was continued for a total of six hours with the results shown in Table XV and curve (a) of Fig.6.

Table XV

Progressive change in lead content of zinc using silver-lead and platinum anodes

Anode	Deposition time hr.	Total deposition time hr.	Lead content of zinc	
			Cell A %	Cell B %
Silver-lead	0.9	0.9	0.0100	0.0095
	1.1	2.0	0.0085	0.0079
	1.0	3.0	0.0066	0.0069
	1.0	4.0	0.0042	0.0050
	1.0	5.0	0.0043	0.0049
	1.0	6.0	0.0040	0.0046
Platinum	1.0	1.0	0.0009	0.0021
	1.3	2.3	0.0006	
	2.0	3.0		0.0012
	2.3	5.3		0.0009
				0.0008
	3.7	6.0	0.0005	
	1.3	7.3	0.0004	
	2.7	8.0		0.0006
				0.0004
	3.8	11.1	0.0003	
	2.5	13.6	0.0003	
	1.4	15.0	0.0003	

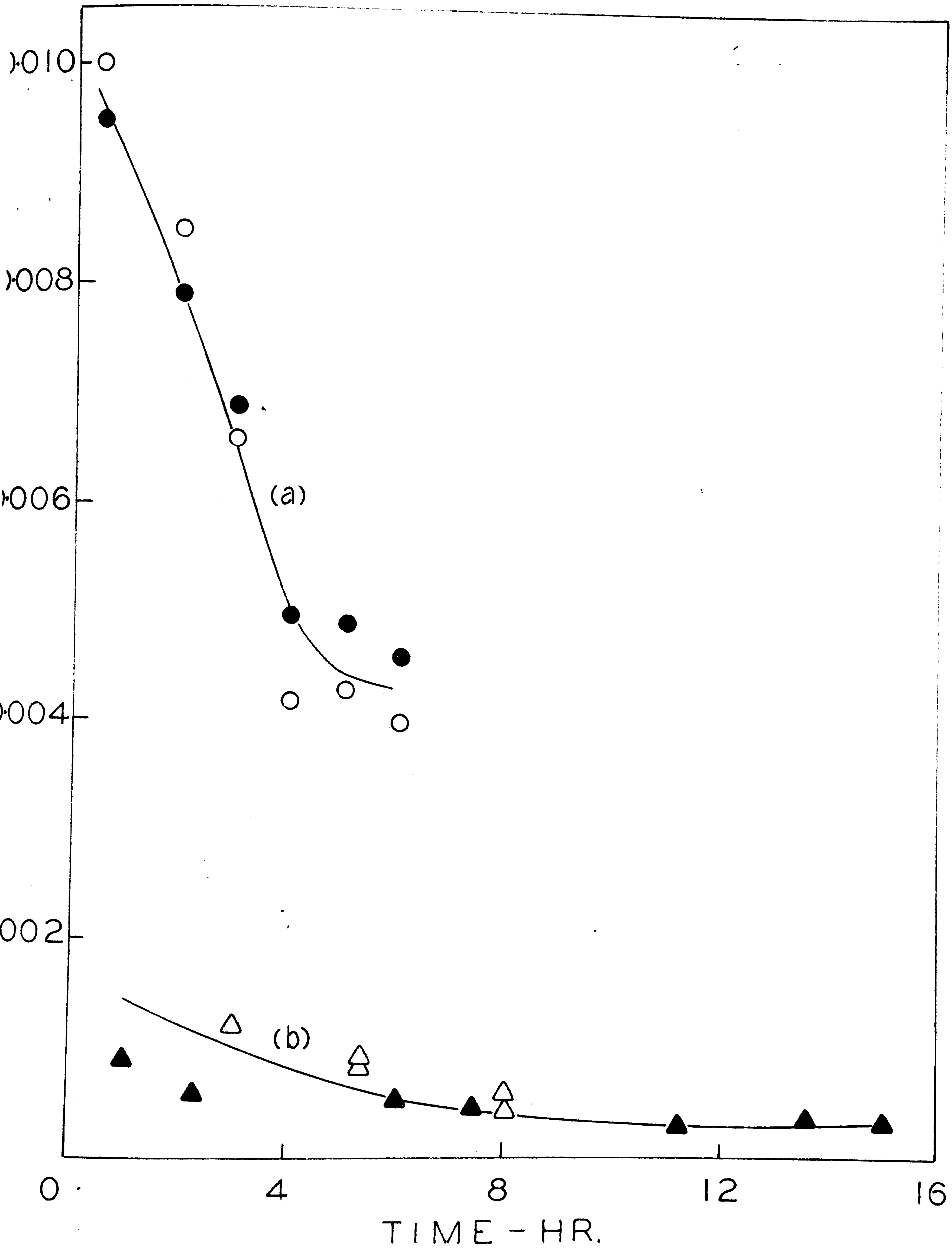
Figure 6

Progressive change in lead content of zinc

Legend

(a) Silver-lead anodes

(b) Platinum anodes


·010
·008
·006
·004
002
(a)
(b)
0
4
8
12
16
TIME - HR.

While it might have been desirable to obtain samples of the zinc deposit shortly after the start of an experiment, this was found to be impractical. The minimum suitable time for electrodeposition on a cathode before replacement with a second cathode was found to be one hour since, with the current density employed, sufficient thickness of deposit to permit its ready removal was obtained only after that time. Shorter deposition periods furnished a very thin deposit which could only be removed with difficulty.

To determine the amount of lead in the zinc deposit as a result of lead initially present in the cell and feed electrolyte, the experiment was repeated using two platinum anodes. Platinum was used instead of graphite to avoid any possible electrolyte contamination originating from the anode. Since only one pair of platinum anodes was available, two separate experiments were made at different times instead of operating two cells in series as previously. Total time of electrolysis for the two experiments was eight hours and fifteen hours respectively. The results of these experiments are given in Table XV and shown graphically in the single curve (b) of Fig.6.

Curve (a) of Fig.6 shows that the lead content of the initial zinc deposits was high, using silver-lead anodes, but that in successive deposits the lead content dropped off quite sharply. After four hours, the rate at which lead deposited on the cathode appeared to level off to a steady value. On the other hand, curve (b) of Fig.6 shows that the lead content of zinc deposited from a cell containing platinum anodes attained only a very small value, namely three parts per million. The somewhat higher values for the lead content at the beginning of the platinum experiments may be attributed to a trace amount of lead impurity initially present on the walls of the electrolytic cell.

The behaviour of silver-lead anodes illustrate very well that they were subject to corrosion at the onset of electrolysis, as a result of which the electrolyte and subsequently the cathode deposit became contaminated. There was naturally a lapse of time before the contamination was removed from the electrolyte by electrodeposition and by overflow of electrolyte from the cell. Meanwhile the layer of lead peroxide, which formed at the anodes and was visible about two minutes after commencement of electrolysis, had formed a partially protective coating over the anode, as a result of which the lead content of the zinc eventually decreased.

Since the protection of the anodes by silver appeared to be incomplete, it became a point of considerable interest to determine whether with the lead peroxide coating present, it retained its partial effectiveness or whether this would be lost when the time of electrolysis was continued for a longer period. An experiment was therefore made in duplicate using silver-lead anodes in two cells operated in series electrically and with other conditions maintained the same as in the previous experiments. In this experiment however the anodes were wrapped in vinyon #2 fabric to study the effect of filters as well as time, on the lead content of zinc during electrodeposition. In Table XVI and Fig.7 are given the results of this extended experiment.

A comparison of the curve of Fig.7 with curve (a) of Fig.6 shows that, as previously the vinyon filter was effective in reducing the lead content of cathode zinc about one-third when electrodeposition was limited to a short period of time of two or three hours. After six hours of electrodeposition however, the curves showing the lead content of zinc deposited with and without the aid of filters approach one another.

The above observations are significant in indicating the behaviour of the anodes. At the commencement of electrolysis, anode lead was converted to lead peroxide which afforded a certain measure of protection to the anode. However, the peroxide coating first formed on the anodes was not uniformly adherent over the entire surface, and particles of this initial coating were shed from the anodes, resulting in a higher lead content of zinc when no filter was used. After a short time, the irregularities in

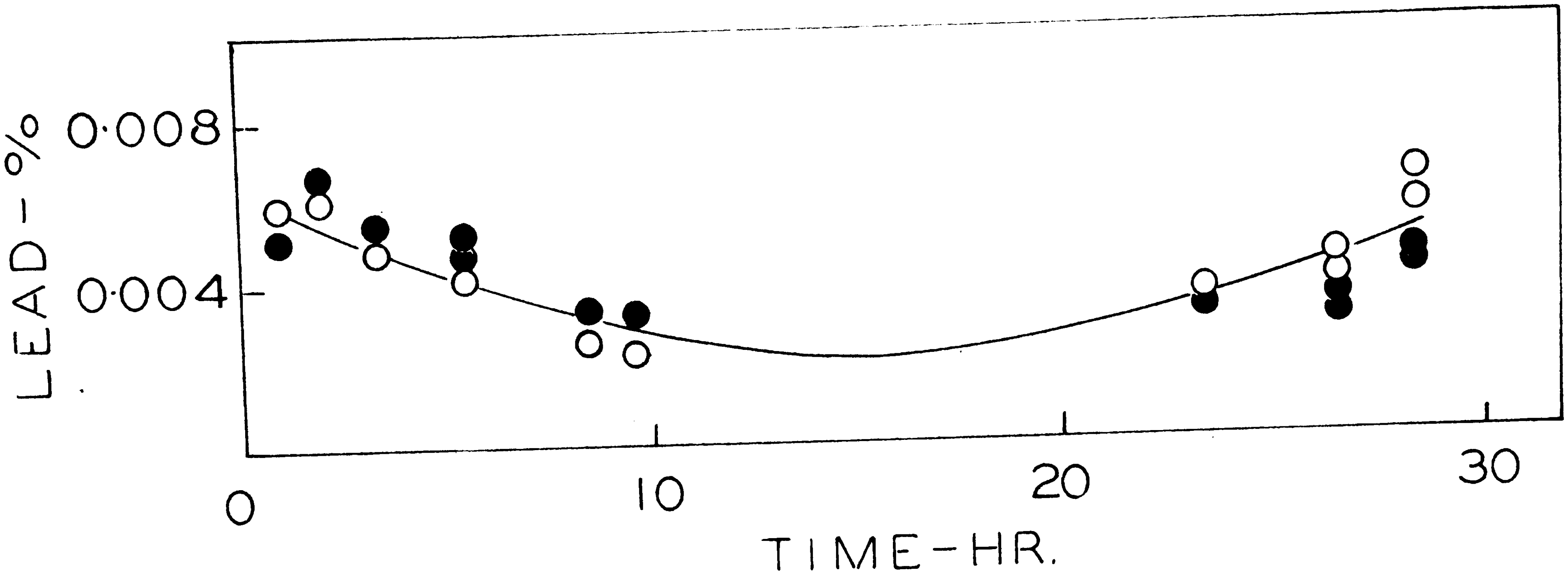
Table XVI

Progressive change in lead content of zinc with silver-lead anodes enclosed in vinyon #2

