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The control of anode corrosion

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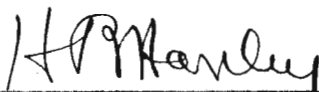
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CONTENTS

INTRODUCTION

This particular study of the control of anode corrosion in connection with the production of zinc by electrolytic deposition from commercial solutions is a continuation of work started at the Missouri School of Mines and Metallurgy in 1929. It is not a new problem or even a new phase of the problem, but rather an attempt to confirm some of the ideas brought out in previous work and to perhaps more definitely establish some of the conclusions drawn from insufficient data, by more extensive tests and by attacking the problem from a slightly different angle.

Before proceeding with the discussion it would be well to review briefly the history as presented before. It is needless to go into the details of past errors and sufficient to say that the turning point came with the discovery that pure solutions are essential to the success of the process. Thereafter all investigation has been conducted on this basis and remarkable advances have been made.

Chief among these advances has been the development of corrosion resistant alloys of lead for use as anodes. The one per cent silver, lead anodes developed by Tainton[1] are now being used in the two large plants at Kellog, Idaho, and East St. Louis respectively. The first year of work[2] on the present problem had to do entirely with alloyed anodes and the following is a summary of the results obtained.

Thallium in amounts up to five per cent alloyed with lead improved the purity of the cathode in direct proportion to the amount of thallium present, changing the lead content from .120% with .5% thallium to .002% with 5.0% thallium. The anodes containing calcium exhibited remarkable lowering of the anode potential amounting to almost 50% below the potential of pure lead. The addition of one per cent silver made the anode passive. The anodes containing over four per cent thallium exhibited remarkable passivity but the anode potential was lowered only slightly.

1. U.C. Tainton, Tr AIMME, 1929, p 192
2. Hanley, Clayton, Walsh, Tr AIMME, #321, part 1 & 2

In the silver-lead alloys, where the silver exceeded the eutectic ratio, the zinc deposits showed lowered efficiency and sometimes resolution. It was deduced that the free silver dissolves in the electrolyte and acts toward the zinc deposit in the same way as would any other noble metal. In this same investigation the value of colloids and manganese as addition agents was brought out, it being concluded that silicic acid prevented the adhesion of hydrogen bubbles to the zinc deposit and that manganese lends a degree of passivity to the anode. In 1930 during the course of this same investigation it was found that silver added to a .1% calcium, 2.0% thallium, 97.9% lead anode increases the stability but lowers the advantage of anode polarization decrease.

Pure lead anodes were employed in the present investigation and there are a great many advantages connected with their use. The very low melting point and high malleability of lead makes it easy to cast, shape, drill, and machine, the latter two items being of great importance where porous anodes are de-

- 3 -

sired. The low melting point makes possible the use of very thin plates which take up less space in the cells. Lead has a constant low voltage as compared to anodes other then the recently perfected alloyed anodes. The chief objection to plain lead anodes is that they do corrode and disintegrate under electrolysis so that their life is relatively short. Part of the lead finds its way to the cathode, lowering the purity of the deposited zinc and decreasing the hydrogen overvoltage. The remainder collects in the manganese dioxide precipitated in the cells, lowering the market value of the by-product. A further disadvantage comes from their tendency to buckle as a result of intercrystalline oxidation, making necessary wide spacing to avoid short circuit, thus necessitating higher power consumption. The power consumption is also affected by the high decomposition potential of a lead peroxide surface.

WORKING BASIS

Certain points have been either definitely or tentatively established before the beginning of this work. Among other things it was concluded that lead contamination of the cathode zinc is, for practical purposes, due to entrainment of the impure anode sludge. This entrainment might take place in somewhat the same manner as does the inclusion of an addition agent. Hunt[3] says that when nucleus formation is prominent, as in the finer grained deposits, the intercrystalline boundaries must necessarily contain the various inclusions which enter the deposit, and conditions approximate more nearly to the views of Tamman[4] who imagines the boundaries in cast metals to consist of impurities.

