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ELECTROLYTIC DEPOSITION of ZINC

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BUTTE, MONTANA,
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ELECTROLYTIC DEPOSITION of ZINC

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THE EFFECT OF HYDROGEN OVERVOLTAGE ON THE
ELECTROLYTIC DEPOSITION OF ZINC

INTRODUCTION

In the deposition of metallic zinc by electro-
lysis from neutral or acid solution, little difficulty
is experienced provided certain impurities are absent
from the electrolyte. The use of the process has long
been considered as a potential source, patents on the
process having been issued as early as 1880. However,
the early experimenters failed to realize the impor-
tance of impurities in the electrolyte, and for this
reason, the process suffered several severe setbacks
when commercial plants were built. Good deposits of
zinc would be obtained in the laboratory where pure
zinc sulphate was used as the electrolyte, but on
leaching commercial zinc ores with sulphuric acid,
poor or no deposits were obtained when the resulting
solution was electrolyzed, so the process was practic-
ally abandoned.

During the early period of the World War, there
came a large demand for pure zinc. The only zinc then
on the market was the Prime Western, a comparatively

impure spelter, and the Horsehead, produced at Franklin, New Jersey, and running slightly over 99% pure. At the time, this brand commanded a large premium, and for this reason a source of pure zinc, cheaply obtained, was again sought. The electrolytic refining of impure zinc was practiced during the period of the World War, but was discontinued due to the extra cost involved when prices dropped. Attention was again directed to the process which involved the leaching of zinc ores with sulphuric acid, and then electrolyzing the resulting solution. Several companies started the investigation almost simultaneously; among these were the Anaconda Copper Mining Co, at their Great Falls plant; the Trail Consolidated Mining Co, at Trail, B. C.; and the General Electric Company at their zinc properties at Bully Hill, Cal. These investigations brought out and drove home the fact that the leached solutions must be purified of all metals more noble than zinc before successful electrolysis can be hoped for. Purifying processes were then perfected, and with this phase of the problem well in control, several commercial plants were built and put into operation. High current efficiencies were generally obtained at these plants, but from time to time the efficiency would drop way off. The solution then had to be withdrawn from the cells and re-purified.

Hydrogen overvoltage according to Tainton[5] is the "be all" of the electrolytic zinc process. If it were not for this phenomenom, the electrolytic zinc process as now in use could not be possible for the simple reason that in aqueous solution hydrogen would be deposited at the cathode rather than zinc. This is due to the fact that metals are deposited electrolytically from solution in the inverse order of their position in the electrochemical series, and since hydrogen is under zinc, it should, practically, be totally depleted from a solution before it could be possible for any zinc to be deposited. However, due to hydrogen overvoltage, hydrogen becomes less noble than zinc, this phenomenom making it possible for the zinc to be deposited from aqueous solution. The single potential of zinc is about -0.8 volts, while the overvoltage of hydrogen on zinc is about -0.76 volts; as long as this condition exists at the cathode, it is possible for both hydrogen and zinc to be deposited simultaneously, whereas if hydrogen did not have an overvoltage on zinc, only hydrogen would be evolved.

The drop in the current efficiency in the zinc cell can be due to either of two causes. First, when more noble metals are deposited on the cathode with zinc, an electric couple is set up between them and

the zinc which causes the re-solution of the zinc
from the cathode; and, secondly, the impurities pre-
sent could cause a lowering of the hydrogen overvolt-
age at the cathode where deposition takes place and
cause hydrogen evolution rather than zinc deposition.
This latter cause was the one elected to be studied.
As far as could be determined from the literature, no
attempts had been made to study this particular phase
of the problem. Tartar and Keyes[1] had done some work
determining the hyrdrogen overvoltage of several metals
under zinc in the electrochemical series, namely nickel,
copper and iron in pure zinc sulphate solution contain-
ing some free sulphuric acid. Ellsworth[2] did some work
in determining the maximum amount of single impurities
with which it was possible to still carry on the electro-
deposition of zinc from sulphate solutions, but he did
not make a specific study of their effect on the hydro-
gen overvoltage. Laist[3], in describing the electrolytic
zinc plant of Anaconda at Great Falls, also mentions
the effect of impurities present on electrolyzing, but
does not explain the causes for the deleterious action
attributed to them.