Deposition time hr.	Total time hr.	Lead content of zinc Cell A %	 Cell B %
1.0	1.0	0.0059	0.0051
1.0	2.0	0.0061	0.0066
1.3	3.3	0.0048	0.0055
2.2	5.5	0.0040	0.0052
		0.0041	0.0047
3.0	8.5	0.0027	0.0034
		0.0026	0.0033
1.2	9.7	0.0023	0.0032
12.0	21.7		
2.0	23.7	0.0035	0.0036
		0.0034	0.0033
3.0	26.7	0.0039	0.0030
		0.0045	0.0034
2.0	28.7	0.0056	0.0041
		0.0063	0.0043

Figure 7

Progressive change in lead content of zinc with silver-lead anodes enclosed in vinyon #2


LEAD - %
0·008
0·004
0
10
20
30
TIME-HR.

adherence of the anode coating apparently disappeared, the coating then offered more uniform protection over the surface of the silver-lead anode, and the beneficial effect of filtering was largely eliminated.

In planning the above experiment it was considered that the twenty-eight hour period of deposition should be more than adequate for conditions in the cell to come to a steady state, beyond which it was thought that the cell would provide zinc deposits with uniform lead content as electrolysis was continued. Consideration of only the first half of the curve in Fig.7 would indicate that steady conditions were attained in the cell. However the data for the last few samples in the experiment showed a tendency towards increasing lead content of the zinc, from which it appeared that the lead content, instead of attaining a steady low value, had passed through a minimum value, to be followed by an increase as electrolysis continued. A further series of experiments was now made to investigate the behaviour of silver-lead anodes during prolonged periods of electrolysis, the results of which will be discussed as a group.

In the first experiment of this series, electrolysis was continued for a total time of forty three hours using an anode that had received the usual surface treatment with emery. An experiment was also made using new rolled anodes, the surface of which were smooth from the rolling operation involved in its fabrication, to compare the relative adherence of the peroxide coating on this and the previous roughened anode. Smooth anodes were next enclosed in vinyon #2 filters to determine the influence of prolonged electrolysis on the effectiveness of such filters.

The results for these various experiments are shown in Tables XVII, XVIII and XIX, and on Figures 8, 9 and 10 respectively. (It might be noted that in these experiments, a fresh stock of feed and cell electrolyte was used.)

The tendency for silver-lead anodes to produce increased contamination of a zinc deposit with prolonged electrolysis is strikingly demonstrated by the results obtained. In all cases, the lead content of successive samples of zinc decreased during the first few hours to a certain minimum value and then progressively increased.

Comparison of Fig.8 and 9 shows that with the smooth anodes not only were the values for the lead content relatively high, but also large differences in lead content were evident for the first few samples of zinc taken for analysis. This presumably was due to initial corrosion of the anode coupled with poor adherence of the resulting thin peroxide coating. Shedding of particles from this thin coating in the initial stages of the experiment would of course expose the underlying anode surface areas to electrolyte and permit further corrosion.

Table XVII

Progressive change in lead content of zinc from rough, rolled silver-lead anodes

Deposition time	Total time	Lead content of Zinc	
		Cell A	Cell B
hr.	hr.	%	%
1.0	1.0	0.0071	0.0069
1.0	2.0	0.0064	0.0062
1.0	3.0	0.0061	0.0059
1.3	4.3	0.0051	0.0051
2.0	6.3	0.0041	0.0040
1.5	7.8	0.0040	0.0034
2.0	9.8	0.0041	0.0040
2.0	11.8	0.0037	0.0044
3.5	15.3	0.0040	0.0044
2.0	17.3	0.0059	0.0054
1.7	19.0	0.0054	0.0058
2.0	21.0	0.0086	0.0083
2.0	23.0	0.0080	0.0102
2.0	25.0	0.0121	0.0120
2.0	27.0	0.0083	0.0091
2.0	29.0	0.0082	0.0127
2.0	31.0	0.0087	0.0104
2.0	33.0	0.0116	0.0202
2.0	35.0	0.0119	0.0141
2.0	37.0	0.0176	0.0188
2.0	39.0	0.0191	0.0276
2.0	41.0	0.0303	0.0226
2.0	43.0	0.0251	0.0238

Figure 8

Progressive change in lead content of zinc from rough, rolled silver-lead anodes

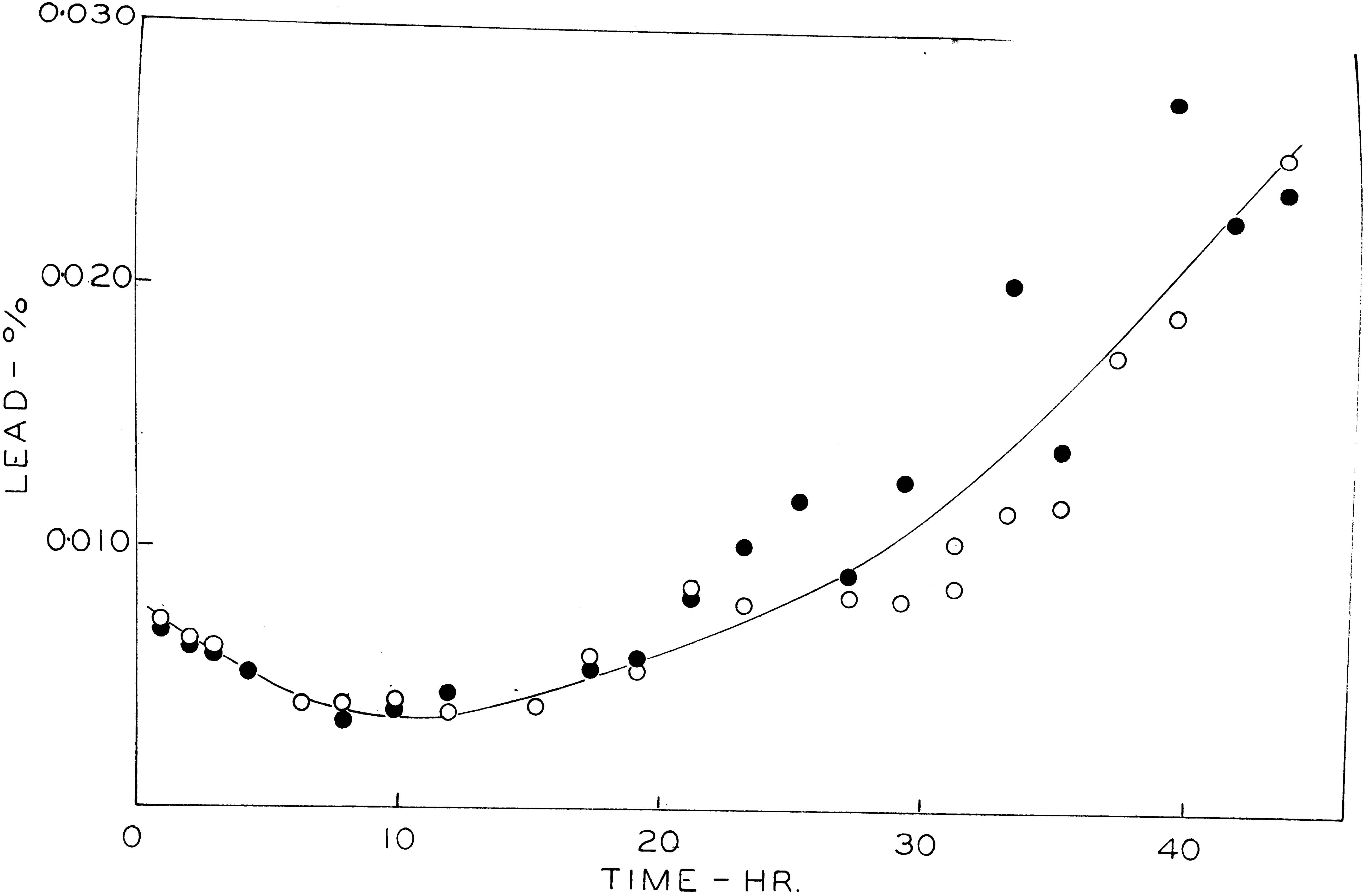

0·030
0·020
0·010
LEAD - %
0
10
20
30
40
TIME - HR.

