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*EFFECT OF IMPURITIES ON THE CURRENT  
EFFICIENCY OF ZINC ELECTRODEPOSITION*

R. C. KERBY AND T. R. INGRAHAM

EXTRACTION METALLURGY DIVISION

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EFFECT OF IMPURITIES ON THE CURRENT EFFICIENCY OF  
ZINC ELECTRODEPOSITION

by

R.C. Kerby\* and T.R. Ingraham\*\*

ABSTRACT

The current efficiency of zinc electrodeposition from acidic zinc electrolytes was found to be adversely affected by a number of single metallic impurities--in particular, rhodium, platinum, gold, silver, tungsten, antimony, germanium, tellurium and copper--and by combinations of metallic impurities such as cobalt, copper and nickel with antimony and arsenic. The decrease in current efficiency of zinc electrodeposition appeared to be related to several factors, including a decrease in hydrogen overvoltage on certain areas of the zinc electrodeposit, the formation of local galvanic cells in the zinc electrodeposit leading to increased corrosion, an increase in catalytic evolution of hydrogen in the case of antimony and mercury, and the possible alteration of the growth morphology of the zinc electrodeposits by impurities. The current efficiency of zinc electrodeposition was determined by measuring the rate of cathodic hydrogen evolution by means of a thermal conductivity cell.

39pp.

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\*Scientific Officer and \*\*Head, Extraction Metallurgy Research Section, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Rapport de recherches R243

EFFET DES IMPURETÉS SUR LE RENDEMENT DU ZINGAGE ÉLECTROLYTIQUE

by

R.C. Kerby\* et T.R. Ingraham\*\*

RÉSUMÉ

L'auteur a mis en évidence que le rendement du zingage électrolytique à partir d'électrolytes acides de zinc était diminué par la présence d'un certain nombre d'impuretés métalliques simples--en particulier, le rhodium, le platine, l'or, l'argent, le tungstène, l'antimoine, le germanium, le tellurium et le cuivre--et par l'effet combiné de certaines impuretés métalliques, comme le cobalt, le cuivre et le nickel, associés à l'antimoine et à l'arsenic. Cette diminution du rendement du zingage électrolytique s'est révélée comme étant imputable à plusieurs facteurs, parmi lesquels: la diminution, dans certaines zones de la couche de zinc, de la surtension due à l'hydrogène; la formation, dans la couche de zinc, de piles voltaïques peu étendues qui provoquent un accroissement de la corrosion; l'augmentation du dégagement d'hydrogène à la cathode, dans le cas de l'antimoine et du mercure; et enfin la déformation possible, due aux impuretés, des dépôts successifs de la couche de zinc. Pour cette étude, le rendement du zingage électrolytique a été déterminé en mesurant le taux de dégagement de l'hydrogène à la cathode, au moyen d'une cellule à conductibilité thermique.

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\*Agent scientifique et \*\* Chef, Section de recherche, Division de la métallurgie extractive, Direction des mines, ministère de l'Energie, des Mines et des Ressources, Ottawa, Canada.

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## INTRODUCTION

The electrolytic zinc industry until recently has lacked a reliable method which would automatically and continuously measure and control the quality of zinc electrolyte supplied to the cell rooms. Because the current efficiency of zinc electrodeposition is critically dependent on the quality of zinc electrolyte, the development of such a method is of some importance.

To supply this need, a program initiated in 1967 at the Mines Branch, Ottawa, has developed a meter which is capable of both automatically and continuously monitoring the quality of zinc electrolyte, and the construction and testing of this meter have been described elsewhere<sup>(1)</sup>.

As a related study, the effects that the impurities present in the zinc electrolyte have on the current efficiency have been determined with this new type of meter, and the results are presented in this research report.

## BACKGROUND

The electrodeposition of zinc from acid sulphate baths is dependent to a large extent on the maintenance of a large hydrogen overvoltage on the surface of the cathode<sup>(2)</sup>. The hydrogen overvoltage is controlled by several variables,

including pH, current density and temperature<sup>(3)</sup>. Operating experience<sup>(2)</sup> has shown that the presence of small concentrations of certain metal ions in the acid sulphate baths can have a detrimental effect on the current efficiency of zinc electro-deposition, by substantially increasing the amount of hydrogen electrodeposited and consequently evolved. The current efficiency can be considered to be the ratio of the amount of zinc deposited per unit of current and time, to the amount of zinc which should have been deposited for the same units of current and time, assuming that Faraday's laws apply and that only zinc is electrodeposited.

A number of studies have been made on the effect of impurities on the morphology of the zinc deposit and the current efficiency of zinc electrodeposition, but the results tend to be somewhat contradictory, particularly for combinations of impurities<sup>(4)</sup>. The presence of metal impurities on the surface of the zinc electrodeposit can increase hydrogen evolution by several means<sup>(5)</sup>. The impurities can act as centres of low hydrogen overvoltage that permit the discharge of hydrogen to occur in preference to zinc electrodeposition<sup>(6)</sup>, or, the impurities can form galvanic couples with zinc and accelerate the corrosion of the zinc electrodeposit, with the consequent evolution of hydrogen<sup>(7,8)</sup>. Because it is difficult to



distinguish between these two mechanisms, it is common practice to relate 100 per cent current efficiency to the total volume of hydrogen evolved plus the weight of zinc deposited.

Several methods<sup>(9,10)</sup> have been used to measure the efficiency of zinc electrolysis; the amount of zinc deposited can be measured, either by weighing or by anodic redissolution, and then compared to that predicted from Faraday's Law. Or, an alternative method is to measure the amount of hydrogen evolved during the electrodeposition of zinc<sup>(11)</sup> and then calculate the loss in current required to produce that amount.

The hydrogen calculation method was used in the present experiments because it permitted the effect of impurities to be assessed.