EXPERIMENTAL

Zinc was first deposited from its sulphate solu-
tion to determine the current efficiency. A control

board was assembled which made it possible to obtain
suitable voltage control. Meters were so placed in
the circuit, as shown in figure 1, that it was possible
at all times to note the EMF and the current. Lead
anodes and a zinc cathode were placed in the solution,
and zinc was deposited on the cathode. The submerged
area of each electrode was two square inches and the
spacing of anode to cathode, two inches. Several con-
centrations of zinc sulphate were used in the electro-
lyte in an attempt to establish one which would give
the most efficient deposition. The results obtained,
as shown in Table I, were variable but seem to indicate
after a little examination and thought that the higher
concentrations give the better efficiency. Acid con-
centrations were also varied and higher acid strengths
seem to indicate higher current efficiencies.

TABLE I

Test made in ZnSO4 solution

	Concentration gm/liter	EMF	Current Density amps/sq/ft.	Current Efficiency
1	50g Zn	3.2v	11.5	80.0%
2	75g Zn	3.2v	12.1	83.0%
3	110g Zn	3.2v	12.7	82.5%
4	75g Zn plus 8.5g H2SO4	3.2v	12.9	82.6%
5	75g Zn plus 17.0g H2SO4	3.2v	14.4	83.6%
6	75g Zn plus 25.5g H2SO4	3.2v	15.2	83.4%
7	75g Zn plus 34.0g H2SO4	3.2v	15.9	83.9%

The efficiencies obtained seemed to be rather low for laboratory work, considering that the solutions used were supposedly pure. The deposits obtained were rough, and examination under the microscope showed that there were many spots on the cathode where no deposition had occurred. The deposited surface was pitted with crater-like holes, with the bottom of the craters at the original surface of the cathode. One of these surfaces was finally polished and again examined under the microscope. The polished surface showed tiny cubes

of copper enclosed in a matrix of zinc. A search for
the source of the copper was then made, and an analy-
sis of the anode material showed that there was a
small amount of copper present. Analysis of the elec-
trolyte also showed the presence of very minute quan-
tities of copper. The copper in the zinc cathode form-
ed an electric couple which caused the re-solution of
the zinc, and resulted in poor deposits and low current
efficiency. When the copper-free lead anode was ob-
tained, this trouble was eliminated and a notable in-
crease in current efficiency and smoothness of deposit
was effected.

Several current efficiency determinations were
made, using normal zinc sulphate solution. As a current
efficiency of over 100% was obtained, it was decided
to assemble a copper coulometer and check the ammeter
scale. A solution containing 150g $CuSO_4$, 50g H_2SO_4, and
50 cc of ethyl alcohol was used with copper electrodes.
The tests with the coulometer indicated that the actual
current flowing in the circuit was 95.5% of the scale
reading on the ammeter. When pure lead was used for
an anode in electrolyzing a pure zinc sulphate solution,
it was possible to obtain a high current efficiency. A
typical test is shown in Table II.

TABLE II

TABLE II

Solution	Voltage	Current Density amps/sq.ft/	Current Efficiency
N-ZnSO$_4$	3.2	10.7	97.5%

It was then decided to assemble suitable apparatus with which to actually measure the hydrogen overvoltage. The setup finally chosen was similar to the one which was used by Tartar and Keyes[1]. As can be seen on the accompanying diagram (figure 2), the apparatus is connected in such a manner that two distinct circuits are available, and by means of a suitable switch control both can be used in conjunction with the zinc cell simultaneously. This setup proved to be very flexible. It employs a standard cell, a battery, a potentiometer, a resistance, and a calomel half-cell with the intermediate bridges necessary to connect it to the electrolyte adjacent to the zinc cathode in the electrolyzing cell. The proceedure for the actual measurement of the overvoltage with this equipment is as follows: The storage battery 'B' is connected to two posts of the potentiometer. By means of the switch 'S', either the standard cell or the system ZnH$_2$/ZnSO$_4$/NZnSO$_4$/SatKCl/Hg$_2$Cl$_2$/Hg, may be made to oppose the current from the battery 'B'. The tip or terminal 't' of the calomel cell is placed at the side of the Zn cathode which faces the anode.