Table XVIII

Progressive change in lead content of zinc from smooth, rolled silver-lead anodes

Deposition time	Total time	Lead content of zinc	
		Cell A	Cell B
hr.	hr.	%	%
1.3	1.3	0.0139	0.0112
1.2	2.5	0.0146	0.0186
1.3	3.8	0.0125	0.0144
2.0	5.8	0.0086	0.0069
2.0	7.8	0.0061	0.0064
2.0	9.8	0.0070	0.0073
2.0	11.8	0.0071	0.0100
1.7	13.5	0.0071	0.0105
2.0	15.5	0.0101	0.0107
2.0	17.5	0.0105	0.0140
2.0	19.5	0.0119	0.0134
2.0	21.5	0.0115	0.0129
2.0	23.5	0.0119	0.0132
2.0	25.5	0.0245	0.0134
2.0	27.5	0.0173	0.0143
2.0	29.5	0.0269; 0.0207	0.0194
2.0	31.5	0.0283; 0.0190	0.0191
2.0	33.5	0.0360; 0.0169	0.0198
2.0	35.5	0.0288; 0.0181	0.0180
2.0	37.5	0.0214; 0.0231	0.0257
2.0	39.5	0.0226; 0.0242	0.0260
(Cell electrolyte replaced by fresh electrolyte)			
1.3	40.8	0.0163	0.0138
1.4	42.2	0.0207	0.0229
1.3	43.5	0.0239	0.0238

Figure 9

Progressive change in lead content of zinc from smooth, rolled silver-lead anodes

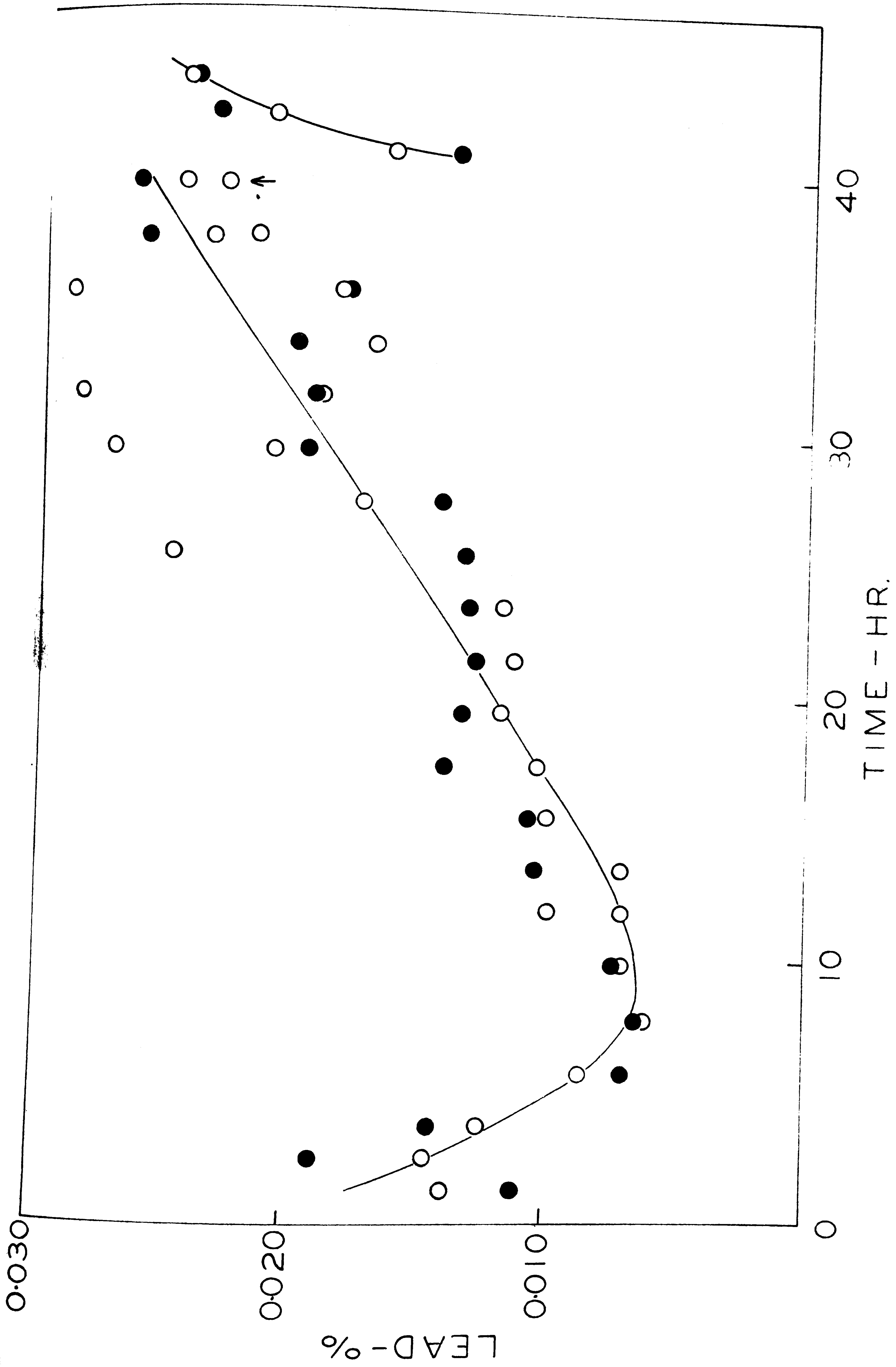

0·030
0·020
0·010
LEAD - %
0
10
20
30
40
TIME - HR.

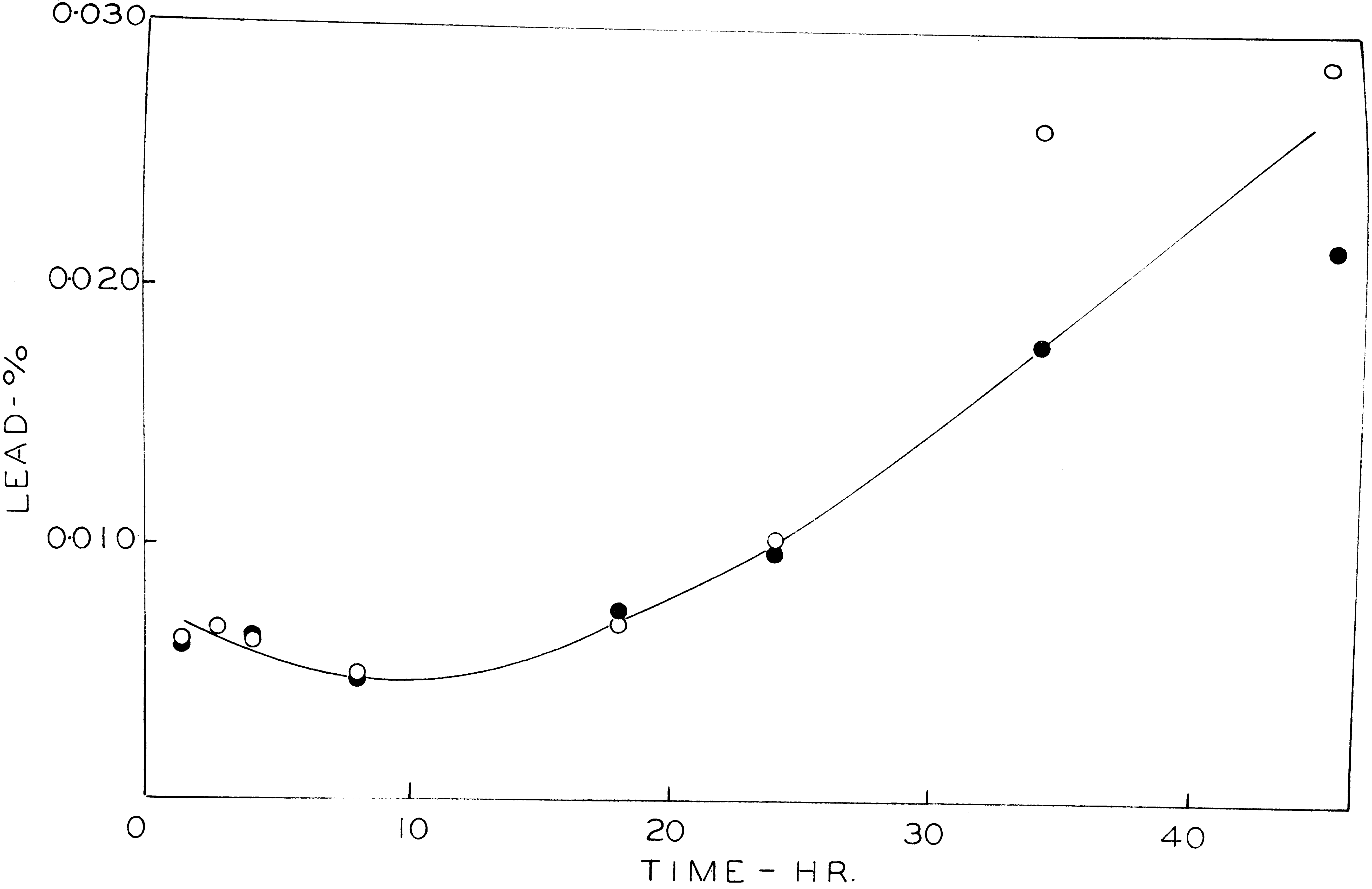
Table XIX

Progressive change in lead content of zinc from smooth, rolled silver-lead anodes in vinyon

Deposition time hr.	Total time hr.	Lead content of zinc Cell A %	Cell B %
1.3	1.3	0.0061	0.0058
1.4	2.7	0.0066	0.0064
1.3	4.0	0.0061	0.0063
2.0	6.0		
2.0	8.0	0.0048	0.0047
8.0	16.0		
2.0	18.0	0.0069	0.0073
4.0	22.0		
2.0	24.0	0.0101	0.0096
8.0	32.0		
2.0	34.0	0.0259	0.0177
8.0	42.0		
3.0	45.0	0.0286	0.0212

Figure 10

Progressive change in lead content of zinc from smooth, rolled silver-lead anodes in vinyon


0·030
0·020
0·010
LEAD - %
0
10
20
30
40
TIME - HR.