#### APPARATUS AND PROCEDURE

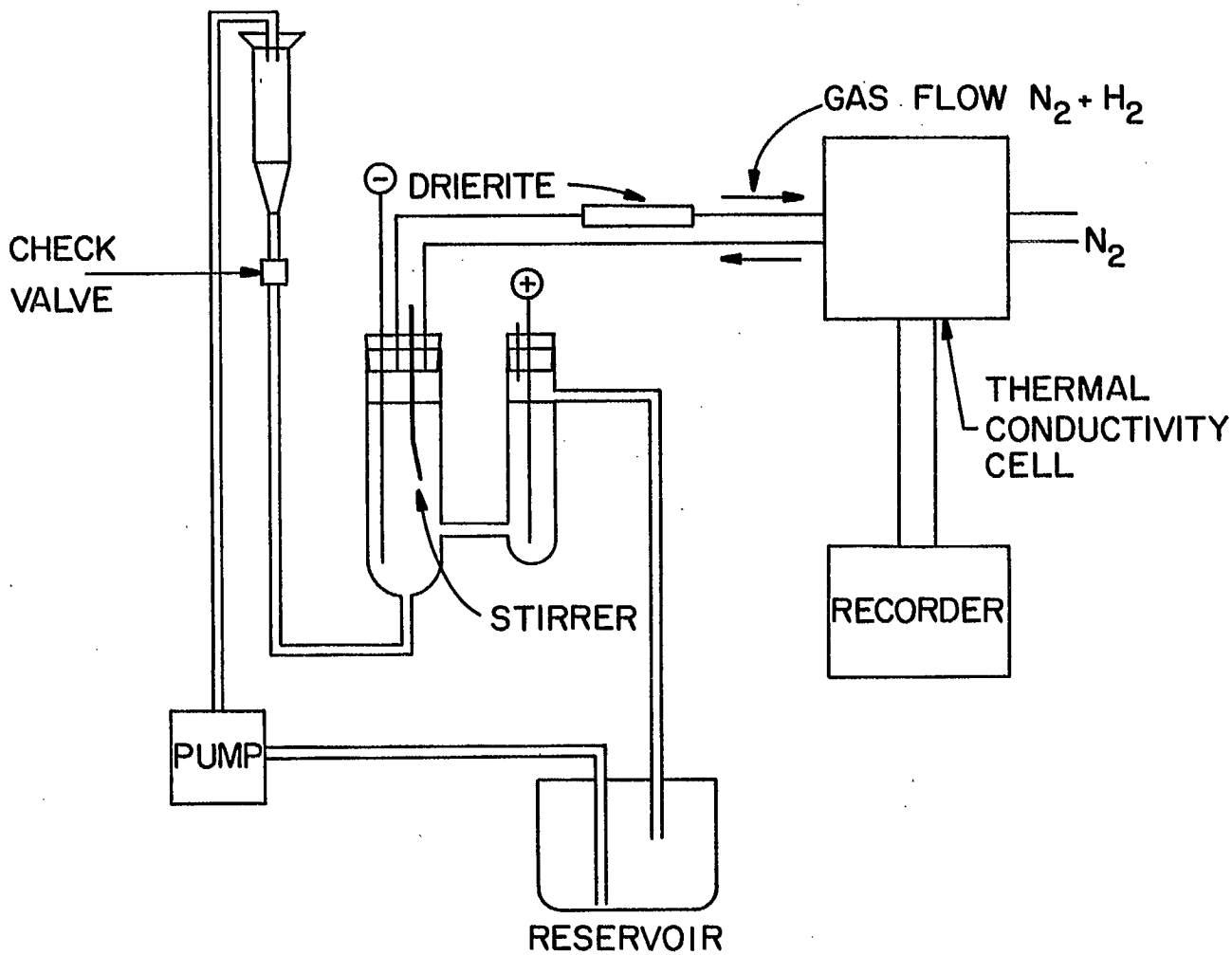
The apparatus consisted of an electrolytic cell (400 ml) with separate compartments for an aluminum cathode and a platinum anode, and a Gow Mac Thermal Conductivity Cell (TCC) which was used to measure the amount of cathodic hydrogen liberated during the electrodeposition of zinc (Figure 1). High-purity nitrogen gas flowing at a rate of 50 cc/min was used to carry the evolved hydrogen from the cathode compartment through a Drierite column and thence to the TCC apparatus. The

differential signal from the TCC apparatus was detected on a Philips recorder.

The cathode was a piece of pure aluminum foil with an effective plating area of 2.8 cm<sup>2</sup>. A teflon stirrer was used in the cathode compartment to provide the gentle stirring action needed (10 RPM) to dislodge, at a uniform rate, the hydrogen bubbles formed at the cathode. A small pump was used to recirculate the zinc electrolyte through the electrolysis cell at a flow rate of 20 ml/min. The zinc electrolyte was maintained at a temperature of 24 ± 1°C.

The zinc electrolytic solution was prepared from high-purity (99.99%) zinc and doubly distilled water, and contained 65 grams of zinc and 200 grams of sulphuric acid per litre. These solutions, which were used as the starting materials to which all impurities were added, had the following impurity content in mg/litre: Al (0.13), Pb (0.013), Cd (<0.001). The metallic impurities were added to the zinc electrolyte as 1-ml aliquots to give an effective concentration of 1 milligram of impurity per litre of solution. Fresh solutions and unused aluminum foil cathodes were used for each twenty-minute test. The solutions of metallic impurities were prepared from either reagent-grade chemicals or dissolved metals and were present as either sulphates (Cu<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Al<sup>3+</sup>, Pb<sup>2+</sup>, Mg<sup>2+</sup>, Zr<sup>4+</sup>, La<sup>3+</sup>, Cr<sup>6+</sup>, Mn<sup>2+</sup>, Ge<sup>2+</sup>, In<sup>2+</sup>, Tl<sup>3+</sup>, Ti<sup>4+</sup>) or

Figure 1



Schematic diagram of the apparatus used to measure cathodic hydrogen evolution during zinc electrolysis.

chlorides ( $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Hg}^+$ ,  $\text{Te}^{4+}$ ,  $\text{Rh}^{3+}$ ). Arsenic and silver solutions were prepared by the dissolution of  $\text{As}_2\text{O}_3$  and  $\text{Ag}_2\text{SO}_4$  in ammonia; selenium and rhenium solutions by the dissolution of their metals in 5N nitric acid; gold solutions by the dissolution of the metal in 5N aqua regia; and tungsten by the dissolution of the metal in a mixture of hydrofluoric and nitric acids. Vanadium was added as a solution of ammonium metavanadate, and antimony as potassium antimony tartrate.

Three sizes of powdered zinc were used for experiments in which the zinc electrolyte was purified by the cementation of metallic impurities on zinc powder. Two sizes of zinc powder, averaging 150 mesh and 60 mesh, were prepared by the air-atomization process. The 10-mesh zinc was reagent-grade, granular zinc metal of constant mesh size. The cementation reaction took place in the reservoir (Figure 1), where the zinc dust was stirred at 250 rpm in the solution.

The electrolysis apparatus was calibrated for current efficiency by two methods. A 4N sulphuric acid solution was electrolyzed with an aluminum foil cathode and the resulting hydrogen gas was passed through the TCC. The volume of hydrogen evolving was calculated from Faraday's Law and used to calibrate the TCC. The current efficiency for zinc electrolysis was determined from the equation:

$$\text{current efficiency (\%)} = 100 (I_{\text{Zn}} - I_{\text{H}_2}) / I_{\text{Zn}}, \quad [1]$$

where  $I_{\text{Zn}}$  was the total electric current consumption per unit time during zinc electrodeposition, and  $I_{\text{H}_2}$  was the electric current per unit time required to produce the volume of hydrogen evolved, as indicated by the TCC. The second method consisted of comparing the weight of deposited zinc, after drying, with the calculated amount of zinc that should have been deposited for current,  $I$ , during time,  $t$ , using Faraday's Law. The hydrogen evolution method tended to give current efficiency readings one to three per cent below that calculated using the weight method, indicating that small amounts of hydrogen were evolved at times by some process other than the electrodeposition of hydrogen. The weight method was used as the primary method of meter calibration to relate hydrogen evolution to the current efficiency of zinc electrodeposition. Acidic zinc solutions containing various concentrations of cadmium and copper were used for the calibration tests.

## RESULTS AND DISCUSSION

The effects of a number of different metal ions, either separately or in combination, on the current efficiency of zinc electrodeposition are listed in Table 1 and shown in Figures 2 to 5. A wide variety of metallic impurities were tested, some

of which are not commonly found in zinc electrolysis solutions.

Two of the mechanisms by which metallic impurities in zinc electrolysis solutions are thought to lessen the current efficiency by increasing hydrogen evolution are: (a) lowering the hydrogen overvoltage on specific sites on the cathodic zinc deposits, and (b) forming galvanic couples on the zinc deposits, thereby increasing the corrosion rate of zinc<sup>(5)</sup>. We have attempted to classify the metallic ion impurities into groups, based on their effect on the current efficiency, the hydrogen overvoltage, and the standard electrode potential of the parent metal<sup>(2)</sup>. The proposed classes are listed below:

CLASS I: Those metals which have sulphate potentials more electronegative than that of zinc sulphate in acid solutions.

CLASS II: Those metals which have hydrogen overvoltages above that of zinc (1.00 volt at 10 milliamperes/cm<sup>2</sup> in 2N sulphuric acid)<sup>(12)</sup>, and sulphate potentials which are less electronegative than that of zinc sulphate but more electronegative than that of sulphuric acid.