The potentiometer dials are set so that they read the same as the voltage of the standard cell. The standard cell is thrown in the circuit to oppose the current from 'B'. By means of the resistance box, 'R', the two potentials are balanced so that no current flows as is indicated by the galvanometer 'G'. This accomplished, the standard cell is thrown out of the circuit and the system $ZnH_2/ZnSO_4/NZnSO_4/SatKCl/Hg_2Cl_2/Hg$ is put in its place. The potentiometer dials are now used until no current flows as shown by the galvanometer. This final setting of the dials indicated the overvoltage referred to the normal calomel cell. Referred to the normal hydrogen electrode, the overvoltage of hydrogen on zinc is the potentiometer reading less 0.283. All overvoltage measurements must be made while electrolysis is taking place and when conditions of voltage and current density in the electrolytic cell are such as <u>to just produce an evolution of hydrogen</u>.

A series of overvoltage readings were then made in N zinc sulphate solutions. It was also attempted to determine the effect of acid concentration on the hydrogen overvoltage; this, however, was not successful due to the fact that when even small quantities of sulphuric acid were present in the electrolyte, an appreciable evolution of hydrogen took place. Since one of the

conditions for measuring hydrogen overvoltage by the direct method is that the EMF be gradually increased until the first bubbles of hydrogen escape from the cathode, and since in acid solution hydrogen was evolved from the cathode even when no current was flowing, it was decided that the conditions required by the direct method could not be maintained in an acid solution.

The effect of silicic acid on the overvoltage was also determined. At first, a solution of sodium silicate was added to the neutral zinc sulphate solution. This tended to precipitate zinc silicate from the solution. After a few measurements were taken, it was decided to make a N $ZnSO_4$ solution containing 8.5 grams of H_2SO_4 and add to it just enough sodium silicate so that the silicic acid formed would stay in solution. Experiment showed that up to 0.2g of sodium silicate could be added to a liter of the above solution before any precipitation occurred. Hydrogen overvoltage measurements were then made using N zinc sulphate solution containing 8.5g H_2SO_4 per liter, to which 0.1g, 0.2g, 0.3g, and 0.4g of sodium silicate had been added, the two latter quantities causing cloudiness in the solution. The result of this series of measurements is also shown in Table III.

TABLE III

All solutions are normal with respect to zinc

	Additions to electrolyte (per liter)	EMF	Current Density amps/sq.ft.	Hydrogen Overvoltage'
1	None	5.5v	35.2	941mv
2	None	5.8v	30.9	918mv
3	8.5g H_2SO_4	2.5v	1.44	825mv
4	17g H_2SO_4	2.75v	1.08	863mv
5	25.5g H_2SO_4	2.6v	0.72	958mv
6	34g H_2SO_4	2.4v	0.36	838mv
7	1g Na_2SiO_3	6.0v	32.3	942mv
8	2g Na_2SiO_3	6.8v	49.0	928mv
9	8.5g H_2SO_4	2.5v	0.722	798mv
10	9 plus 0.1g Na_2SiO_3	2.6v	"	808mv
11	9 plus 0.15g Na_2SiO_3	2.6v	"	803mv
12	9 plus 0.2g Na_2SiO_3	2.6v	"	793mv
13	9 plus 0.3g Na_2SiO_3	2.6v	"	792mv
14	9 plus 0.4g Na_2SiO_3	2.6v	"	790mv

'Measured at a potential which just causes the evolution of H_2 from the cathode.

NOTE: The overvoltages given are referred to the normal hydrogen electrode as zero.

Solutions 3, 4, 5, and 6 were obtained by adding

acid in the proper amount to Solution 1. Solutions 7

and 8 were obtained by adding sodium silicate as spec-
ified to solution 2.

In using this method for determining overvoltage,
it is specified that the measurements take place at an
EMF which just causes the evolution of hydrogen at the
cathode. This works out all right in the case of neu-
tral solutions, but the addition of acid to the solu-
tion causes an evolution of hydrogen at the cathode
even when there is no current flowing. 8.5g of H_2SO_4
per liter of solution is sufficient to bring about such
an evolution. Hence, overvoltage measurements by the
method just outlined are of little value when using
acid solutions. Since all commercial electrolytic
work is done in acid solution, it was decided that
measurements made in neutral solutions would have
little or no bearing upon the working conditions
actually encountered. For this reason the above method
was abandoned, and work started in another direction.