It has been shown in at least two cases[1-10] that anode sludges containing lead in quantities of two per cent or less show very low lead in the cathode deposit, but no definite arithmetical relationship exists between the lead determined in the cathode and the lead in the anode sludge. It follows then that any impurity causing

a corrosion of the anode, e.g. chlorine, would have the effect of increasing the lead in the deposit.

Manganese in small amounts, five grams or under per liter, has the effect of lowering the lead in the anode sludge and consequently the lead in the deposit. There is a large degree of protection which the MnO_2 deposit gives to the anode but the definiteness of the degree has not been determined. The operation of a cell in the absence of manganese will always produce cathodes too high in lead to be classed as grade A zinc.

Glue definitely has an influence in producing smooth deposits, and smooth deposits entrain less anode sludge, hence there will be less lead in a cathode produced from solutions containing glue. The influence of glue on the stability of the anode surface is unknown and afford a problem for research.

A solution temperature of 45° tends to produce a cathode with less lead than does a solution temperature of 25°. According to H. R. Hanley: "this

- 6 -

is most likely due to the relatively greater continuous removal of hydrogen bubbles from the surface of the cathode at higher temperatures. Cold solutions tend to cause the hydrogen bubbles to adhere to the deposit. It is known that corrosion is initiated around the bubbles of adherent gas and that a gas free plate will produce smoother deposits than one to which bubbles are adherent. So long as the high temperature doesnot initiate corrosion of the cathode by the acid we should expect a cathode low in lead, but when chemical corrosion is started we may expect a cathode containing a high percentage of lead". According to the latest hypothesis[3] as to the mechanism of deposition, an increase in temperature, by causing an increase in speed of diffusion and an increase in mobility, should increase the ratio of metal to other bodies in the cathode film and decrease the tendency of foreign particles to adhere to the cathode. Graham[5] found that a slight decrease in polarization accompanied an increase in temperature and that an unexpectedly large increase of grain size was brought about at the same time. He concluded

3. Journ Phys Chem V 36, #3, p 1006
5. Tr. Am Electro Chem 121, p 275

that the effect was due to an increase in metal ion
supply and that the tendency for foreign particles
to adhere to the cathode was reduced to some extent.

Low acid solutions produce cathodes lower in
lead than do high acid solutions (unless it be in
combination with high current density). The reason
for this is not apparent. High acid probably loosens
the flakes of anode sludge and may put a greater con-
centration of them in suspension than does low acid.

High current density cathodes produced from or-
dinary solutions of low acid content contain more
lead than do cathodes produced at low current densi-
ties. Knowing that the purest zinc is produced from
a combination including high current density and high
acid, this is probably due to the mechanical dislodg-
ment of the flakes of anode sludge, probably richer
in lead because of their force detachment from the
lead sheet, and the greater concentration of them at
the cathode. They are directed toward the cathode by
the excape of anodic oxygen which as stated is forced.

EXPERIMENT I

Theory

While it is rather evident that at least the major portion of lead enters the deposit by the entrainment of the anode sludge and that by improving the character of the deposit by the addition of a colloid the lead content may be lowered, the decreased corrosion of the anode, which in turn lowers the lead content, is not even partially explained. Igareshev[6], using gelatin, found that a colloid increased both cathode and anode overvoltages but this does not explain lowered anode corrosion. In nearly all scientific investigations the only colloidal particles considered are positive, i.e. the ones that migrate toward the cathode. As a result little is known of the possible effects it might have at the anode.

Since the principle interest lies in the improvement of the density and structure of the deposit and its concomitant benefits, the mechanism of this action will be considered. The theory of the mechanism of

6. Z. Electro Chem. V 28, p 40 to 47

deposition as advanced by Blum and Rawdon[7] has been strongly contested and declared untenable, but in that a certain parallelism exists between this theory and the observed phenomena it serves as a working hypothesis in the explanation of the effect of a colloid on the structure of electro-deposited metals. The principle idea of the theory is as follows: the union of one or more electrons with a positively charged ion takes place at the cathode surface at a point determined both by the orientation of the metal atoms on the cathode surface, and by the effective concentration of the metal ions in the cathode film. The latter concentration is approximately measured by the dynamic potential of the cathode. When this ion concentration is high, the cathode polarization will be low and conditions will be favorable for the growth of existing crystals. Conversely, when the metal ion concentration is low, and the cathode polarization is high the conditions are less favorable for crystal growth and more favorable for the formation of new crystals. This assumption is based on the well-known