CLASS III: Those metals which have hydrogen overvoltages less than that of zinc, and which have sulphate potentials less electro-

TABLE I - CURRENT EFFICIENCY (%) OF ZINC ELECTRODEPOSITION

IMPURITY	CONCENTRATION (mg/litre)								
	0	1	2	3	4	5	10	15	20
Mg	92	--	--	--	--	91.5	91	90	88
Sr	92	89	85	--	--	70	--	--	--
Ti	92	--	--	--	--	62	--	--	--
Zr	92	--	83	--	--	81	79	--	--
V	92	86	--	77	--	68	--	--	--
Cr	92	88	--	84	--	81	--	--	--
W	92	62	55	53	--	--	--	--	--
Mn (2+)	92	--	--	--	--	82	74	--	--
Mn (4+)	92	--	--	--	--	89	87	85	83
Re	92	--	89	--	--	85	80	75	70
Fe	92	--	--	--	--	91	86	82	--
Co	92	--	--	--	--	90	84	77	--
Rh	92	33	--	--	--	--	--	--	--
Ni	92	--	--	--	--	88	80	70	--
Pt	92	80	23	--	--	--	--	--	--
Cu	92	--	--	--	--	83	72	56	--
Ag	92	--	--	--	86	82	13	--	--

--cont'd

TABLE I - CURRENT EFFICIENCY (%) OF ZINC ELECTRODEPOSITION (cont'd)

IMPURITY	CONCENTRATION (mg/litre)								
	0	1	2	3	4	5	10	15	20
Au	92	--	54	--	9	--	--	--	--
Cd	92	--	--	--	--	90	88	85	80
Hg	92	94	56	10	--	--	--	--	--
Al	92	--	--	--	--	92	92	91	90
In	92	91	89	79	61	38	--	--	--
Tl	92	95	93	87	83	--	--	--	--
Ge	92	62	50	--	--	--	--	--	--
Sn	92	78	--	--	--	69	60	--	--
Pb	92	--	--	--	--	91	90	88	--
As	92	--	--	--	--	94	96	--	--
Sb	92	38	15	--	--	--	--	--	--
Se	92	93	94	--	--	96	97	--	--
Te	92	74	57	22	--	--	--	--	--
La	92	90	89	--	--	88	87	--	86
Ce	92	--	--	--	--	91	87	82	--
Cu + Ni	92	90	89	88	--	84	78	67	--

--cont'd



TABLE I - CURRENT EFFICIENCY (%) OF ZINC ELECTRODEPOSITION (concluded)

IMPURITY	CONCENTRATION (mg/litre)								
	0	1	2	3	4	5	10	15	20
Cu + Co	92	92	--	90	--	89	82	--	--
Cd + As	92	--	90	--	88	87	83	81	79
Co + As	92	89	--	83	62	28	--	--	--
Cu + As	92	--	47	--	--	--	--	--	--
Fe + As	92	--	--	--	--	86	82	80	--
Ni + As	92	88	80	44	--	--	--	--	--
Co + Cu + As	92	90	88	84	57	--	--	--	--
Cd + Sb	92	89	83	77	--	--	--	--	--
Co + Sb	92	27	--	--	--	--	--	--	--
Cu + Sb	92	68	43	--	--	--	--	--	--
Fe + Sb	92	36	--	--	--	--	--	--	--
Co + Cu + Sb	92	87	80	74	68	21	--	--	--

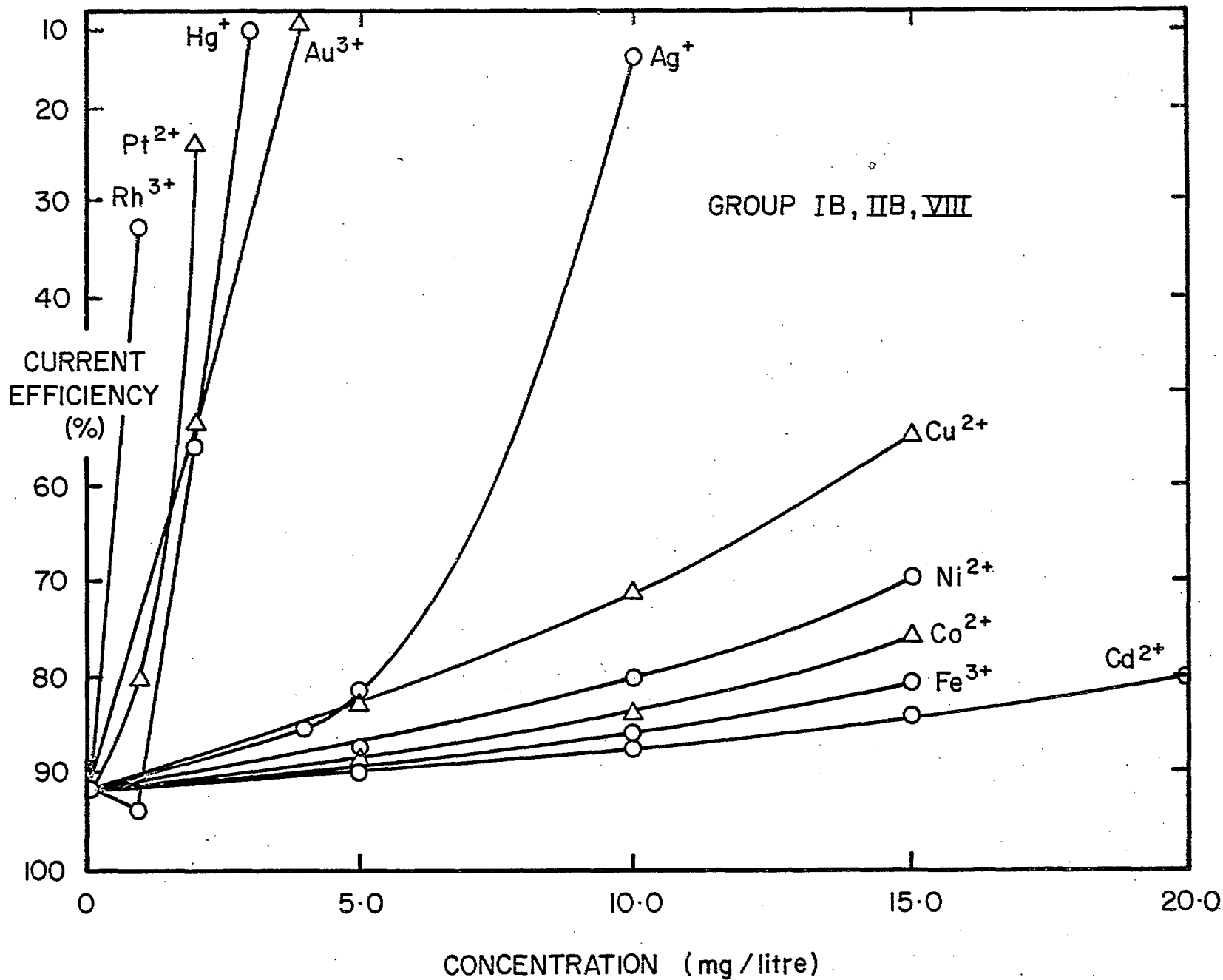


Figure 2. Effect of the metallic impurities of groups IB, 2B, and 8 of the periodic table on the current efficiency of zinc electrolysis.