Minimum values for the lead content of the deposits using either smooth or roughened anodes were obtained after about ten hours. It is interesting, however, that smooth anodes not only gave less protection at this time but also had a much shorter period of time over which maximum protection was offered. Also, whereas with roughened anodes it required a period of electrolysis of twenty four hours to form a film on the bottom of the cell and to give a brown tinge to the electrolyte from particles liberated from the anodes, only twelve hours elapsed before similar effects were observed with smooth anodes. Since protection of the anode by "mechanical passivity " was much less pronounced with smooth than with roughened anodes, it seems quite probable that variability of results of duplicate experiments such as encountered in many of the experiments reported previously might well be attributed in part to dissimilarities in anode surfaces as a result of variations produced by repeated use and cleaning by abrasion.

The effect of filters in reducing the lead content of zinc deposits with prolonged electrolysis is shown by Fig.9 and 10, since smooth anodes were used in these two cases. During the first five hours of electrolysis the anode filter reduced the lead content of the zinc by two thirds, while after ten hours the reduction amounted to one third. When the time of electrolysis was extended from ten to forty hours, the curves of Figs. 9 and 10 became almost parallel. During that time, reduction in lead content brought about by the use of filters decreased from one third to one sixth. The shape of the curves, suggest that if the time of electrolysis had been extended to a still longer period, the effectiveness of filters would have been further decreased. Obviously, with prolonged electrolysis, the electrolyte became contaminated to about the same extent when a vinyon #2 filter was used as it did with no filter.

The break in the curve of Fig.9 comes as a result of changing the cell electrolyte after a period of electrolysis of thirty nine hours. The anodes were discarding peroxide particles freely at that time and quickly contaminated the fresh electrolyte and the zinc deposits.

When pure lead anodes were used in prolonged electrolysis (c.f. Table XIII), a random distribution of values was obtained for the lead content of the deposit. The average value was roughly 0.06%. Since the cause of contamination of the electrolyte and zinc deposit was presumably the same with lead and silver-lead anodes, an average value for the lead content of zinc greater than 0.06% is not to be expected from cells containing silver-lead anodes even after very prolonged periods of electrolysis.

Using a value of 0.06% for the lead content of zinc samples with pure lead anodes, the presence of silver in the anodes was apparently effective in reducing the lead content of zinc deposits by more than ninety percent for short periods of electrolysis and by about fifty percent when electrolysis was carried on for around forty hours. It would further seem from these experiments that the presence of silver in lead anodes was effective in reducing the lead content of zinc by virtue of its ability to hinder but not prevent the formation of lead peroxide at the anode surface. It must be noted however, that effectiveness of silver-lead anodes in decreasing lead contamination of deposits might have been decreased somewhat by their interrupted use (to obtain zinc samples) during these experiments. It may also be pointed out that if such anodes were removed and replaced after cleaning off the peroxide layer at ten hour intervals, their effectiveness might remain unimpaired.

Electrolyte containing cobalt

When present in the electrolyte in large amounts, cobalt decreases current efficiency for deposition of zinc but when present in small amounts it has a beneficial effect in reducing anode corrosion (2,35,36). It was therefore of interest to determine whether silver-lead anodes in electrolyte containing cobalt would give satisfactory performance in reducing the lead content of cathode zinc when electrolysis was prolonged. An experiment was made in duplicate using silver-lead anodes and with both cell and feed electrolyte containing 3.5 mgm. of cobalt per liter as cobaltous sulphate. Electrolysis was continued for forty hours in this experiment, the results of which are given in Table XX and Fig.11.

To determine the extent to which lead from the particular electrolyte used in the experiment was responsible for the lead content of the cathode, an experiment was made using platinum anodes in electrolyte similar to that above but containing no cobalt, with the results shown in Table XXI.

Table XX and Fig.11 show that as in previous experiments, the lead content of successive zinc samples decreased during the first few hours, the higher lead content of the first few samples being due probably to the initial production of lead sulphate at the anodes prior to formation of a lead peroxide coating. The important result of this experiment, however, is that the lead content of zinc samples was maintained at a very low level even when electrolysis was continued as long as forty hours.

With pure electrolyte, i.e. without the presence of cobalt, the thickness of the lead peroxide coating on the silver-lead anodes increased as electrolysis continued, until after ten hours the coating was of such a thickness that particles of lead peroxide became detached. However, when cobalt was added to the electrolyte, the formation of a

Table XX

Progressive change in lead content of zinc using Ag-Pb anodes in electrolyte containing cobalt

Deposition time hr.	Total time hr.	Lead content of zinc	
		Cell A %	Cell B %
1.3	1.3	0.0054	0.0058
1.4	2.7	0.0041	0.0046
2.0	4.7	0.0029	0.0026
2.0	6.7	0.0025	0.0029
2.0	8.7	0.0032	0.0041
2.0	10.7	0.0030	0.0036
2.0	12.7	0.0029	0.0043
3.6	16.3	0.0027	0.0032
2.0	18.3	0.0027	0.0032
2.0	20.3	0.0028	0.0033
2.0	22.3	0.0027	0.0026
2.0	24.3	0.0029	0.0028
2.0	26.3	0.0037	0.0037
2.0	28.3	0.0026	
2.0	30.3	0.0030	0.0030
2.0	32.3	0.0028	
2.0	34.3	0.0029	0.0027
2.0	36.3	0.0031	0.0027
2.0	38.3	0.0027	0.0035
2.0	40.3	0.0030	0.0030
2.0	42.3	0.0030	0.0031

Figure 11

Progressive change in lead content of zinc using Ag-Pb anodes in electrolyte containing cobalt

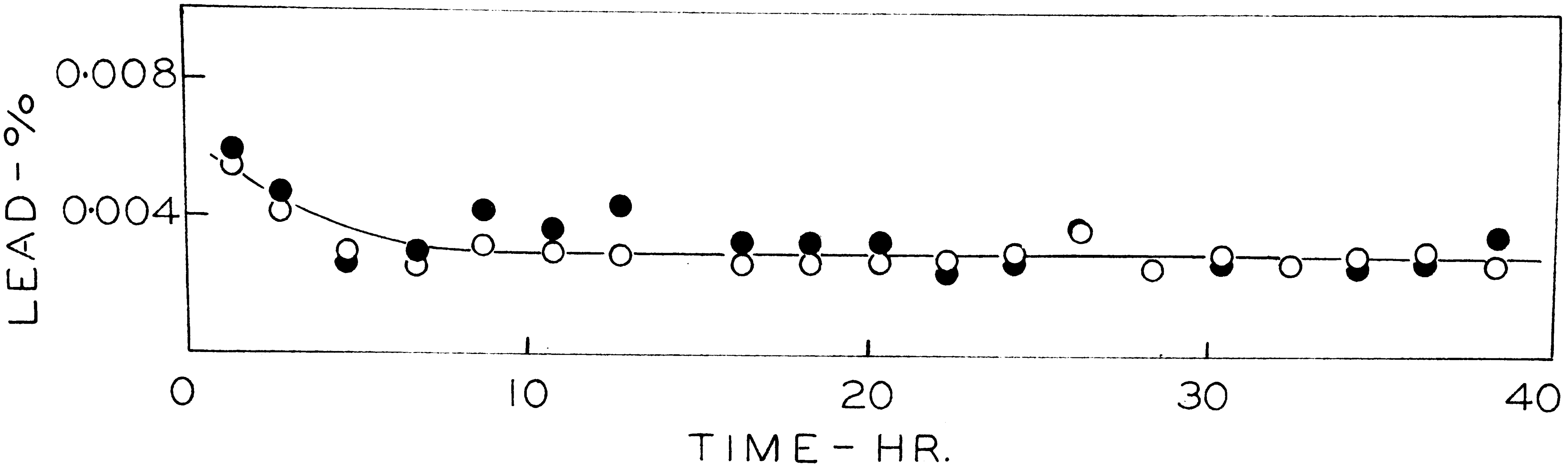

LEAD - %
0·008
0·004
0
10
20
30
40
TIME - HR.

Table XXI

Progressive change in lead content of zinc using platinum anodes

Deposition time hr.	Total time hr.	Lead content of zinc %
2.0	2.0	0.0022
2.0	4.0	0.0027
2.0	6.0	
2.0	8.0	0.0029
2.0	10.0	0.0028

thick brown coating did not occur. Instead, the anodes after being in use in the cell for more than forty hours had merely turned a dull bronze colour, probably with an extremely thin, adherent film of lead peroxide.

A comparison of Table XX and XXI reveals a remarkable similarity. With platinum anodes, the lead content of zinc samples was 0.003% due to lead initially present in the electrolyte, while with cobalt in the same electrolyte, silver-lead anodes produced zinc deposits which had a lead content also of approximately 0.003%. The addition of cobalt to the electrolyte therefore rendered silver-lead anodes almost completely passive. It would seem that with silver-lead anodes in an electrolyte containing cobalt the lead content of the deposited zinc is essentially dependent on the purity of the electrolyte used.

EFFECT OF IONS AND THEIR OXIDATION POTENTIALS

Oxidation potentials of ions

The use of cobalt to control the purity of cathode zinc raises the interesting possibility that other materials might be added to the electrolyte to bring about the same effect. Lead anodes containing about 1% silver in place of pure lead anodes have found wide-spread acceptance as a means of reducing the lead content of cathode zinc. Since cobalt is useful either incorporated in the anodes (63) or when present in the electrolyte, it was thought that silver in the electrolyte might also prove beneficial.

At the time this investigation was made, no report was found in the literature concerning the possible use of silver at low concentrations in solution as a method of controlling lead content of zinc deposits. Although the electrolytic zinc plant at Risdon, Tasmania (10) uses silver sulphate to reduce the chloride content of their electrolyte, checks are made to ensure that there is still chloride in solution and therefore no excess of silver.