7. Tr Am Electro Chem Soc, V 44, p 397 (1923)

fact that small crystals have a higher solution pressure and a more negative potential than large crystals and that more negative potentials will be required for the productions of fine crystals. Their contention is then that any factors which would increase cathode polarization, such as the addition of a colloid, would tend to yield a finer deposit.

The absolute effect of colloids in increasing cathode polarization and improving the structure of the deposit has been shown rather conclusively by Taft and Messmore [8] to be an absorption phenomenen. This is in confirmation of the idea advanced by Igareshev[9] in 1921.

We are not so much interested in the mechanism of the effect of the colloid as in the fact that in one way or another it works to yield a better, denser deposit and to lengthen the normal life of the anode.

In previous work only a suggestion has been made of the possibility of a relationship between the lead

8. Journ Phys Chem, V 35, p 2585 (1931)
9. Colloid Chem, V 14, p 25-26

in the anode sludge and that in the cathode deposit.
Tainton[1] concluded that there could be no relation
whatever but a close study of his results might yield
information. He expressed the lead in the sludge as
per cent rather than in actual corrosion or weight
and it is possible that the variation in sludge weight
due to differing amounts of Zn particles and to une-
qual formation of manganese dioxide might have changed
the appearance of his results. For this reason it was
proposed to make a series of runs of such duration
that any irregularities and variations so often mis-
leading in the interpretation of data might be over-
come. The tests represent about four thousand ampere
hours of deposition for two cells operated at six am-
peres, and the large amounts of sludge obtained to-
gether with the great number of analyses of deposits
should be somewhat representative. Although the in-
dividual runs do not agree with one another, the av-
erage appears to give rather good evidence of certain
facts.

1. Tr AIMME, 1929, p 192

PROCEDURE

Certain conditions as suggested before were kept constant throughout the experiment. Since the possible temperature range in practice does not vary much from forty degrees centigrade, and since the maximum current efficiency is obtained in this neighborhood, that temperature was adopted. Due partly to the fact that authorities are more or less in agreement as to the beneficial effect of manganese when present in small amounts and since all commercial solutions contain this element it was decided to have it present in every case in amounts varying from .6 to 1%.

The solutions contained at all times eighty grams per liter of sulfuric acid and fifty grams per liter of zinc at the beginning of each run of eight hours and no replenishment was made until the end of this time. The current density was maintained as near thirty-six ampered per square foot as possible. Each cell had a capacity of three and three-tenths liters. Two anodes and three cathodes were used in each cell and the two outside had their unused faces covered

with acid resistant paint. The cathode edges were covered with rubber strips to make the surfact as nearly as possible equal to the anode surface and to minimize the formation of trees at the points of high current density, i.e. the edges and corners.

LEACHING

The preparation of pure Zn sulphate solution for use in the tests followed the same procedure as given in "A Study of Anode Corrosion" except that some difficulty was encountered when the supply of clean Joplin calcine was exhausted. An attempt was made to leach a mixture of British Columbia calcine and crushed sinter together with C.P. ZnO in proportions of about three parts calcine and sinter to two parts ZnO. On the suggestion of Professor Hanley the ZnO was mixed with the roasted ore before adding it to the leach solution, and this arrangement proved quite satisfactory and eliminated the inordinately long time necessary to leach pure ZnO. .