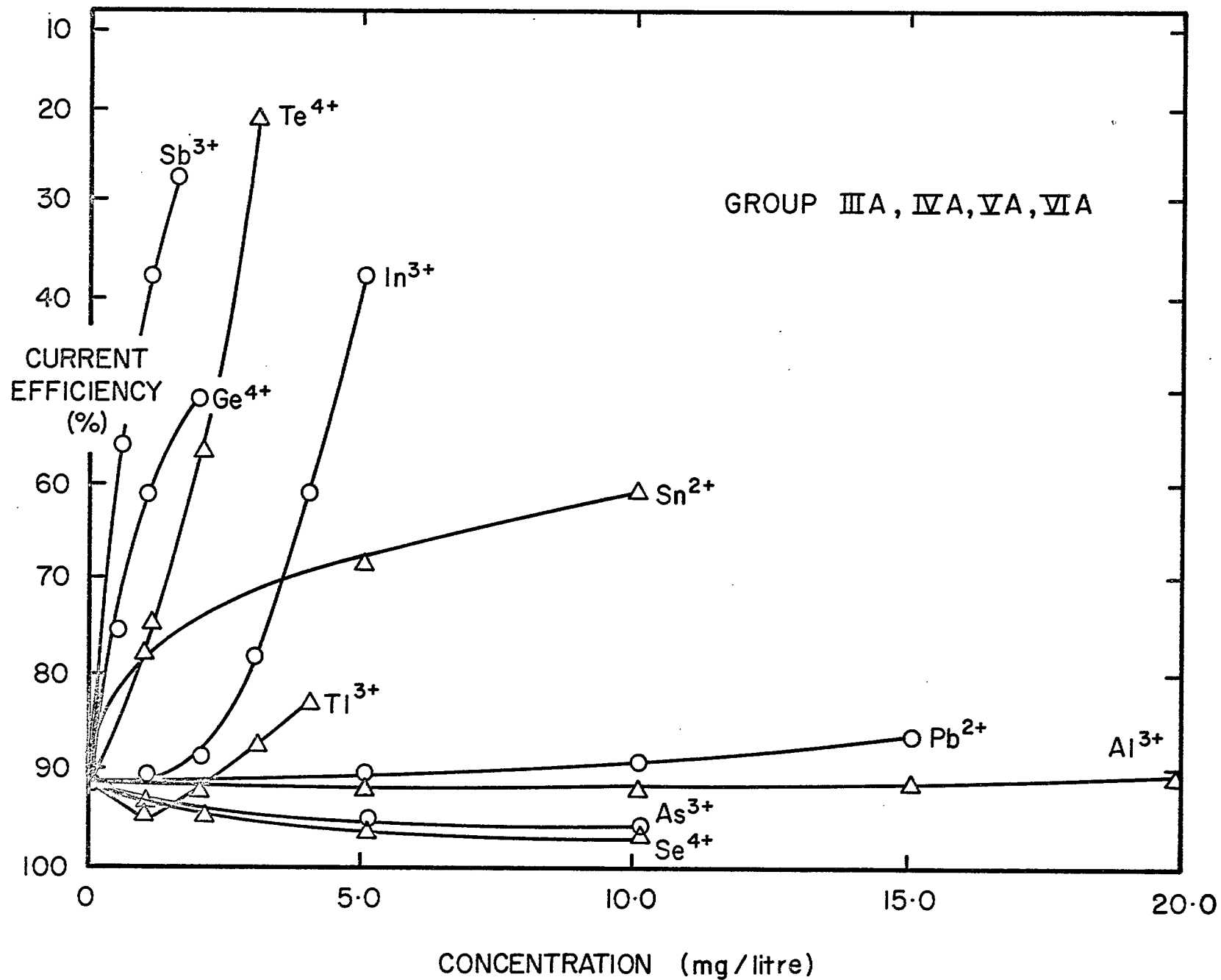


Figure 3. Effect of the metallic impurities of groups 3A, 4A, 5A and 6A of the periodic table on the current efficiency of zinc electrolysis.

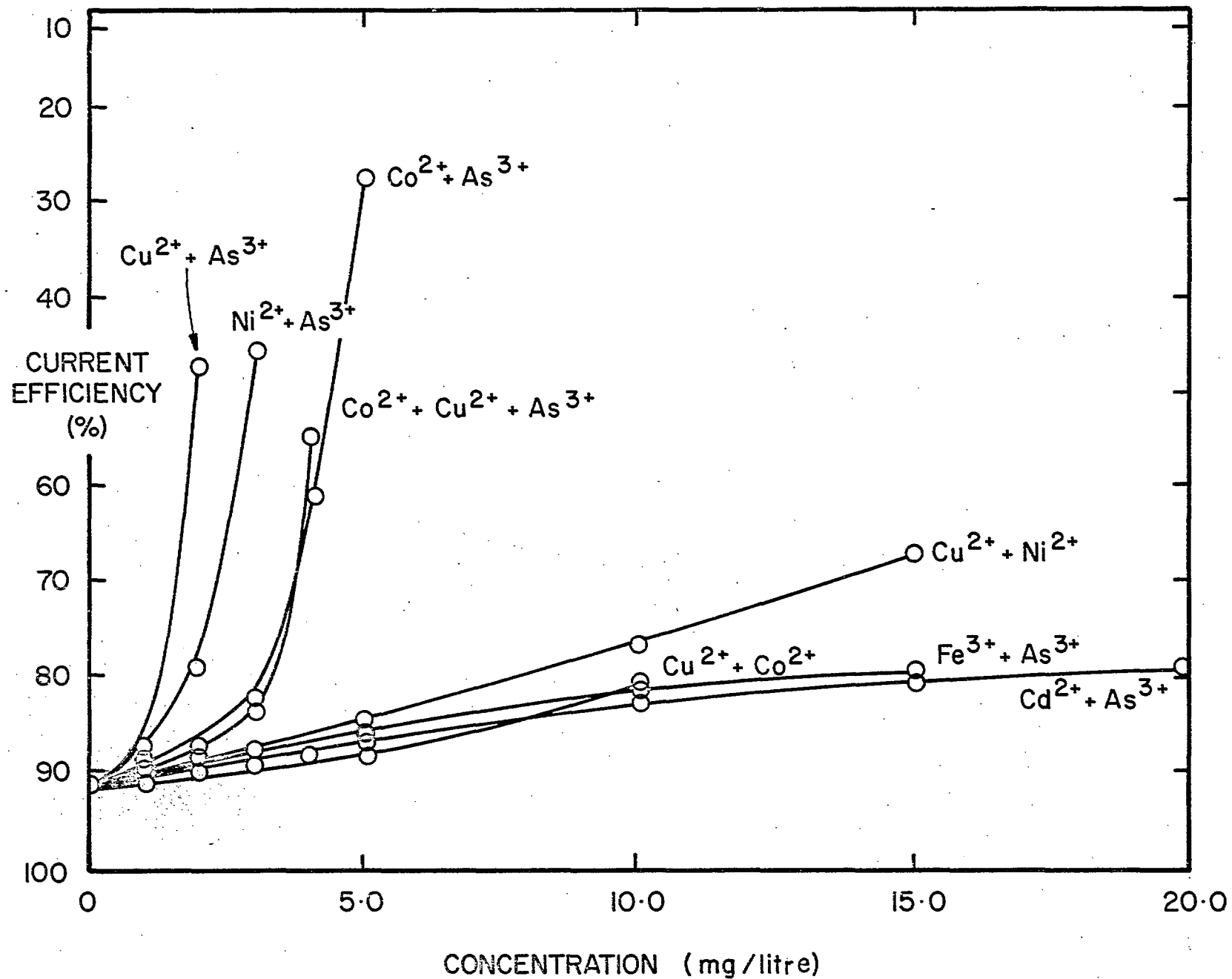


Figure 4. Effect of combinations of metallic impurities with arsenic on the current efficiency of zinc electrolysis.