Attention was directed towards determining the
effect of certain impurities on the current efficiency.
The impurities added to the solution were cobalt, arsen-
ic, and sodium silicate. These were added singly; cer-
tain combinations were also tried. In this set of ex-
periments a copper coulometer was run in series with
the zinc cell. The coulometer was the one which had
been previously used in standardizing the ammeter. A

set of experiments showed that the ammeter readings
were variable and could not be depended upon. This
necessitated the weighing of a copper cathode, as well
as weighing the zinc cathode with each run, but the
extra accuracy obtained in this manner is undoubtedly
worth the extra work. The results obtained from these
combinations are shown in Table IV.

TABLE IV

All solutions are N with respect to zinc and
contain 17g H_2SO_4 per liter.

Additions	EMF	Current Density (calculated)	Time (minutes)	Current Efficiency
1 None	4.31	66.3 amps per ft^2	20	92.7%
2 0.1g Co/L	4.30	66.3 amps	20	91.4%
3 0.26g Co/L		67.1 amps	60	97.2%
4 0.25g Co/L	4.30	58.3	60	90.0%
5 0.25g Co/L Excess As_2O_3	4.4	62.5	60	91.5%
6 0.25g Co/L 0.2g Na_2SiO_3	4.2	58.8	60	93.7%
7 0.25g Co/L	4.3	52.5	60	92.4%
8 0.1g Co/L 0.2g Na_2SiO_3	4.3	33.2	60	90.4%
9 None	3.8	45.3	60	92.0%

The results gathered here seem to point to the fact
that the impurities added have no considerable effect in

lowering the current efficiency in the zinc cell.
This is quite contrary to general opinion as quoted
by Laist[3], Ellsworth[2], and Ralston[4]. The amounts of
cobalt present are far in excess of that which is gen-
erally accepted as the allowable maximum. Laist[3] gives
the maximum permissable quantity as 0.0015%, whereas
most of the solutions run contained 0.025% cobalt. The
presence of silicic acid seemed to increase the current
efficiency (see Table IV). Of course, it may be pos-
sible that the runs made were not of sufficient dura-
tion for the bad effect of the impurities to set in.
The most noticeable results of the presence of these
impurities was the effect that it had on the character
of the deposit. When zinc is deposited from pure sul-
phate solution, a fairly rough and non-coherent deposit
is obtained. With increased acidity, the deposit be-
comes smoother, but does not adhere any better to the
surface on which it is deposited. The presence of co-
balt gives a much smoother deposit, but does not parti-
cularly increase the adherence to zinc. The stripped
material is also fairly brittle. Chemical analysis did
not show the presence of cobalt in the cathode zinc.
The presence of silicic acid in the electrolyte not
only gave a much smoother deposit, but it also increased
the adhering properties of the deposited metal, and re-
duced the brittleness considerably. Pieces of the material

deposited from solutions containing silicic acid could be bent a number of times before they showed any cracks in their surface. Further research may show that the presence of silicic acid will be a valuable aid in obtaining a smooth and coherent electrolytic zinc deposit wherever electro-zinc plating is resorted to.

CONCLUSIONS

The most important conclusion drawn from the work done is that hydrogen overvoltage on zinc cannot be measured in an acid solution. The drop in current efficiency can undoubtedly be attributed to the fact that the detrimental elements have more than one valence, and are reduced at the cathode and oxidized at the anode. This cycle absorbs considerable energy which can in no manner be recovered as zinc at the cathode as long as they are present. The evolution of hydrogen at the cathode is also responsible for the reduction of current efficiency. As far as could be determined, the impurities studied had no appreciable effect on the hydrogen overvoltage.

Chemical analysis did not disclose the presence of either cobalt or arsenic in cathode material deposited. This would tend to support the theory that they are in a cycle of oxidation and reduction within the electrolyte.

Perhaps the most important fact brought out was that the presence of silicic acid in acid sulphate solution greatly improved the character and coherence of the deposit. No explanation can be ventured as to the reason for this, nor has any mention of it been made in any of the literature which has been studied.