After completing the customary steps in purification of the solution it still showed a strong test

for nickle. After several attempts to remove the nick-
le by additions of silver sulphate at the rate of 50
gms/L, followed by the addition of an excess of Zn dust
at successively higher temperatures, it was found that
at least two precipitations were required at a temper-
ature of 50 C or one precipitation at 80C. It is prob-
able that low concentrations of Ni could be removed in
one precipitation at the lower temperature or that even
the large concentration could have been removed in one
precipitation at a higher temperature, since Tainton[1]
found that complete elimination of nickle was effected
at temperatures near the boiling point in solutions
used at the Kellog Zn plant. This point is important
in the above mentioned process since the use of a
strong acid leach brings all solutions to a tempera-
ture near the boiling point for the subsequent puri-
fication by Zn dust.

During the time that the nickle was being remov-
ed a standard test was adopted for use on the solution
and its sensitivity investigated. It was found that
nickle could be detected in solutions carrying 135 gm/L

1. Tainton & Leyson, Tr AIMME., V LXX, p 486

of zinc sulphate, in concentrations as small as one part per million.

After eliminating the nickle and starting electrolysis it was found that corrosion and deposition alternated in such a way that no deposit remained for more than a few hours. Sometimes the deposition would continue undisturbed for as long as eight hours and then resolution would set in. The deposit had a porous or network structure. No analysis was made to determine the cause of this action, but from Tainton and Clayton's[2] description of the action of germanium it is probable that that was the element present.

In describing the effects of germanium he says: "the Zn deposition would continue normally for several days and then quite suddenly would start to redissolve. When present in small amounts, say, for example one part in ten million, the germanium lowers the hydrogen overvoltage at a Zn surface only where the current density is low, consequently the fact of a Zn deposit will remain fairly good, but if it is at all

2. Tainton & Clayton, Tr Am Electro Chem Soc, vol. 47, p 279 (1930)

porous the acid will redissolve the Zn at the back of the plate. This re-solution will spread rapidly until the whole back of the plate is redissolved, the face remaining practically untouched". He found that precipitated ferric hydrate in reasonable amounts completely removed the germanium. By mixing ores low in iron with others containing high iron, the iron content was kept at a point which would insure complete removal of this impurity in all cases.

RESULTS

Test number I represents 1724 amp hours of deposition with no glue present and the other conditions constant as outlined. The individual analysis do not agree perfectly but with a few exceptions are of the same order. It will be noted that the first run, samples 1 and 5, represents eight hours of deposition rather than sixteen as in every other case, and this might account in part for its higher lead content if we consider that the greater part of the lead is deposited when the anode is new. This was noticed in every case where new anodes, freshly cleaned surfaces, were used. In order to ascertain if the difference might be due to an extreme change in current density or in temperature, two runs were made represented by samples 17, 18, 19, and 20. One of these was made at double the current density, the second at room temperature, but the results indicate that the high lead in 1 and 5 was due only to the new anode surface; and it was further deduced that to all practical purposes the aging of the anode takes place in the first few hours

of electrolysis.

No attempt was made to show a gradual improvement by increasing the glue addition by degrees. Test number II with a small addition of glue shows some improvement over test number I, the improvement being more in the was of uniformity than in a lowering of the lead content. It might be deduced from this that the first function of a colloid is to smooth out the irregularities, any further addition acting to lower both the anode corrosion and the lead in the deposit. This latter is shown by the marked improvement in test number III.

Test number III shows more nearly the ideal conditions not only in regard to anode corrosion but to the purity of the deposit, and although this condition could probably be more closely approached with some other addition factor, the contrast is sufficient to stress the point. In the table comparing the overall results of tests I, II, III, the calculations are made on the basis of tons of Zn produced in order to relate it more closely to plant practice.

Test # I   Table I

Sample No.	Age of Anode in hours	% Pb in cathode	Gms of Pb in cathode
1	New	.058	.040
2	8	.029	.030
3	24	.028	.028
4	40	.034	.037
9	56	.022	.022
10	72	.013	.013
11	88	.013	.013
12	104	.093	.090
17	120	.025	.026
19	136	.031	.030

ROLLED ANODES

Manganese .6 gm/ liter; current density 35 amp/sq ft.
Electrode spacing 1.5 inches, center to center; Average acidity 91.5 gm/liter. Zn content 50 gm / liter.