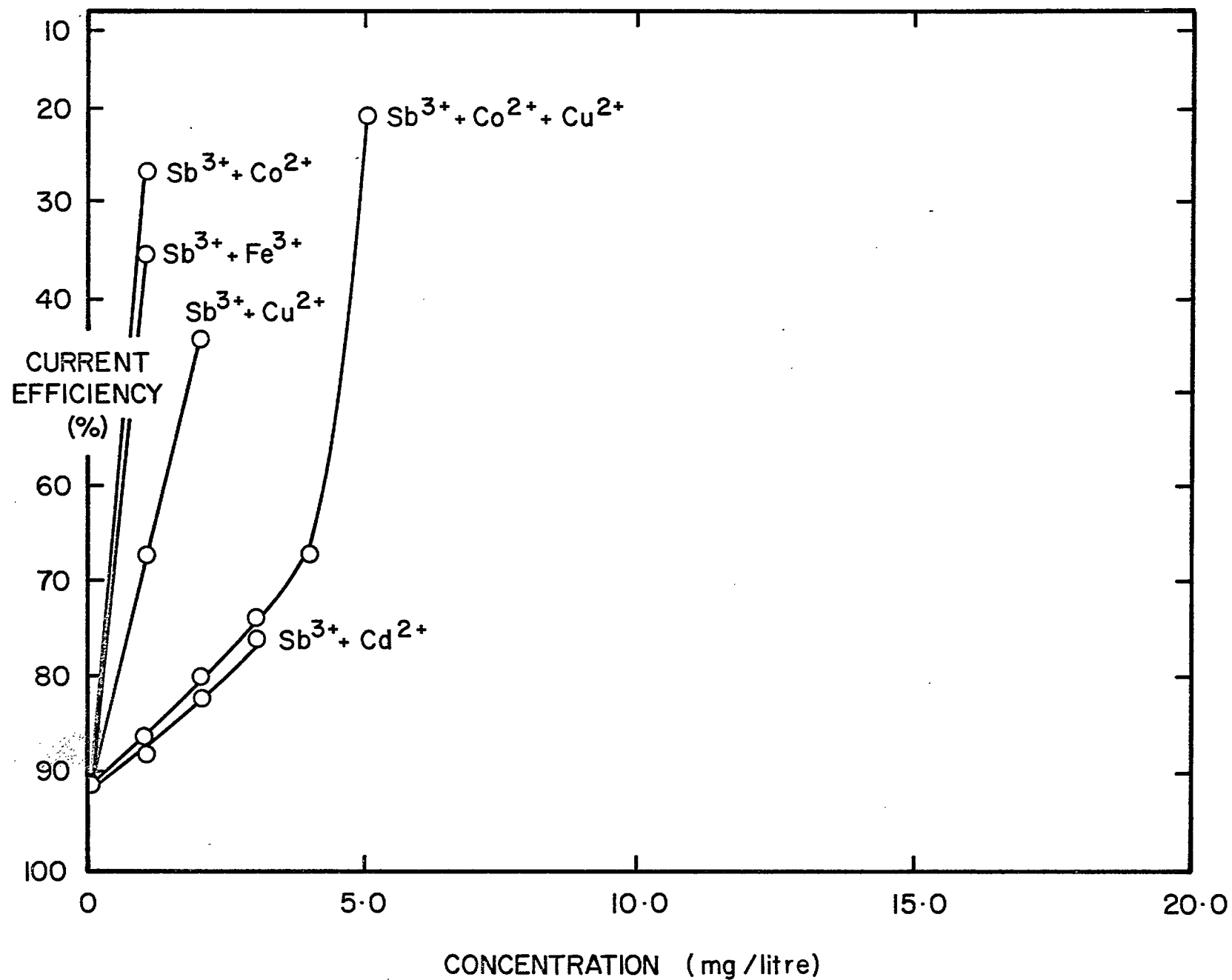


Figure 5. Effect of combinations of metallic impurities with antimony on the current efficiency of zinc electrolysis.

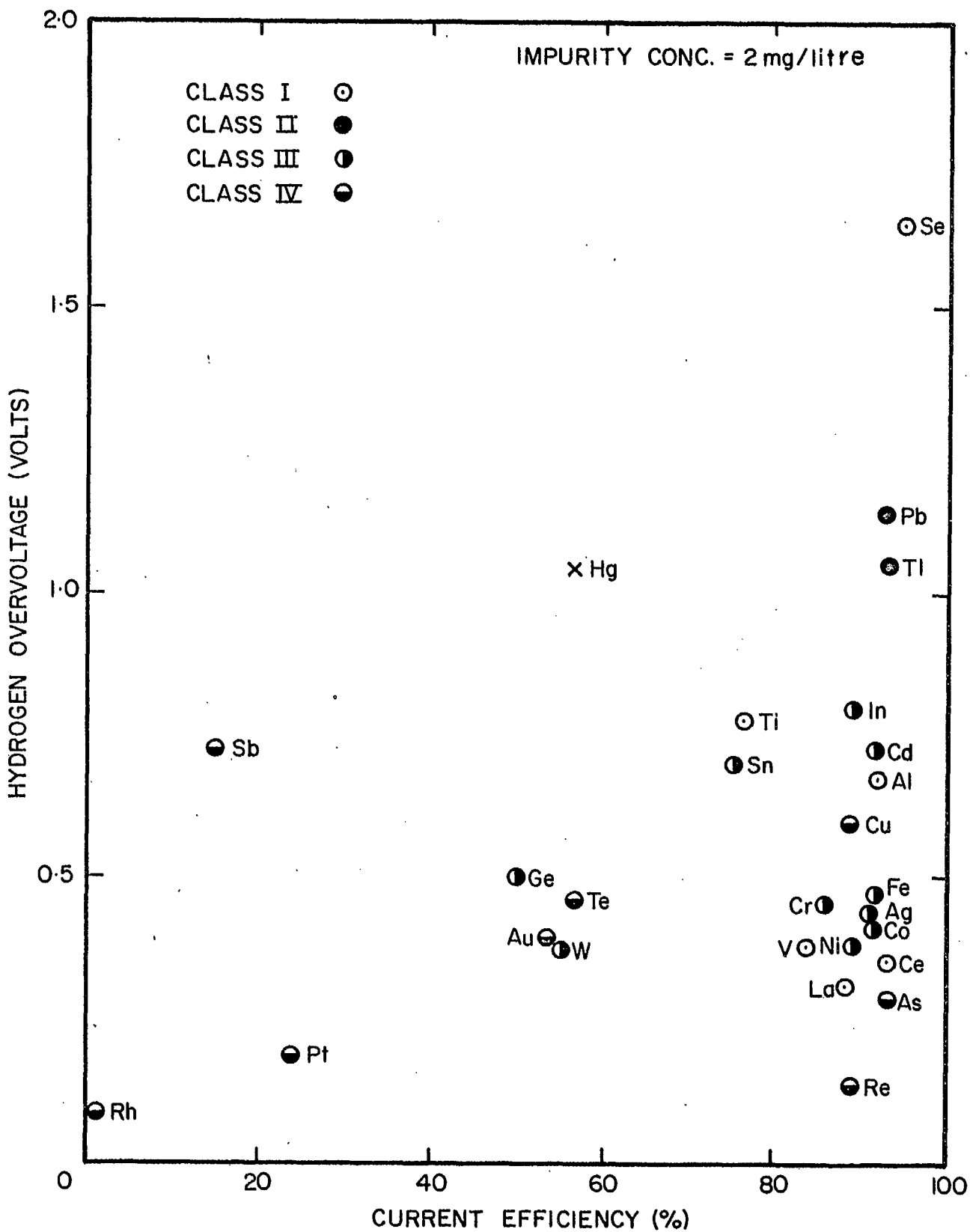
negative than that of zinc sulphate but more electronegative than that of sulphuric acid.