The possibility that silver might behave in a manner similar to cobalt is strengthened from a study of their standard oxidation potentials shown in Table XXII. This table, abstracted from Latimer (64), shows that the oxidation potentials of silver and cobalt are highly negative

Table XXII

Standard oxidation potentials

Reaction	E° (volts)
$Zn = Zn^{++} + 2e$	+ 0.7620
$Pb = Pb^{++} + 2e$	+ 0.126
$Sn^{++} = Sn^{++++} + 2e$	-0.15
$CH_3OH = HCHO + 2H^+ + 2e$	-0.24
$2CNS^- = (CNS)_2 + 2e$	-0.77
$Fe^{++} = Fe^{+++} + e$	-0.771
$Hg_2^{++} = 2Hg^{++} + 2e$	-0.910
$2Br^- = Br_2 + 2e$	-1.065
$Tl^+ = Tl^{+++} + 2e$	-1.25
$Mn^{++} + 2H_2O = MnO_2 + 4H^+ + 2e$	-1.28
$2Cl^- = Cl_2 + 2e$	-1.358
$Pb^{++} + 2H_2O = PbO_2 + 4H^+ + 2e$	-1.456
$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e$	-1.52
$Ce^{+++} = Ce^{++++} + e$	-1.61
$IO_3^- + 3H_2O = H_5IO_6 + H^+ + 2e$	-1.7
$Ni^{++} + 2H_2O = NiO_2 + 4H^+ + 2e$	-1.75
$Co^{++} = Co^{+++} + e$	-1.84
$Ag^+ = Ag^{++} + e$	-1.98
$2F^- = F_2 + 2e$	-2.85

and close to one another. Their potentials are more than 1 volt more negative than iron.

The presence of iron in the electrolyte has been reported by Koenig et al (36) to lower the lead content of cathode zinc. The effectiveness of iron, however, was much less than that of cobalt. For example, pure acid zinc sulphate and lead anodes gave zinc deposits containing 0.0029% lead. This was reduced to 0.005% by the use of 2.5 mgm. per liter of cobalt, whereas to lower the lead content to 0.010% required 100 mgm. per liter of iron. Since the standard oxidation potential of iron is much less negative than that of cobalt or silver, it immediately became of interest to determine whether protection of zinc deposits was in any way related to oxidation potentials.

Effect of added anions

To investigate the possible relation between oxidation potentials of anions and extent of lead contamination, two experiments were made. Into each of five 200 ml. beakers containing 150 ml. of standard acid zinc sulphate electrolyte were placed an aluminum cathode and a lead foil anode, each measuring 1.8 cm. wide by 8.9 cm. long, and immersed to a depth of 6.4 cm. The first cell contained only pure electrolyte while the electrolyte in the second cell was made 0.0018M in $FeSO_4$, being equivalent to 100 mgm. per liter of iron. These two cells were used for purpose of comparison.

The remaining three cells were made 0.0018M in NaBr, NaCl and KHF_2 respectively. The five cells were connected in series and electricity passed through the cells for two hours using a current density of 40 amp. per sq. ft. In the second experiment, the conditions were identical but the electrolytes of the remaining three cells in this case were 0.0018M in KIO_3, KCNS and CH_3OH respectively.

Observations were made during electrolysis for the appearance of a brown film of PbO_2 on the bottom of the cells. Previous experience had shown that when peroxide particles appeared in the cells, the lead content of zinc deposits increased considerably. Although methyl alcohol is not an electrolyte, it was added to one cell as a matter of possible interest. In Table XXIII are summarized the observations made during these experiments.

Table XXIII shows that fluoride ion increased corrosion of the lead anode. When the electrolyte contained ferrous sulphate, no film of lead peroxide was seen on the bottom of the cell after 2 hours of electrolysis. (In a separate experiment no film was observed on the bottom of a cell containing ferrous sulphate even when electrolysis was carried on for more than 3 hours). The electrolytes containing NaCl, KCNS, KIO_3, NaBr and CH_3OH all offered a small amount of protection, but there was no apparent relation between oxidation potentials of the anions and protection against

Table XXIII

Effect of added anions on passivity of anodes

Substance added	Time for first appearance of film on bottom of cell
None	1 hr. 15 min.
KHF_2	1 hr.
KCNS	1 hr. 20 min.
NaCl	1 hr. 20 min.
CH_3OH	1 hr. 20 min.
KIO_3	1 hr. 25 min.
NaBr	1 hr. 45 min.
$FeSO_4$	. . . .

anode corrosion. Also, since the protection was slight, even in comparison with that offered by iron, further investigation with anions was discontinued.

Effect of added cations

Since previous experiments had clearly demonstrated the beneficial effects of cobalt in decreasing the lead content of cathode zinc, a relation between the oxidation potentials of cations and passivity of lead anodes was next sought, by investigating the behaviour of various metal salts added to the electrolyte. The experiments were made using a flowing acid zinc sulphate electrolyte in cells containing two anodes and one cathode. Electric current was passed through the cells for 1 1/4 hr. after which time the cathode containing the zinc deposit was removed, replaced by another cathode and electrolysis continued for an additional 3 hr. The zinc deposits from these cathodes were then analyzed polarographically for lead content.

For the different experiments, solutions of various metal sulphates, in their lower valence states, were added to the electrolyte at the start and also at 1 hr. intervals during electrolysis. For example, from a sample of stock electrolyte was prepared a solution containing 0.35 mgm. of cobalt as cobaltous sulphate per ml. Sufficient of this solution was added to the cell so that the initial cell electrolyte contained 3.5 mgm. per liter of cobalt. In this way, the only added impurity was the cobalt ion. With flowing electrolyte, 100 ml. of electrolyte (or 0.35 mgm. of cobalt) passed out of the cell every hour. Consequently 1.0 ml. of cobaltous sulphate solution was added hourly to the cell during electrolysis.

The anodes used in the first set of experiments were rolled pure lead anodes. These anodes were cleaned with emery paper and rinsed in a jet of distilled water prior to each experiment. In the second set, gold assay lead foil was used as anodes, with new anodes being used in each experiment. The lead foil provided anodes having a uniformly smooth surface, whereas the surface of the rolled lead anodes changed during successive experiments. The results of these two sets of experiments are shown in Tables XXIV and XXV respectively.

Table XXIV

Effect of added cations using rolled lead anodes

Added cation, mgm./L		Lead content of zinc (%) after:	
		1 1/4 hr.	4 1/4 hr.
Nil		0.0088	0.0276 0.0155 0.0221
		0.0107	0.0336 0.0142
Co	0.035	0.0084	0.0149
		0.0192	0.0319 0.0187
Co	0.35	0.0082	0.0207
		0.0072	0.0121
Co	3.5	0.0102	0.0064
Ag	3.5	0.0078	0.0033 0.0041
Fe	100	0.0099	0.0078
Ce	8.35	0.0075	0.0174
Ce	835	0.0602	0.0594 0.0809
Hg	359	0.0220	0.133 0.146
Sn	213	0.110	0.0752 0.0945

Table XXV

Effect of added cations using lead foil anodes

Added cation, mgm./L		Lead content of zinc (%) after:	
		1 1/4 hr.	4 1/4 hr.
Nil		0.0068	0.0448
		0.0064	0.0691
		0.0064	0.0198 0.0302
Co	3.5	0.0055	0.0043 0.0044
Ag	1.0	0.0054	0.0053 0.0075 0.0259 0.0163
Ag	3.5	0.0053	0.0017 0.0014 0.0027 0.0025
Ag	10	0.0067	0.0023 0.0023 0.0025 0.0029
Fe	100	0.0074	0.0047 0.0116 0.0093 0.0089
Fe	100	0.0095	0.0092 0.0104 0.0087 0.0099
Ce	8.35	0.0101	0.0455 0.0368
Mn	98	0.0128	0.0640 0.0780
Ni	105		0.0705

Certain effects of added metallic ions were readily observed during the course of electrolysis. Cerous ions on being oxidized to the ceric state at the anode produced a yellow coloured solution, while the cathode deposit had a number of pin-head projections on the surface. Manganous ions were oxidized to purple permanganate solution and to brown manganese dioxide at the anode, and the cathode deposit was pitted and contained long vertical slits.

Stannous, thallous and mercurous sulphate on being added to the electrolyte caused the zinc deposit to be brittle. Thallous sulphate also caused the formation of small pits in the deposit. Polarographic solutions from this deposition formed a film on the mercury pool of the polarographic cell which prevented lead analyses on these samples. Mercurous sulphate caused severe corrosion along the edges of the aluminium cathode. On addition of hydrochloric acid to samples of zinc from this deposit, small droplets of metallic mercury were observed. Nickel sulphate exhibited an interesting but deleterious behaviour, previously described by Koenig et al (36). With this cation, zinc appeared to deposit in a normal manner for approximately one hour, after which it dissolved quite rapidly and after 15 minutes almost the entire deposit had disappeared. This cycle was repeated during electrolysis.

The effect of various metal ions on anode passivity was visible during electrolysis. With pure electrolyte, a fine film of lead peroxide was observed at the bottom of cells after approximately 1 hour. In 2 hours a rather heavy layer of sediment had formed and in 3 hours the electrolyte was tinged a distinct brown due to suspended particles. This progression of events was followed in most cases but with a certain increase or decrease in time necessary for the successive steps. However, when the concentration, per liter of electrolyte, reached 3.5 mgm. of silver, 3.5 mgm. of cobalt or 100 mgm. of iron, the electrolyte remained free of visible peroxide contamination.

Since the behaviour of various electrolytes was similar with either rolled lead or lead foil anodes, the results of experiments shown in Tables XXIV and XXV have been averaged in Table XVI, in which electrolytes are arranged in order of decreasing lead content of the zinc samples obtained after electrolysis for 4 1/4 hours. The influence of various metal ions on the transport of lead to cathode zinc during electrodeposition is immediately evident from Table XXVI. Mercury, tin and nickel increased anode corrosion, hence increased the lead content of the cathode zinc. Manganese was also found deleterious although it has been reported (6) that in larger amounts (600 mgm. per liter), it may decrease anode corrosion. Small amounts of cerium had little effect although larger amounts caused increased lead content of the zinc.