TEST # I   TABLE II

Sample No.	Age of Anode in hours	% Pb in cathode	Gms Pb in Cathode
5	New	.064	.042
6	8	.027	.028
7	24	.028	.027
8	40	.024	.024
13	56	.023	.023
14	72	.021	.021
15	88	.021	.020
16	104	.096	.090
18	120	.026	.026
20	136	.036	.033

CAST ANODES

Manganese .6 gm / liter; current density 35 amp/sq ft
Electrode spacing 1.5 inches, center to center; Aver-
age acidity 91.5 gm / liter. An content 50 to 34
gm / liter.

TEST # II   TABLE III

Sample No.	Age of Anode in hours	% Pb in Cathode	Gms Pb in Cathode
21	16	.024	.024
23	32	.020	.019
25	48	.020	.020
27	64	.024	.022
29	80	.024	.024
31	96	.019	.018
33	112	.024	.022
35	128	.022	.023
37	144	.014	.015

ROLLED ANODES   GLUE ADDED

Manganese .7 gms / liter; current density 35 amp/sq ft
Electrode spacing 1.5", center to center; average aci-
dity 92 gms / liter; GLUE added at rate of 2 lbs. per
ton of Zn produced and solution originally conditioned
with .03 gms / liter.

TEST # II   TABLE IV

Sample No.	Age of Anode in hours	% Pb in Cathode	Gms Pb in Cathode
22	16	.023	.023
24	32	.024	.023
26	48	.019	.018
28	64	.022	.020
30	80	.026	.027
32	96	.016	.015
34	112	.022	.020
36	128	.022	.023
38	144	.022	.022

CAST ANODES   GLUE ADDED

Manganese .7 gms / liter; current density 35 amp/sq ft
Electrode spacing 1.5", center to center; average aci-
dity 92 gms / liter; GLUE added at rate of 2 lbs. per
ton of Zn produced and solution originally conditioned
with .03 gms / liter.

TEST # III   TABLE V

Sample No.	Age of Anode in hours	% pb in Cathode	Gms Pb in Cathode
39	New	.014	.014
40	16	.0075	.0076
41	32	.0088	.0090
42	48	.0063	.0065

Manganese 1.0 gms / liter; current density 36 amp /
sq ft.; Electrode spacing 1.5", center to center;
Average acidity 92 gms / liter; GLUE added at rate
of 3.5 lbs per ton of Zn produced and solution ori-
ginally treated with .05 gms of glue / liter.   In
addition there was added .025 gms / liter to re-
habilitate the solution after each eight hours of
deposition.

TABLE VI

Comparison of Tests I, II, and III

Test No.	Addition agent in gms/ liter.			Average % Pb in Cathode Zinc	Pb in deposit in lbs of Pb / ton of Zn produced	Pb in anode sludge in lbs / ton of Zn produced	Total corrosion in lbs of Pb / ton of Zn produced
I	Mn	--	.6	.038	.76	6.25	7.01
II	Mn	--	.7				
	Glue	--	.03	.022	.44	6.15	6.59
III	Mn	--	1.0				
	Glue	--	.05	.0091	.18	1.3	1.48

Test # I   No Glue

Test # II   No addition of Glue to rehabilitate solution. 2 lbs glue / ton of Zn.

Test # III   An addition of .025 gms glue / liter made each eight hours to rehabilitate solution and 3.5 lbs added per ton of Zn produced.

All during the first three tests the two cells were run under like conditions with the exception that cell number I contained anodes made of rolled lead while cell number II held cast anodes. It was thought to establish any difference in corrosion rate through this long series of runs, but there is little apparent advantage in either case. It was suggested[10] that the freshly cast surface of an anode might have an effect but this condition would be destroyed on scraping or brushing the anode surface. The density difference in case and worked lead is sufficient to be effective since in the case of chromium plating with lead anodes it was found[11] that cast anodes were entirely unsatisfactory while worked lead could be used. In any case it would be unsafe to draw conclusions as to their relative values from the results of the above tests, but if there be any advantage it is in favor of the rolled anode.