CLASS IV: Those metals which have hydrogen overvoltages less than that of zinc and which have sulphate potentials that are more electropositive than that of sulphuric acid.

The relationship between the current efficiency of zinc electrodeposition, the hydrogen overvoltage, and the standard electrode potentials of the metallic impurities is shown in Figure 6, in which the elements have been separated into the four classes described above. Mercury does not fit into the above classes, and has therefore been listed separately. The hydrogen overvoltage data were taken from references 12 to 23 and are for the parent metals in 2N sulphuric acid at a current density of 10 milliamperes, except for lanthanum and cerium (phosphate-buffered phosphoric acid) and germanium and chromium (1N sulphuric acid). Standard electrode potentials were used (24).

It was found that the harmful effect of the metallic impurities on the current efficiency of zinc electrodeposition generally increased as the hydrogen overvoltage of the parent metals decreased. However, there were several exceptions.

Figure 6



The relationship between the current efficiency of zinc electrodeposition, the hydrogen overvoltage, and the standard electrode potentials of the metallic impurities.

Class IV impurities were generally the most harmful to zinc electrodeposition, followed in order by Class III, Class I and Class II impurities. These results are discussed below in more detail for the individual metallic impurities.

#### Class I

The metallic impurities in this class would not be expected to have much influence on the current efficiency of zinc electrolysis, because zinc would be preferentially electrodeposited. However, they might affect the growth kinetics and morphology of the zinc deposit and the electrical conductance of the acid zinc electrolyte.

The metallic impurities aluminum, cerium and magnesium were found to have little effect on the current efficiency of zinc electrodeposition at concentrations up to 20 mg/l. Manganese, which is usually present in appreciable quantities in zinc electrolytes, was found to have little effect on current efficiency when present in the (+4) valence state, but it did decrease the current efficiency somewhat when present in the (+2) valence state. Other investigations have shown that manganese in either valence state had a minimal effect on current efficiency and improved the structure of the zinc deposit by distributing zinc evenly over the electrode<sup>(2,25-28)</sup>.

Permanganate ion caused a large decrease in current efficiency.



Selenium increased the current efficiency of zinc electrodeposition when present in concentrations of up to 20 mg/l. The effect could be related to both the large hydrogen overvoltage of selenium and the poisoning of hydrogen evolution centres on the zinc deposit, caused by the formation of selenium hydrides<sup>(29)</sup>. Some reports indicate that selenium decreases the current efficiency of zinc electrodeposition<sup>(2,10,30)</sup>, but this decrease could be caused by the presence of other impurities or it might depend on the ionic form in which the selenium exists in solution.

Titanium, lanthanum, zirconium, strontium and vanadium (as metavanadate) were found to decrease the current efficiency significantly when present in concentrations up to 20 mg/l. The effect may be related to an alteration of the growth kinetics and morphology of the zinc electrodeposit, resulting in an increased number of centres for hydrogen evolution. It has been reported that, in some instances, titanium may increase the current efficiency of zinc electrodeposition<sup>(31)</sup>.

## Class II

Lead had little effect on the current efficiency of zinc electrodeposition. The effect is most likely related to the large hydrogen overvoltages shown by the parent metal. Lead is reported to slightly increase the current efficiency of zinc

electrodeposition<sup>(7,10)</sup>. However, large concentrations will result in the incorporation of the lead into the zinc deposit<sup>(2,4)</sup>.

Increasing the thallium concentrations initially increased, then decreased slightly, the current efficiency of zinc electrodeposition. A similar effect has been reported by Bratt<sup>(6)</sup>. Other investigations have shown that thallium either increases the current efficiency slightly<sup>(10)</sup> or has no effect<sup>(2)</sup>. The effect appears to depend somewhat on which other impurities are present.

### Class III

Iron, cobalt, nickel and chromium impurities all had much the same effect on the current efficiency of zinc electrodeposition. Their presence decreased the current efficiency by up to 25% at a concentration of 20 mg/l. Chromium had the largest effect, followed in turn by nickel, cobalt, and iron. On the basis of their hydrogen overvoltages, which are approximately one-half that of zinc, these metallic impurities would be expected to have a greater effect on the current efficiency of zinc electrodeposition than was actually observed. However, they have higher deposition overpotentials than zinc<sup>(3)</sup>, indicating that the concentration of these metallic impurities in the zinc deposit would be somewhat limited.

Nickel and cobalt impurities appear to reduce the current efficiency by depositing with zinc as mixed alloy phases,

which then redissolve into solution, resulting in the evolution of hydrogen on cathodic sites<sup>(7,32,33)</sup>. Thus, successive cycles of electrodeposition and redissolution take place on the surface of the electrodeposited zinc<sup>(34)</sup>. It has been shown that cobalt ions tend to discharge on cobalt crystals that have already been formed, whereas nickel ions are deposited more evenly over the surface<sup>(35)</sup>. Cobalt impurities would be expected, therefore, to increase the corrosion of zinc more than that of nickel<sup>(8)</sup>. However, the observation that nickel reduces the current efficiency more than cobalt would indicate that the lower hydrogen overvoltage of nickel also plays an important part in decreasing the current efficiency of zinc electrodeposition.

Iron tends to lower the current efficiency by consuming power while being successively reduced at the cathode to the ferrous state and oxidized at the anode to the ferric state<sup>(2,28)</sup>. Chromium probably has much the same effect. This effect would not be detected by measuring the evolution of hydrogen but would be noticeable from measurements of the weight of zinc deposited. Chromium, which had a greater effect on the current efficiency than iron, increased the evolution of hydrogen on the zinc deposit. Iron ions are reported to partially block the evolution of hydrogen at cathodic sites on the zinc electrodeposit, because they hydrolyze next to the deposit surface<sup>(7)</sup>.

Silver and indium impurities have to exceed some critical concentration in the zinc electrolyte (5 mg/l for silver and 3 mg/l for indium in the experiments reported here) before the current efficiency of zinc electrodeposition is seriously affected. In these respects, the effects resemble that of copper, a Class IV impurity. Studies of zinc electrodeposition on silver cathodes showed that the zinc deposit did not cover the whole surface, leaving areas of low hydrogen overvoltage at which hydrogen could be evolved<sup>(36)</sup>. The same effect could have occurred in the present case, when sufficient silver had deposited on the cathode. Black, powdery deposits were obtained when silver was present as an impurity in the zinc electrolyte.

Germanium, tungsten, tin, indium and cadmium impurities can be classed in a group, because they lower the current efficiency of zinc electrodeposition in proportion to the hydrogen overvoltage of the parent metals (Figure 6). Cadmium, which has a relatively high hydrogen overvoltage, had little effect. Cadmium is usually found to be distributed evenly in the zinc electrodeposit<sup>(37)</sup> and would be expected to have little effect on the current efficiency in quantities up to 150 mg/l<sup>(2)</sup>. Indium and tin, even though they have relatively high hydrogen overvoltages, greatly decreased the current efficiency when present at concentrations greater than 2 mg/l. Several other

studies also reported that tin was detrimental to the current efficiency of zinc electrolysis<sup>(6,10)</sup>. The presence of tin tends to alter the crystalline structure of the zinc deposit<sup>(2)</sup>, possibly allowing hydrogen evolution to occur at preferred sites on the deposit. Indium is not normally found in zinc electrolytes, and little has been reported about its effect on zinc electrodeposition.