Table XXVI

Effect of added cations using lead anodes

Added cation, mgm./L		Lead content of zinc (%) after;	
		1 1/4 hr.	4 1/4 hr.
Hg	359	0.022	0.140
Sn	213	0.110	0.085
Mn	98	0.013	0.071
Ni	105		0.071
Ce	835	0.060	0.070
Ce	8.35	0.0088	0.033
Nil		0.0078	0.031
Co	0.035	0.014	0.022
Ag	1.0	0.0054	0.014
Co	0.35	0.0072	0.012
Fe	100	0.0089	0.0090
Co	3.5	0.0079	0.0050
Ag	3.5	0.0062	0.0026
Ag	10	0.0067	0.0025

While 100 mgm. per liter of iron gave an appreciable lowering of lead content, much smaller amounts of silver or cobalt gave even greater reduction. The results show that silver or cobalt when present in the electrolyte at concentrations in the order of one part per million brought about a significant decrease in the amount of lead present in the cathode zinc.

As with the anions, the cations showed no apparent correlation between standard oxidation potential and the extent of anode protection. For example, cerium with an oxidation potential between that of iron and silver, both of which offered protection, caused increased anode corrosion. However, cobalt and silver which both have large negative oxidation potentials provided remarkable anode passivity.

Whereas it has previously been known that silver-lead anodes lower the lead content of cathode zinc, the results shown here demonstrate that silver ions in the electrolyte were also capable of bringing about a similar result. Since this study was made, a patent has been issued to Griffith and Isherwood (65) covering the use of silver ion in the electrolyte to reduce the lead content of zinc when it is electrolytically recovered using a lead-containing anode.

Cathode current efficiency

For practical use of certain agents to reduce lead content, these substances must not at the same time bring about a serious loss of current efficiency. Thus, even if nickel were to lower the lead content, it would be undesirable since it causes considerable re-solution of the zinc deposit. With pure electrolyte, cathode current efficiency was 89.5%. The efficiency was lowered 1% by the use of 100 mgm. per liter of iron in the electrolyte. Using 3.5 mgm. per liter of silver or cobalt, or 10 mgm. per liter of silver, the efficiency was reduced by 3%. This slight lowering of current efficiency was however compensated by the greater purity of the zinc deposit. Since it has been reported (43) that the change in current efficiency caused by cobalt can be decreased by addition of gelatin, other colloids or ammonium sulphate, the same might be true when silver is used.

Reactions of lead peroxide with cations

Although the extent of anodic corrosion in the presence of various metal sulphates showed no apparent relation with the standard oxidation potentials of various cationic impurities, there existed the possibility that such a relation did exist but was masked by direct chemical attack of these substances on the anode. For example, both cerium and iron may undergo reactions at the anode as a result of electrolysis which contribute to anode passivity, the extent of this protection being related to their standard oxidation potentials. Nevertheless, cerium may at the same time react chemically more vigorously than iron with the anode to cause corrosion, and thus obscure the above relation.

An attempt to study the rate of chemical reaction of various substances on lead anodes was first made in the following manner. A platinum and a saturated calomel electrode were placed in a beaker containing cell electrolyte with added lead peroxide. To the beaker was added ferrous, cerous, mercurous or stannous sulphate in amounts smaller than required to react completely with the lead peroxide present. Changes in potential of these cells with time were then measured by a potentiometer.

It was considered that the change in potential of these systems might vary in a manner similar to the usual change that occurs during a potentiometric titration. When for example a solution containing a reducing agent is titrated with an oxidizing agent the potential of the system is governed by the reducing agent and changes but slightly during the early stages of titration. Near the equivalence point however, the potential changes considerably and is controlled by the oxidizing agent. Hence, it was believed that with the ferrous-lead peroxide system, the potential might remain at a nearly constant value until the time when ferrous ions had all reacted, after which an appreciable change might be observed. If similar changes occurred with cerous, mercurous and ferrous ions, the different times required for the change in potential to occur would be a measure of the speed of reaction.

Unfortunately the systems under consideration were not amenable to this method of investigation. The potentials of the systems changed in an irregular, irreproducible fashion so that the results were of little value. Substituting the calomel electrode by a lead-lead peroxide electrode showed no improvement.

Since the electrochemical method was not suitable to study the reaction rates owing to the lack of consistent electrode potentials, the systems were studied by titration methods. Solutions of cations and suspensions of lead peroxide were made to contain 105 gm. per liter of sulphuric acid so that their acidity would be comparable with that of cell electrolyte. In all cases, the solutions were allowed to react with a suspension containing 0.6 gm. of lead peroxide per liter. The stock lead peroxide suspension was agitated for two hours with an electric stirrer. The flask was also subsequently shaken thoroughly to obtain an uniform suspension before removing samples.

The reaction between ferrous iron and lead peroxide was investigated in the following manner. Two solutions were prepared to be 0.004 molar in ferrous ions and ceric ions respectively. To a flask containing 10.0 ml. of PbO_2 suspension was added 10.0 ml. of ferrous solution. The resulting mixture, containing approximately 100 mgm. per liter of iron, was agitated for a given time after which the remaining ferrous iron was titrated with ceric sulphate solution, using osmium tetroxide and ferrous-phenanthroline indicator. The experiment was repeated, allowing different periods of time for the ferrous iron and lead peroxide to react before titration. For each given time of reaction, four determinations were made.

From the volume of 0.004 molar ceric solution used in titration was calculated the number of moles of ferric iron produced. The average values obtained from these experiments are recorded in Table XXVII and Fig.12.

The reaction between cerous ion and lead peroxide was studied in a manner similar to that outlined above. To 10.0 ml. of 0.004 molar cerous solution was added 10.0 ml. of lead peroxide suspension. After a given time of agitation, the ceric ion produced in this system was titrated with 0.004 molar ferrous solution again using osmium tetroxide and ferrous-phenanthroline indicator. The average values obtained from these experiments are also given in Table XXVII and Fig.12.

In studying the reaction between mercurous ions and lead peroxide, difficulty was at first encountered in obtaining a suitable titrating substance for use in a system containing both lead and mercury in the oxidized and reduced

Table XXVII

Reaction of lead peroxide with cations

Time min.	Millimoles ferric ion formed	Millimoles ceric ion formed	Millimoles mercuric ion formed
0.5	0.010	0.007	0.019
1	0.016	0.014	0.029
2	0.022	0.023	0.034
5	0.030	0.033	0.036
10	0.034	0.035	0.037
15	0.035	0.036	0.037

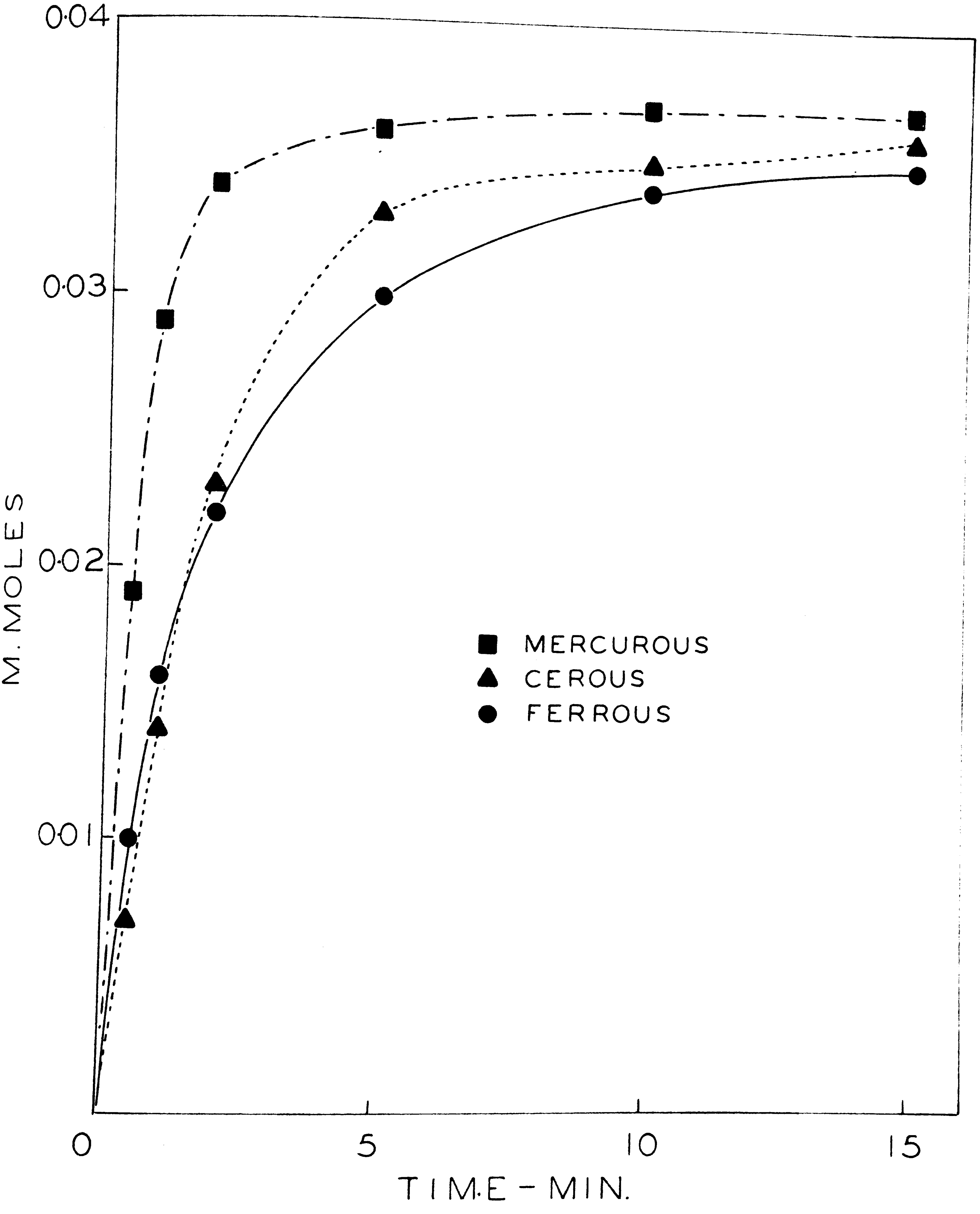
state. To overcome this handicap the following procedure was adopted. To 10.0 ml. of solution, 0.0016 molar in mercurous ion, was added 10.0 ml. of lead peroxide suspension. After shaking for a given period of time there was added 2.0 ml. of dilute hydrochloric acid (2 ml. of conc. hydrochloric acid diluted to 1 liter). At the concentrations used, the mercurous ion was precipitated as mercurous chloride while the mercuric ion produced during the reaction remained in solution. The mixture was filtered through a fine filter paper and to the filtrate was added a few drops of carbon tetrachloride and 2.0 ml. of conc. nitric acid containing brown fumes of oxides of

Figure 12

Reaction of lead peroxide with cations

Legend

■ Mercurous → Mercuric.
▲ Cerous → Ceric.
● Ferrous → Ferric.