10. AIMME paper #321 Discussion
11. M.S.M. Thesis #   , Study of Anode Corrosion

EXPERIMENT #2

After finishing the investigation of the effects of glue on anode corrosion and cathode purity and assuming that the lead in the cathode is a function of the amount of lead corroded from the anode, it was proposed to study the effects of various depolarizers, organic and inorganic, on these two factors. The agents chosen were formaldehyde, formic acid, oxalic acid, tartaric acid, and ferrous sulphate.

Among other reducing agents mentioned in the literature as depolarizers are sulphur dioxide gas and a superposed alternating current. Thompson and Sullivan[1] found that the presence of sulphur dioxide lowered the potential at the anode saving power and in addition making sulphuric acid. It is also known that depolarization is dependent on current density and the nature of the anode. Theoretically the action of an organic acid is to combine with the oxygen at the anode forming carbon dioxide which

1. Met and Chem Eng., V 18, p 178   and
   Journ Am Chem Soc, V 46, p 545

will escape, there being no noxious products formed
in the reaction. The reaction should decrease the
force of evolution of anodic oxygen, i.e. the pres-
sure of release, and in effect lower the tendency to
throw out particles of lead which might be partially
or completely corroded from the anode. In the case
of an inorganic salt like ferrous sulphate there will
be formed ferric sulphate which will accumulate in the
solution. It would, of course, be removed by precip-
itation in the leaching cycle. In this connection
there seems but one possible practical application;
the case of an ore of iron content inadequate for the
removal of arsenic, antimony, germanium, etc. In view
of the large available supply of iron ores and the rel-
atively high cost of pure reagents it is not likely
that the situation will ever be encountered.

It was believed at first that the behaviour of the
reducing agents would be in a sense parallel to that of
manganese, and an added advantage. The coating of man-
ganese dioxide formed on the anode is a large factor in
its stabilization and anything which might help retain

this coating would obviously be beneficial. It was
partly due to this fact that manganese was kept pres-
ent in the solution. It became apparent later that
the reagents had no effect until present in sufficient
concentration to prevent the formation of manganese
dioxide. It is probable that permanganic acid is for-
med and immediately reduced by the added reagent. The
agents which did not prevent the continued formation
of permanganic acid had no apparent effect on the
rate of corrosion, while those reagents which did re-
duce the permanganic acid and prevented the formation
of manganese dioxide caused a marked reduction in the
rate of corrosion. The results of the ferrous sul-
phate addition would lead one to believe that the de-
colorization of the solution by reduction of the per-
manganic acid might serve as an indicator as to the
amount to be added.

One of the three cells operated in series was
maintained with no addition agent other than mangan-
ese in order that comparative results be obtained.

Any variation of results due to a change of current density, the nature of the neutral solution added, or other operating condition was checked by this cell. The other conditions, temperature, solution strength, etc., were maintained constant as outlined in Experiment #I.

The reagents were added on the basis of the amount necessary to reduce one tenth of one per cent of the oxygen evolved at the anode. Subsequent additions were some multiple of this factor. The solutions were first conditioned with the reagent at the required concentration and the addition made from dispensing burrettes arranged to drop the solution uniformly during the run. The addition factors are given in table VII. At the end of sixteen hours of deposition the cathodes were analyzed for lead; the results then, as shown by the tables represent the average of two analyses. After thirty-two hours of deposition the solution was filtered, the sludge dried, weighed, and analyzed for lead.

On completing the first sixteen hours of electrolysis with formaldehyde in cell number 1 and formic acid in cell number 2, it was noticed that the strips of rubber on the cathodes had swelled slightly and their changed surfaced indicated decomposition. To eliminate the possibility of poisoning the solution with antimony or other elements used as mordants in the rubber, the strips were removed. This resulted in decreased cathode current density, but to partly compensate for the lowering of overvoltage, the cathodes were stripped at the end of each eight hours of deposition rather than sixteen. Since the blank cell was operated under the same conditions the results remained comparable.