Germanium and tungsten were found to cause a large decrease in the current efficiency of zinc electrodeposition when present in small concentrations in the zinc electrolyte. This effect might be expected, because their hydrogen overvoltages are only half that of zinc. Most reports on the effect of germanium in zinc electrolytes indicate it greatly decreases the current efficiency of zinc electrodeposition<sup>(7,10,11,38)</sup>, although two papers report no effect<sup>(39,40)</sup>, possibly because of the difficulty in getting germanium into solution<sup>(7)</sup>. A radioisotope study<sup>(41)</sup> indicated that germanium is deposited at preferred centres on the cathode when the solution contains as little as 0.3 mg/l. The zinc deposit is blistered on the cathode at these spots. Excessive amounts of hydrogen are subsequently released and the zinc deposit becomes spongy with a large number of pinholes. There is also the possibility that germanium hydride may be evolved at the cathode<sup>(42)</sup>.

Class IV

The metallic impurities rhodium, platinum, gold and tellurium caused large decreases in the current efficiency of zinc electrodeposition when present in small amounts in the zinc electrolyte. Rhodium, which had the lowest hydrogen overvoltage, also caused the largest decrease in current efficiency. These metallic impurities probably decrease the current efficiency by providing cathodic sites of low hydrogen overvoltage at which the electrodeposition and evolution of hydrogen can readily occur. Larger concentrations of tellurium are reported to cause large areas of the zinc deposit to redissolve<sup>(2)</sup>.

Antimony had a very harmful effect on the current efficiency of zinc electrodeposition, though the parent metal has a relatively high hydrogen overvoltage. The zinc deposits tend to be friable and porous, with the formation of dendritic growths<sup>(7,28,36)</sup>, probably because of the formation of gaseous antimony hydride on the surface of the zinc deposit<sup>(27)</sup>.

Antimony is known to act as a catalyst in the decomposition of gaseous antimony hydride<sup>(43)</sup>. This could account for the large volumes of hydrogen released at the cathode<sup>(7)</sup>, where a reaction involving the formation and decomposition of gaseous antimony hydride could occur on the surface of the cathode.

Copper did not cause a large decrease in current

efficiency until a concentration of 5 mg/l had been exceeded. Loss in current efficiency probably resulted from the dissolution of zinc into the solution as a result of local cells set up on the surface of the zinc electrodeposit<sup>(7)</sup>. Copper is known to deposit with some regularity over the surface of the zinc electrodeposit<sup>(7)</sup>, so it would appear that a certain concentration of copper in solution must be exceeded before enough copper deposits to form local galvanic cells.

Arsenic had a beneficial effect, while rhenium had little effect on the current efficiency of zinc electrodeposition, even though these metallic impurities have low hydrogen overvoltages when present as the parent metal. These findings agree with the more recent literature<sup>(2,7,38)</sup>, although some reports indicate that arsenic tends to reduce the current efficiency<sup>(10,11)</sup>. The effect of arsenic is probably one of poisoning the centres for hydrogen evolution, possibly by the formation of intermetallics such as  $ZnAs_2$ <sup>(7)</sup>. There is also evidence of the formation of a small amount of hydrogen arsenide.

Many of the Class IV impurities were added as chloride salts, so it was possible that the chloride ions could have some effect on the current efficiency. However, tests made with an equivalent amount of hydrochloric acid added to the zinc electrolyte showed no change in current efficiency from that of zinc electrolytes.

Mercury does not fit into any of the four classes, because of its high hydrogen overvoltage and electropositive potential. Mercury increased the current efficiency at a concentration of one mg/l, but at greater concentrations it decreased the current efficiency. The large hydrogen overvoltage normally present on liquid mercury would be expected to apply in this case and decrease the efficiency of hydrogen evolution on the surface of the zinc deposit<sup>(2,7,10)</sup>. However, at certain concentrations, mercury apparently catalyzes the evolution of hydrogen. Studies involving the deposition of ruthenium onto mercury from acid solutions of ruthenium chloride have shown that high rates of catalytic hydrogen evolution occur on the edges of the growth centres<sup>(44)</sup>. It is possible that a similar mechanism involving zinc electrodeposition on areas of mercury could account for the large amount of hydrogen evolution observed in the present case. Another possibility is that the mercury is evolved from the cathode along with hydrogen. Recent studies<sup>(45)</sup> have shown that this is the case for the metal electrodes iron, nickel, cobalt and platinum.

#### Combinations of Impurities

The literature on acid zinc electroplating contains numerous references on the harmful effects toward current efficiency of various combinations of impurities<sup>(2,39)</sup>. The



effects do not appear to be always additive and are, therefore, difficult to predict<sup>(10,46)</sup>. Several tests were made on the effects on current efficiency of combinations of metals with arsenic and antimony. The results are listed in Table 1 and shown in Figures 4 and 5.

The combination of equal amounts of cobalt and of iron with antimony resulted in the same decrease in current efficiency as when antimony was present as the only impurity. Because the concentration of antimony had been reduced by a half in these tests as compared to the tests involving antimony alone, cobalt and iron doubled the harmful effect of antimony towards zinc electrodeposition. The combination of an equal amount of copper with antimony reduced the current efficiency to one-half that of antimony alone, indicating that copper had no influence on the harmful effects of antimony towards zinc electrodeposition.

The combination of equal amounts of cadmium and of cobalt and copper greatly reduced the harmful effect of antimony towards zinc electrodeposition. All these observed effects are probably related to the kinetics of the formation and decomposition of gaseous antimony hydride on the surface of the zinc deposit, which was considered to be the process by which the large volumes of hydrogen were evolved. There is also the possibility of increased corrosion of the zinc electrodeposits due to a multiplicity of local cells formed on the surface of the deposit.

Combinations of equal amounts of iron and of cadmium with arsenic had little effect on the current efficiency as compared with that observed for iron and cadmium present individually. However, combinations of equal amounts of copper, of cobalt, of nickel, and of cobalt and copper with arsenic, all greatly decreased the current efficiency when present in small amounts. The most likely explanation for this behaviour is that a number of local cells are set up on the surface of the zinc electrodeposit, which greatly increase the corrosion rate of the deposit. Arsenic apparently does not "poison" the evolution of hydrogen in this case, possibly because it exists as an intermetallic.

#### Organic Additives

The effect of several organic and inorganic additives on the current efficiency of zinc electrodeposition was briefly examined. Sodium silicate, gum arabic and gelatin are often added to the zinc electrolyte to obtain smooth cathodic deposits<sup>(47,48)</sup>. Dimethyl-glyoxime is sometimes added to the zinc electrolyte during the purification stage to remove copper, lead, and tin<sup>(49)</sup>. A zinc electrolyte containing 15 mg/l of cupric sulphate and having a current efficiency of 56% was used for the experiments. One mg/l of gum arabic and of gelatin increased the current efficiency by 2%, while sodium silicate

reduced it 1%. Gum arabic and gelatin are known to increase the hydrogen overvoltage on the zinc surface, which would account for the increased current efficiency<sup>(48)</sup>. The presence of 10.0 mg/l of dimethyl-glyoxime in the zinc electrolyte increased the current efficiency 15% by reducing the copper concentration in the electrolyte.

#### Cementation by Zinc Dust

One of the important steps in zinc electrolyte purification is the cementation of the more electropositive metallic impurities by zinc dust<sup>(47)</sup>. The kinetics of the cementation of cadmium by zinc had previously been examined in this laboratory<sup>(50)</sup> and it was considered of interest to examine the effect on current efficiency of zinc electrodeposition while the electrolyte was being purified by cementation.