0·04
0·03
0·02
0·01
M. MOLES
0
5
10
15
TIME - MIN.
■ MERCUROUS
▲ CEROUS
● FERROUS

nitrogen. The mercuric ions in the filtrate were titrated with potassium iodide solution (0.3 gm. KI per liter) which precipitated mercuric iodide. The nitric acid oxidized excess iodide to iodine after the end-point was reached, and the presence of free iodine was detected by its discolouration of the carbon tetrachloride. From the amount of potassium iodide added was calculated the number of moles of mercuric ion produced.

The average results for the reaction between mercurous ion and lead peroxide are summarized in Table XXVII and shown graphically in Fig.12. Owing to the low solubility of mercurous sulphate, the mercurous ion concentration in the solution used was only 0.0016 molar compared to 0.004 molar for the ferrous and cerous ion concentration. Consequently the values obtained in the experiments with mercurous ion were multiplied by a factor of 40/16 to facilitate comparison.

Table XXVII and Fig.12 show that lead peroxide is attacked by all three ions, namely mercurous, cerous and ferrous ions. While mercurous and cerous ions both gave considerably greater contamination to cathode zinc than that caused by iron (c.f. Table XXVI), the mercurous, but not the cerous ion reacted more readily with lead peroxide than did ion. The experiments indicated then that the rate at which these cations attack lead peroxide has no bearing on the cathode contamination.

DISCUSSION

The formation of lead peroxide on the lead anodes used in zinc electrowinning, and its possible contamination of the electrolyte if it flakes off has been reported by the various investigators who have studied these systems. While it may be a reasonable assumption that contamination of the cathode zinc is due mainly to the occlusion of particles of the peroxide, it must be realized that the presence of lead in the form of such particles cannot be taken as proof of their sole responsibility for contamination of the deposited zinc. For such contamination to occur, the particles must, of course, be brought to the cathode face, be then adsorbed there, and eventually be incorporated into the deposit. All these steps would seem to be probable, but obviously are not necessary consequences of the mere presence of the particles.

Furthermore, there is no a priori reason to suppose that an accelerated formation of the peroxide may not be accompanied by a greater rate of formation of lead ions, and an increased extent of cathode contamination from these or from colloidal lead sulphate formed therefrom. The brief study with a canvas filter, reported by Koenig et al (36) indicates that the major cause of lead entering the cathode is, in fact, the occlusion of peroxide, but the investigation does not appear to have been sufficiently extensive to take into consideration the possible influence of such factors as inadequate electrolyte replenishment within the filter. It was with a view to obtaining as incontrovertible evidence as possible on the relative significance of lead ion, as opposed to peroxide particle contamination that the rather tedious and time-consuming experiments were made with various filters in the present study. As pointed out previously, it was felt that an answer to this problem was prerequisite as a directive for further investigation.

From the data recorded on the effect of filters with platinum anodes, it became evident that the lead ion content of the electrolyte contributed but little to the lead content of the deposit (0.003%). Similarly when lead anodes under conditions such that only lead ions could be involved in the contamination of the cathode (cellophane filters), the lead content of the zinc remained at a low level (~0.006%). By comparison, the experiments with lead anodes in which filters were not used, or in which the filters did not prevent completely the access of lead peroxide particles to the cathode, showed beyond reasonable doubt that the majority of the lead content of the zinc deposit was directly attributable to adsorption and occlusion of particles of the peroxide. The change in extent of contamination with change in porosity of the filter, the large variations in extent of contamination in the absence of a filter, the increase in extent of contamination with increased agitation of the electrolyte and by the use of smooth anodes to which adherence of the peroxide was less effective than on rough anodes, may all be regarded as direct consequences of the predominant part played by peroxide particles as opposed to ions, in the transport of lead to the cathode. The unspectacular but important conclusion to be drawn from the various experiments with filters is, of course, that means for reducing the extent of cathode contamination by lead, and the mechanism by which any agency functions to bring about such a reduction, must both be sought in a study of the factors governing the oxidative corrosion reaction of the lead anode.

The use of silver alloyed with the anode to effect a reduction in its rate of corrosion unquestionably has its merits, but the results of the experiments in which deposition was continued for prolonged periods showed that such a procedure was by no means a complete solution to the problem. It will be recalled that in these experiments, the lead content of the zinc decreased at first (as the cell electrolyte became depleted of lead contamination) but that after about ten hours deposition, the rate of lead transport increased to a value comparable with that for an unalloyed anode. Such behaviour would seem to be interpretable only on the assumption that silver is lost from the surface of the anode at a rate in excess of that at which it can be replenished by diffusion from below the surface of the anode. This conclusion that silver is lost from the anode is in agreement with the observations of Tainton et al (33) and also with those of Koenig et al (36). On the other hand, the presence of cobalt enabled deposition to be continued for prolonged periods under similar conditions without an increase in lead content of the cathode zinc, and without any large amount of peroxide formation on the anode. From these observations, it seems reasonable to conclude that whether or not the added substance is incorporated initially into the electrode, its beneficial effect may be regarded as exercised by the corresponding ions in solution. Presumably, adsorption of these ions on the anode surface is prerequisite to their inhibition of corrosion.

Before attempting an explanation of the beneficial effects of added substances, it seems reasonable and necessary to inquire into the reactions involved in the oxidative corrosion of an unalloyed lead electrode in acid zinc sulphate electrolyte containing no foreign substance. As pointed out in the introduction, the sequence of reactions responsible for the formation of lead peroxide appears to be some preliminary formation of lead salt on the anode surface, followed by an increase in potential until hydroxyl ion discharge becomes possible. The discharged hydroxyl ions are then assumed to react with the metal to produce a discontinuous film of the peroxide. When the peroxide film effectively covers the surface, oxygen evolution occurs.

There is little doubt that the species actually responsible for the attack on the anode metal when the potential has attained a sufficiently high value is the hydroxyl radical. It is generally agreed that the first step in the process of oxygen evolution at an anode is the formation of hydroxyl radicals, and this may be represented by the reaction

$$OH^- = OH + e \qquad (3)$$

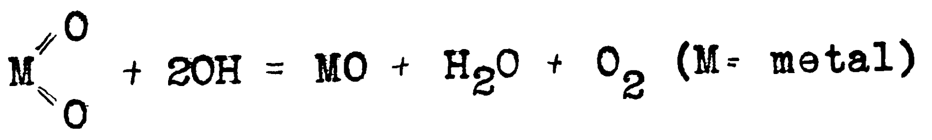
or in highly acid solution by

$$H_2O = OH + H^+ + e \qquad (4)$$

There is, however, some controversy about the subsequent steps. The view that combination of hydroxyl radicals occurs to form hydrogen peroxide, which subsequently decomposes with formation of oxygen (17,26,66-72) has been criticized (73-76) in favour of the opinion that disappearance of hydroxyl radicals occurs by the reaction

$$2OH = H_2O + O \qquad (5)$$

followed by combination of oxygen atoms. Haissinsky (77) assumes that hydroxyl radicals would immediately react with active oxygen of the anodic deposit with mutual reduction.



$$M\begin{smallmatrix}\diagup\!\!\!\diagup O\\ \diagdown\!\!\!\diagdown O\end{smallmatrix} + 2OH = MO + H_2O + O_2 \text{ (M= metal)} \qquad (6)$$

According to Latimer (64) an equally plausible mechanism for oxygen evolution is the preliminary formation of a surface oxide of the metal, followed by a reaction of the type

$$MO_2 + OH^- = MOH + O_2 + e \qquad (7)$$

It is important to note that the formation of peroxide by the mechanism suggested above occurs not only with unalloyed anodes in pure electrolyte, but also with silver-lead and other lead alloy anodes, and in the presence of silver, cobalt and iron in the electrolyte, all of which have been found to reduce the lead content of zinc deposits. This observation immediately poses the problem of why reduction of the rate of corrosion is effected by the presence of these substances only after initial formation of a peroxide film over the anode surface.

One possible explanation for the "delayed protective action" of the substances mentioned is that they or more likely their oxides function to render the lead peroxide film impermeable by the purely mechanical action of filling pores in the film. An explanation of this type has been offered for the passivity of silver-lead anodes in the electrolysis of brine solutions, where it was shown that silver chloride and oxide are present as layers in the peroxide film (29). However, a high concentration of silver (49.3%) was present in the anodes where identification of such layers was made. Rey et al (35), in describing the protective action of cobalt in the electrolyte, have also suggested that the anode behaves as if the current no longer had access to the metallic lead, or as if a thin impermeable film of lead peroxide was formed. Apparently, however, they do not ascribe the protection to mere mechanical action of cobalt to render the lead peroxide film impermeable, since they express the opinion that the cobalt on the anode probably acts as an oxygen carrier.