TABLE VII

Reagent	Efficiency ratio in gms of reagent per bm of oxygen reduced.	Amount necessary to reduce .1% of the oxygen evolved at the anode. gms / liter.
Formaldehyde	1.0	.016
Formic Acid	2.9	.046
Oxalic Acid	56.0	.896
Tartaric Acid	1.7	.027
Ferrous Sulphate	9.1	.146

RESULTS

The additions of formaldehyde and formic acid
even at concentrations of four times the original
factor had no apparent effect on either the forma-
tion of manganese dioxide or anode corrosion. Even
on adding an inordinate amount to the solution, no
decolorization was obtained. Its reducing action
must in some manner be inhibited.

TABLE VIII

Sample No.	Addition Agent	Conc. of agent / liter.	% Pb in Cathode	Pb in Cathode lbs/ton Zn	Total cor-rosion in lbs / ton Zn.
1	Formalde-hyde	.016	.020	.42	3.55
2	Formic Acid	.046	.019	.40	2.50
3	———	———	.015	.32	2.99
4	Formalde-hyde	.064	.013	.31	3.72
5	Formic Acid	.184	.015	.31	3.72
6	———	———	.016	.24	3.05

TABLE IX

Sample No.	Addition Agent	Conc. of agent in gms/liter	% Pb in Cathode	Pb in Cathode lbs Pb / ton of Zn	Total corrosion in lbs Pb / ton of Zn
1	Oxalic Acid	.896	.022	.44	1.7
2	Tartaric Acid	.027	.011	.22	2.93
3	--------	-----	.022	.44	2.60

Table IX represents the results obtained by the addition of oxalic acid and tartaric acid in concentrations four times the calculated value for .1% of the oxygen evolved. This concentration of the oxalic acid was just sufficient to decolorize the solution, as indicated by the appearance of a slight color on slowing up the rate of addition. A small amount of white precipitate was formed on the first addition which set-

tled to the bottom of the cell and did not redissolve.
This precipitate was weighed and analyzed for lead
just as were the other sludges.

There was some doubt at first as to the nature
of this precipitate but it was explained that since
zinc oxalate is very insoluble and lead oxalate even
less soluble any addition of oxalic acid over that
amount necessary to reduce the permanganic acid would
form lead oxalate and zinc oxalate in turn, part of
each being precipitated to the bottom of the cell.
Tests of successively larger additions of oxalic acid
to samples of the solution showed this to be the case
any amount of precipitate being formed with suffici-
ent concentration of the acid.

There is shown a marked decrease in the lead in
the cathode with the addition of tartaric acid. At
the same time the tartaric acid did not decolorize
the solution and there was a large corrosion of the
anode. The improvement of the purity of the cathode
seems justified since it has been demonstrated[2] that

2. Am Electro Chem Soc., Tech Pub #7, 1926

tartaric acid, among other organic salts and acids, forms complexes with the cation of the salt of the electrolyte in the same manner as do colloidal addition agents, decreasing the crystal size and improving the density and character of the deposit. That these substances are occluded in many deposits has been confirmed by careful checks.

TABLE X

Sample No.	Addition Agent	Conc. of Agent in gms / liter	% Pb in Cathode	Pb in Cathode lbs Pb / ton of Zn	Total corrosion in lbs Pb / ton Zn
1	Ferrous Sulphate	.292	.010	.20	.80
2	"	.146	.0125	.25	.91
3	-----	-----	.019	.38	1.80

The best results were obtained with ferrous sulphate as shown by table X. In the higher of the **two** concentrations the solution was practically decolorized, there being scarcely enough sludge formed to be weighed and analyzed. Tests were made at concentrations of ten and twenty times the factor given in the table, but the results were difficult of interpretation. The formation of sludge was, naturally, negligible but at the same time there was a relatively high percentage of lead in the cathode. It is possible that the high concentration of the ferric sulphate formed by the oxidation of the ferrous sulphate caused resolution of the zinc lowering the overvoltage and resulting in a poor deposit. It is certain that the deposit was inferior from its appearance. Coupled with this is the possibility that some particles of lead otherwise tending to fall to the bottom of the cell might have been dissolved and plated out with the zinc.