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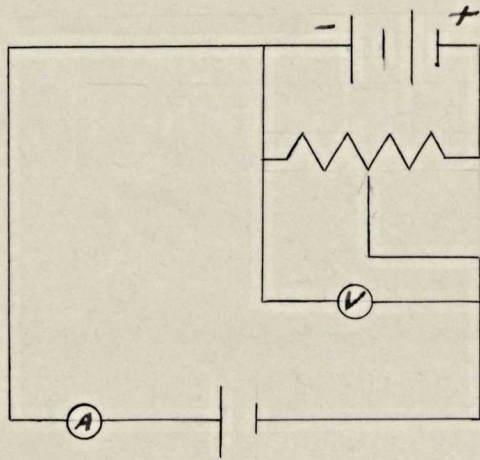
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Figure 1.
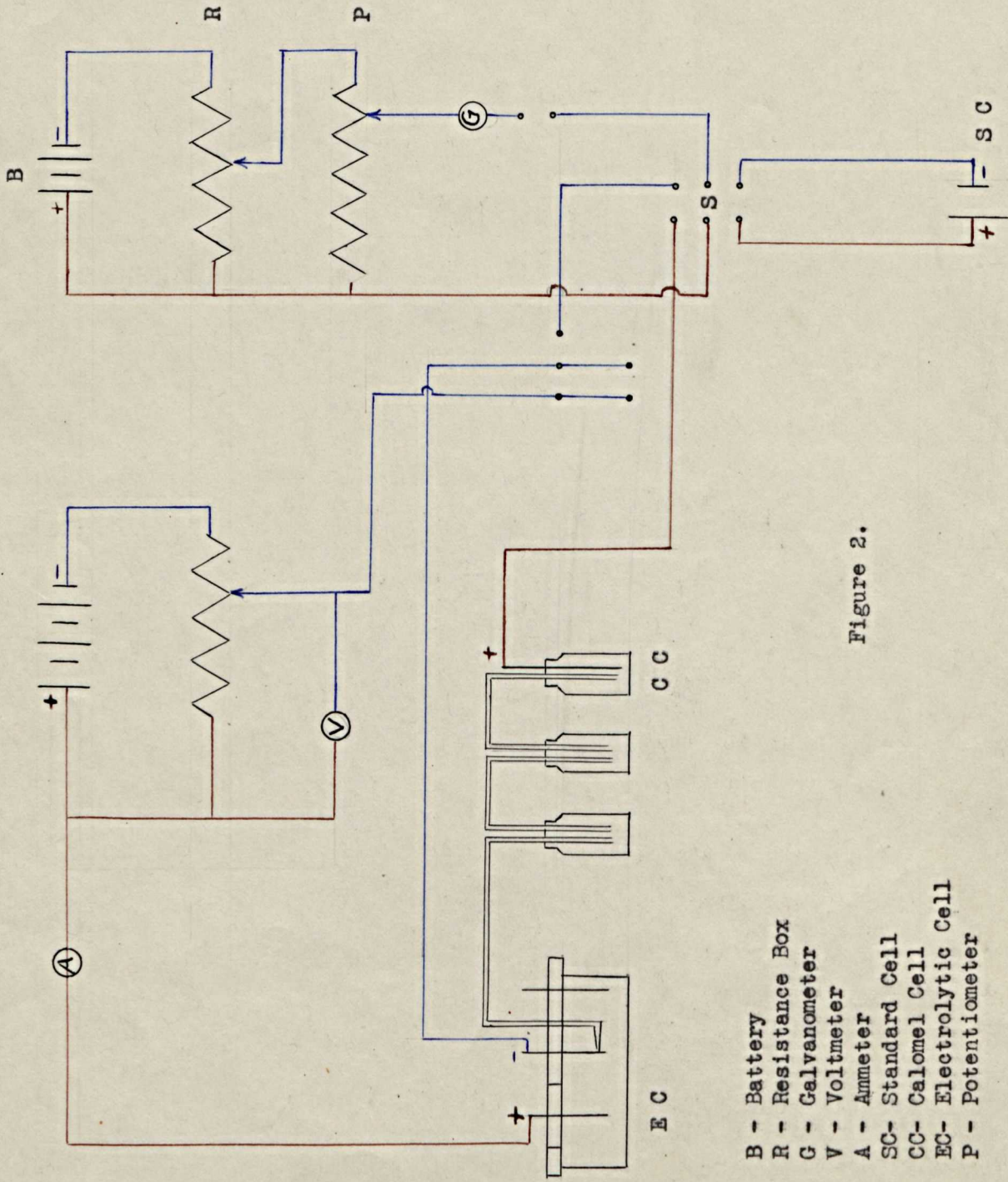
Figure 2.

B – Battery
R – Resistance Box
G – Galvanometer
V – Voltmeter
A – Ammeter
SC– Standard Cell
CC– Calomel Cell
EC– Electrolytic Cell
P – Potentiometer