A zinc electrolyte containing 15 mg/l of iron, 2 mg/l of cobalt, 4 mg/l of lead, 5 mg/l of cadmium, 5 mg/l of copper and 0.1 mg/l of arsenic was used for the tests. The coarse zinc dust (10 mesh) increased the current efficiency of zinc electrodeposition from 59% to 67% in fifty-five minutes, the medium zinc dust (60 mesh) from 59% to 83% in ninety minutes, and the fine zinc dust (150 mesh) from 59% to 92% in one hundred and five minutes. After the current efficiency had reached its maximum value in each case, it then remained constant for the

duration of the test (two hours). The results suggest that a surface coating is formed on the zinc dust which retards the cementation reaction. Previous studies had shown that the combination of cobalt and arsenic in solution could retard the cementation reaction<sup>(50)</sup>. Increasing the surface area of the zinc dust allowed the cementation reaction to proceed closer to completion.

#### CONCLUSIONS

1. The current efficiency of zinc electrodeposition can be determined by measuring the volume of hydrogen evolved from the cathode during electrodeposition. The method used in the experiments reported here, which involved the measurement of the rate of hydrogen evolution using a thermal conductivity cell, could be used to give rapid and reliable data for the quality control of zinc electrodeposition on an industrial scale.
2. A number of metallic impurities were found to decrease the current efficiency of zinc electrodeposition. As a general rule, the current efficiency decreased in proportion to the decrease in hydrogen overvoltage of the metallic impurities in their massive form, although there were several exceptions. The metallic impurities could be divided into four classes, depending on their effect on the current efficiency of zinc

electrodeposition, their hydrogen overvoltage, and the standard electrode potential of the parent metal.

The metallic impurities rhodium, platinum, gold, silver, tungsten, antimony, germanium, tellurium and copper are particularly harmful to the current efficiency of zinc electrodeposition when present as single impurities in the acid zinc electrolytes. The combinations of cobalt, copper and nickel with arsenic, and of cobalt, copper and iron with antimony, in the acid zinc electrolytes were also very harmful to the current efficiency of zinc electrodeposition. In combination they reduced the current efficiency to less than 20% for concentrations of 5 mg/l or greater.

REFERENCES

- (1) Ingraham, T.R., and R.C. Kerby. Can. Met. Quarterly (in press).
- (2) Weimer, F.S., G.T. Wever and R.J. Lapee. Zinc (ed. by C.H. Mathewson). Reinhold, New York. Ch.6. 1959.
- (3) Vagramyan, A.T., and Z.A. Soleveva. Technology of Electrodeposition. R. Draper Ltd., Teddington. 1961.
- (4) Mantell, C.L. Electrochemical Engineering. McGraw-Hill, New York. Ch. 10. 1960.
- (5) Salin, A.A. Sbornik Nauch.-Tekh. Trudov, Nauch.-Issl. Inst. Met. Chelyabinsk Sovnarkhoza. 2: 131. 1960.
- (6) Bratt, G.C. Electrochem. Tech. 2: 323. 1964.
- (7) Turoshima, U.F., and V.V. Stender. Zhur. Prikl. Khim. 28: 372. 1955.
- (8) Pakhomova, G.N. Tsvetn. Met. 6: 35. 1965.
- (9) Salin, A.A., G.G. Rannev and I.M. Kogol. Tsvetn. Met. 5: 32. 1964.
- (10) D'Este, A., and R. Guerriero. Montevecchio. 16: 1. 1965.
- (11) Kett, M. Hutnicke Listy. 16: 669. 1961.
- (12) Petcherskaia, A.G., and V.V. Stender. Zhur. Fiz. Khim. 24: 856. 1950.
- (13) Ferguson, A.L. Nat. Bur. Stand. Circ. No. 524. 227. 1953.

- (14) Knobel, M. International Critical Tables. VI: 339. 1929.
- (15) Petrenko, A.T. Zhur. Fiz. Khim. 36: 1527. 1962.
- (16) Saltzberg, H.W., and B. Goldschmidt. J. Electrochem. Soc. 107: 348. 1960.
- (17) Morse, S.L., and N.D. Greene. Electrochim. Acta. 12: 179. 1967.
- (18) Wilde, B.E., and F.G. Hodge. Electrochim. Acta. 14: 619. 1969.
- (19) Gerischer, H. Anales de Fisica y Quimica. 56: 535. 1960.
- (20) Bockris, J.O'M. Trans. Faraday Soc. 43: 417. 1947.
- (21) Hoare, J.P., and S. Schuldiner. J. Chem. Phys. 25: 786. 1956.
- (22) Gobrecht, H., R. Kuhnkies and A. Tausend. Z. Elektrochem. 63: 541. 1959.
- (23) Konochuk, T.I., and I.B. Barmashenko. Ukrain. Khim. Zhur. 26: 25. 1960.
- (24) de Vries, T. Handbook of Chemistry and Physics. Chem. Rubber Pub. Co., Cleveland. 44th ed. 1743. 1963.
- (25) Kletenik, Iu.B. J. Appl. Chem. (USSR). 8: 1320. 1957.
- (26) Vekhidov, R.S., and G.Z. Kir'yakov. Izvest. Vysshikh. Ucheb. Zavedenii, Khim. i Khim. Technol. 2: 238. 1959.
- (27) Pecherskaya, A.G., and V.V. Stender. Zhur. Priklad. Khim. 23: 920. 1950.

- (28) Ellesworth, J.T. Trans. Amer. Electrochem. Soc. 42: 62. 1922.
- (29) Coughlin, R.W. Ind. Eng. Chem. 59: 45. 1967.
- (30) Raub, E. Metalloberflaeche. 22: 1. 1968.
- (31) Bundzhe, V.G., G.Z. Kir'yakov and F.K. Bainietova. Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR. 12: 18. 1964.
- (32) Yunus, M., C. Capel-Boute and C. Decroly. Electrochim. Acta. 10: 885. 1965.
- (33) Volkov, L.V., and B.P. Yurev. Electrokhimiya. 5: 1143. 1969.
- (34) Maja, M., and S. Pozzoli. Chim. Ind. 51: 133. 1969.
- (35) Pecherskaya, A.G., and V.V. Stender. Zhur. Fiz. Khim. 24: 856. 1950.
- (36) Kiryakov, G.Z. Zhur. Prik. Khim. 35: 2661. 1962.
- (37) Fink, C.G., and C.B.F. Young. Trans. Electrochem. Soc. 82: 311. 1935.
- (38) Liebscher, R. Neue Huette. 14: 651. 1969.
- (39) Ross, S.T., and J.L. Bray. Trans. AIME. 191: 465. 1951.
- (40) Lyons, E. Trans. Electrochem. Soc. 89: 290. 1946.
- (41) Fischer-Bartelk, Ch. Freiburger Forschungshefte. B47: 21. 1960.
- (42) Zelezny, W.F., J.H. Foreman and G.T. Wagner. Paper presented to Amer. Inst. Mining Met. Petr. Engineers. New York. February 15-18, 1960.



- (43) Iofa, Z.A., and E.I. Lyakhovetskayn. Proc. Acad. Sci. USSR. 86: 577. 1952.
- (44) Fleischmann, M., J. Koryta and H.R. Thirsk. Trans. Faraday Soc. 63: 1261. 1967.
- (45) Vondrak, J., and J. Balej. Electrochimica Acta. 16: 1331. 1971.
- (46) Steintveit, G., and H. Holtan, Jr. J. Electrochem. Soc. 107: 247. 1960.
- (47) Jephson, A.C., A.Y. Bethune and R.C. Kelahan. J. Metals. 18: 947. 1966.
- (48) Pring, J.N., and U.C. Tainton. J. Chem. Soc. 105: 710. 1914.
- (49) Khan, O.A. Rudneyj Altaj-Sovnarch. Vost. Kazek. Adm. Raj. 1: 28. 1958.
- (50) Ingraham, T.R., and R. Kerby. Trans. AIME. 245: 17. 1969.