The results of the oxalic acid test was rather
inconclusive and for this reason it was proposed to
check it by an additional run in the presence of a
certain amount of glue to ascertain if by improving
the cathode in this way the effects of lowered anode
corrosion might not be more clearly brought out. At
the same time the ferrous sulphate test was repeated
in the presence of a like concentration of glue to
verify its effect also.

The results are rather interesting and at least
indicate that the presence of these agents have a no-
ticeable effect. Even this is not entirely conclu-
sive since the same variations in cathode impurity
have been noted under conditions otherwise identical,
but where the addition agents were not present. How-
ever, it does further prove that the presence of
these agents lowers the rate of corrosion of the an-
ode. To definitely establish this relationship it
would be necessary to make a long series of tests
with them present in the solution.

TABLE   X

Addition Agent	Conc. of Addition Agent gms/liter	Gms Pb in sludge	% Pb in deposit	Pb in deposit in lbs Pb / ton of Zn	Total Corrosion of anode in lbs. Pb / ton Zn
Ferrous Sulphate	.584	.04	.008	.082	.482
Oxalic Acid	.896	.024	.009	.093	.333
-------	-----	.151	.012	.121	1.631

Glue in all cells at a concentration of .05 gms / liter
.025 gms / liter added each eight hours to rehabilitate
solution. 3.5 lbs. added / ton of Zn produced.

It is to be regretted that tests were not made
on small changes of concentration of ferrous sulphate
near the point of maximum lowering of anode corrosion
to determine the exact value of this factor. It is
possible that the point might lie at the concentration
necessary to just prevent the formation of permanganic
acid.

In closing it might be suggested that to defini-
tely determine the effect of various addition agents
on anode corrosion it would be more feasible to con-
trol the concentration of corroding agent, e.g. chlor-
ine, rather than attempt to maintain a complete absence
of it. In addition, the presence of a definite amount
of glue, which, by regulating the character of the de-
posit, should facilitate the establishment of a rela-
tionship between the two factors, anode corrosion and
cathode impurity.

SUMMARY OF CONCLUSIONS

A definite relationship exists between the amount of lead corroded from the anode and the amount of lead contained in the cathode although due to the variability of operating conditions no mathematical relationship has been established.

The presence of glue decreases both the rate of corrosion of the anode and the amount of impurity in the deposit.

The aging of an anode, for all practical purposes takes place in the first few hours of deposition and if any further change takes place it is so slight as to be negligible.

If any difference exists between the corrosion resistant properties of rolled and cast lead it is very slight and in favor of the rolled lead.

Oxalic acid lowers the rate of corrosion of the anode and when a stabilizing substance is present this lowered corrosion results in purer deposits. Tartaric acid

tends to improve the purity of the deposit but has
little, if any, effect on the rate of corrosion. Fer-
rous sulphate lowers the rate of corrosion, the lower-
ing depending on the concentration of the salt present.
After a certain maximum concentration is reached its
effects are deleterious.

INDEX

BIBLIOGRAPHY

1.   Tr AIME., 1929, p 192.

2.   AIMME, paper, # 321, parts 1 & 2.

3.   Journ Phys Chem., Vol XXXVI, # 3, p 1006.

4.   Z. Anorg Chem., Vol 121, p 275.

5.   Tr Am Electro Chem Soc., Vol 52, p 157.

6.   Z Electro Chem., Vol 28, p 40 to 47.

7.   Tr Am Electro Chem Soc., Vol 44, p 397.

8.   Journ Phys Chem., Vol 35, p 2585.

9.   Colloid Chem., Vol 14, p 25 to 62.

10.   AIMME paper # 321, Discussion.

11.   A Study of Anode Corrosion, Thesis, MSM.

12.   Tr AIMME, Vol LXX, p 486.

13.   Tr Am Electro Chem Soc., Vol 47, p 279.

14.   Met and Chem Eng., Vol 18, p 178.

15.   Journ Am Chem Soc., Vol 46, p 545.

16.   Am Electro Chem Soc., Tech Pub. # 7, 1926.