While it is perhaps rather imaginative, even naive, to consider that the added substances function only by filling pores in the lead peroxide film, it must be admitted that it is not at all easy to disprove such a view. True, it would require a relatively high degree of specificity in the type of material capable of fulfilling such a function, both in respect of permeability and adsorption, but this is not an impossible condition to meet. Granting such a specificity, an explanation is obvious for the protective action of such added materials as iron, cobalt and silver, together with the differences in their effectiveness. It is equally obvious, however, that such an explanation takes refuge in a lack of the very information that might serve to disprove its validity, and that its simplicity is only apparent.

It seems possible to suggest a more satisfying and perhaps more satisfactory type of explanation for the inhibition, by certain substances, of oxidative corrosion at a lead anode, by consideration of the reactions responsible for the corrosion and their relation to the main anodic process, the liberation of oxygen.

Since the formation of lead peroxide may be attributed to attack of the metal by hydroxyl radicals, after attainment of a sufficiently high potential for hydroxyl ion discharge, the inhibition of corrosion would appear to be associated with prevention of the metal-radical reaction. This essentially must involve the introduction of an alternative elimination of hydroxyl radicals such that their rate of reaction with lead is vastly reduced, and, from previous remarks, it would seem essential that the alternative reaction must occur with an adsorbed ion of the substance responsible for the inhibition of corrosion. (It is not necessary to specify the precise form in which the substance is adsorbed, but it seems probable that it may be as an oxide). The type of reaction that may accomplish the desired purpose is suggested by a study made by Noyes et al (78) on the oxidation-reduction reactions of argentic salts in acid solution. To explain their results, the authors suggest the occurence of a rapid reaction as follows:

$$2Ag^{++} + H_2O_2 = 2Ag^{+} + O_2 + 2H^{+} \qquad (8)$$

If now it is assumed that an adsorbed silver ion may be oxidized at the potential prevailing for hydroxyl ion discharge on the anode, the following analogous reaction may be postulated:

$$Ag^{++} + OH = Ag^{+} + O + H^{+} \qquad (9)$$

It is true that non-equilibrium conditions prevail during the discharge of hydroxyl ions, and therefore an argument based on equilibrium values for oxidation potentials cannot be rigorously applied. However the recently corrected value of -2.00 volts given by Hickling and Hill (79) for the standard oxidation potential of the reaction

$$OH^- = OH + e \qquad (3)$$

makes it quite plausible for the reaction

$$Ag^+ = Ag^{++} + e \qquad (10)$$

to proceed at the anode, for which the standard oxidation potential is -1.98 volts (64).

Since the oxidation potential for the reaction

$$OH = 1/2O_2 + H^+ + e \qquad (11)$$

is + 0.34 volt (corrected to the new value of 2.00 volts for reaction (3)), the reaction assumed in (8) should occur quite readily.

It is immediately apparent that disposal of hydroxyl radicals, in the manner suggested, by a silver ion adsorbed on a metal site would prevent corrosive attack at that point. Moreover, it will be noted that re-oxidation of the argentous ion enables repetition of the process of hydroxyl radical elimination. Obviously, a small amount of silver should suffice to prevent a relatively large amount of corrosion, but if silver is gradually lost from the system, the extent of corrosion should increase, as observed.

It should be noted that, in the above scheme, discharge of an hydroxyl ion is not assumed to occur necessarily at the silver site. There is no reason to suppose that it could not occur on a neighbouring lead peroxide site, and the radical subsequently be brought into contact with the silver, where it would suffer decomposition rather than attack the lead substrate.

An entirely similar representation may be made for the inhibitory effect of cobalt, where the hydroxyl radical may react accofding to

$$Co^{+++} + OH = Co^{++} + O + H^{+} \qquad (12)$$

The protective action of thallium (6,34) and of iron (36) may be represented by

$$Tl^{+++} + 2OH = Tl^{+} + O_2 + 2H^{+} \qquad (13)$$

and

$$Fe^{+++} + OH = Fe^{++} + O + H^{+} \qquad (14)$$

respectively.

While the suggested mechanism appears to give a satisfactory account of the protection from corrosion afforded to lead anodes by the added substances mentioned above, it must also allow an explanation of the failure of certain substances to provide protection. For example, calcium-lead anodes considerably lower the anode potential (6), but such electrodes corrode readily. On the other hand, the presence of silver in the anode along with calcium gives the same protection as that observed with a silver-lead anode, yet the overvoltage for oxygen evolution remains at the value for a calcium-lead anode.

Although the available information indicates that the oxygen overvoltage on a calcium-lead anode is lower than that on lead or silver-lead anodes, it does not follow, of course, that discharge of hydroxyl ion occurs at a calcium site. The rate governing step in oxygen evolution at an anode still seems to be obscure (26,80), but whatever it may be, calcium presumably functions to reduce the energy barrier associated with it. It might be, for example, that discharge of the hydroxyl ion occurs elsewhere on the electrode, and that combination of oxygen atoms is promoted by the presence of calcium. If, however, calcium is capable of existing on the electrode only in the divalent state, it would be incapable of destroying hydroxyl radicals by the mechanism proposed previously, and these would still be available to attack lead in the vicinity. If, now, silver is also present, decomposition of the radical may be promoted as before and corrosion of the lead prevented. The overvoltage for oxygen evolution would remain at the value for a calcium-lead anode if calcium facilitated a subsequent step in the ultimate evolution of oxygen, e.g., perhaps combination of oxygen atoms to oxygen molecules.

In the present study, no beneficial effect of manganese was observed, although at high concentrations and in the presence of addition agents, it has been reported (6) to be effective in inhibiting corrosion to some extent. Its failure to give protection under the conditions of the present experiments probably emphasizes a fundamental consideration which has not yet been mentioned. Since manganese can exist in several valence states, it might be expected that the following sequences of reactions should serve to inhibit corrosion at a lead anode, in the manner described previously:

$$Mn^{++} = Mn^{++++} + 2e \qquad (15)$$

$$Mn^{++++} + 2OH = Mn^{++} + O_2 + 2H^{+} \qquad (16)$$

While the latter reaction is thermodynamically possible, it seems entirely reasonable to assume that it would be a relatively slow reaction, since MnO_2 is a stable oxide of manganese. In such an event, the threat of reaction between hydroxyl radicals and lead would remain practically as serious as in the absence of manganese. It is, perhaps, interesting to note that similar considerations probably apply to lead itself. While the sequence

$$Pb^{++} = Pb^{++++} + 2e \qquad (17)$$

$$Pb^{++++} + 2OH = Pb^{++} + O_2 + 2H^{+} \qquad (18)$$

is possible, again the second reaction is probably quite slow since PbO_2 is a stable oxide of lead. Hence, it is incapable of providing inhibition to further corrosion of the anode such as may be obtained with silver, cobalt etc.

It might be mentioned in conclusion that it is possible to arrive at a satisfactory explanation for the inhibition of corrosion by silver, cobalt, etc. by arguing from the reactions usually postulated for formation of lead peroxide in a lead accumulator. To present the argument in detail would be, perhaps, superfluous, but an outline might be of interest. Formation of peroxide in the accumulator has been described in terms of the reaction sequence

$Pb = Pb^{++} + 2e$ (19) (Solution of lead and formation of a coating of lead sulphate)

$Pb^{++} = Pb^{++++} + 2e$ (17) (Oxidation of Pb^{++} as a result of increased current density and potential at the uncovered metal)

$Pb^{++++} + 4OH^{-} = PbO_2 + 2H_2O$ (20) (Formation of lead peroxide)

Reduced corrosion may now be regarded as dependent upon reduction in the extent of reaction (19). As an example, when silver is present this may be accomplished if the reaction

$$Ag^{+} = Ag^{++} + e \qquad (10)$$

occurs at the potential attained for discharge of hydroxyl ions, such that electrons may be transferred to the anode by the reaction

$$Ag^{++} + OH = Ag^{+} + O + H^{+} \tag{9}$$

rather than (effectively) by solution of lead to form lead ions to a corresponding extent.

SUMMARY AND CONTRIBUTION TO KNOWLEDGE

1. While radioactivity measurements, using radium D may be used to follow progressive changes in the rate of lead transport during electrodeposition of zinc, the method is not adaptable to routine use. Bismuth is transported more readily than lead from anode to cathode during zinc electrodeposition.

2. By a series of experiments in which various filters were placed around the cathode or anode during the electrodeposition of zinc, using lead anodes, it has been shown unequivocally that practically all of the lead contamination appearing in the zinc deposit has its origin in the occlusion of lead peroxide particles shed by the anode. With pure lead anodes and short periods of electrolysis, up to three quarters of the lead appearing in the deposit is due to coarse particles of lead peroxide, approximately one tenth is due to finer particles, while the remainder is due to lead in colloidal or ionic form. The use of carbon anodes provided direct evidence for the occlusion of particles in the zinc deposit.

3. It has been found that the use of silver-lead anodes to prevent contamination of the zinc deposit

provides only temporary protection in the absence of other materials added to the electrolyte. While silver-lead anodes in pure electrolyte exhibit increasing protection for periods of electrolysis of up to ten hours, the contamination of the zinc deposit increases when electrolysis is continued beyond this time. With prolonged electrolysis in pure electrolyte, the lead contamination of zinc deposits using silver-lead anodes becomes comparable with that obtained with pure lead anodes. On the other hand, the continued presence of cobalt ion in the electrolyte results in virtually complete protection of the cathode even over prolonged periods.

4. No apparent relation existed between the protection against anodic corrosion and the oxidation potentials of various anions and cations, nor did the relative protection provided by various cations appear to be related to their rate of attack by lead peroxide.

5. It has been found that the presence of silver ion in the electrolyte is equally as effective as cobalt ion in preventing contamination of the zinc deposit by lead.

6. A mechanism is suggested to account for the inhibition of anodic corrosion by such ions as silver, cobalt, etc. The action of these substances is attributed essentially to their ability to pass between higher and lower oxidation states, in such a way as to prevent hydroxyl radicals from attacking the metal of the anode.

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