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The Measurement of Current Efficiency in Zinc Sulphate Electrolytes Containing Antimony and Cobalt by Hydrogen Evolution

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THE MEASUREMENT OF CURRENT EFFICIENCY IN ZINC SULPHATE ELECTROLYTES CONTAINING ANTIMONY AND COBALT BY HYDROGEN EVOLUTION

By

Arthur R. Hard

A Thesis
Submitted to the Department of Metallurgy
In Partial Fulfillment of the Requirements
of the Degree of Bachelor of Science in
Metallurgical Engineering

MONTANA SCHOOL OF MINES
BUTTE, MONTANA
MAY 1, 1940

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INTRODUCTION

It has long been realized that minute quantities of impurities present in the zinc sulphate solution for the production of electrolytic zinc have a marked effect on the current efficiency obtained during electrolysis and on the properties of the zinc sheet. Before this fact was recognized, the low current efficiency was accredited to the presence of free acid. Much time and money were wasted in attempts to neutralize the acid as it formed. Since that time many investigators have shown the effects of single impurities. In all cases the time-honored method of determining current efficiency was used. The cathode was weighed before and after electrolysis, the difference in weight being divided by the theoretical weight of zinc that should have been deposited by the quantity of current passed. There is little fault to be found with the accuracy of this method. It will always be the best measure of efficiency in practice. In the laboratory, however, it would be ideal to have a method which would show the operation of the cell at any particular instant. So far this has not been achieved, but the hydrogen evolution method is the closest approach to continuous observation and is worthy of investigation.

CURRENT EFFICIENCY BY THE HYDROGEN EVOLUTION METHOD

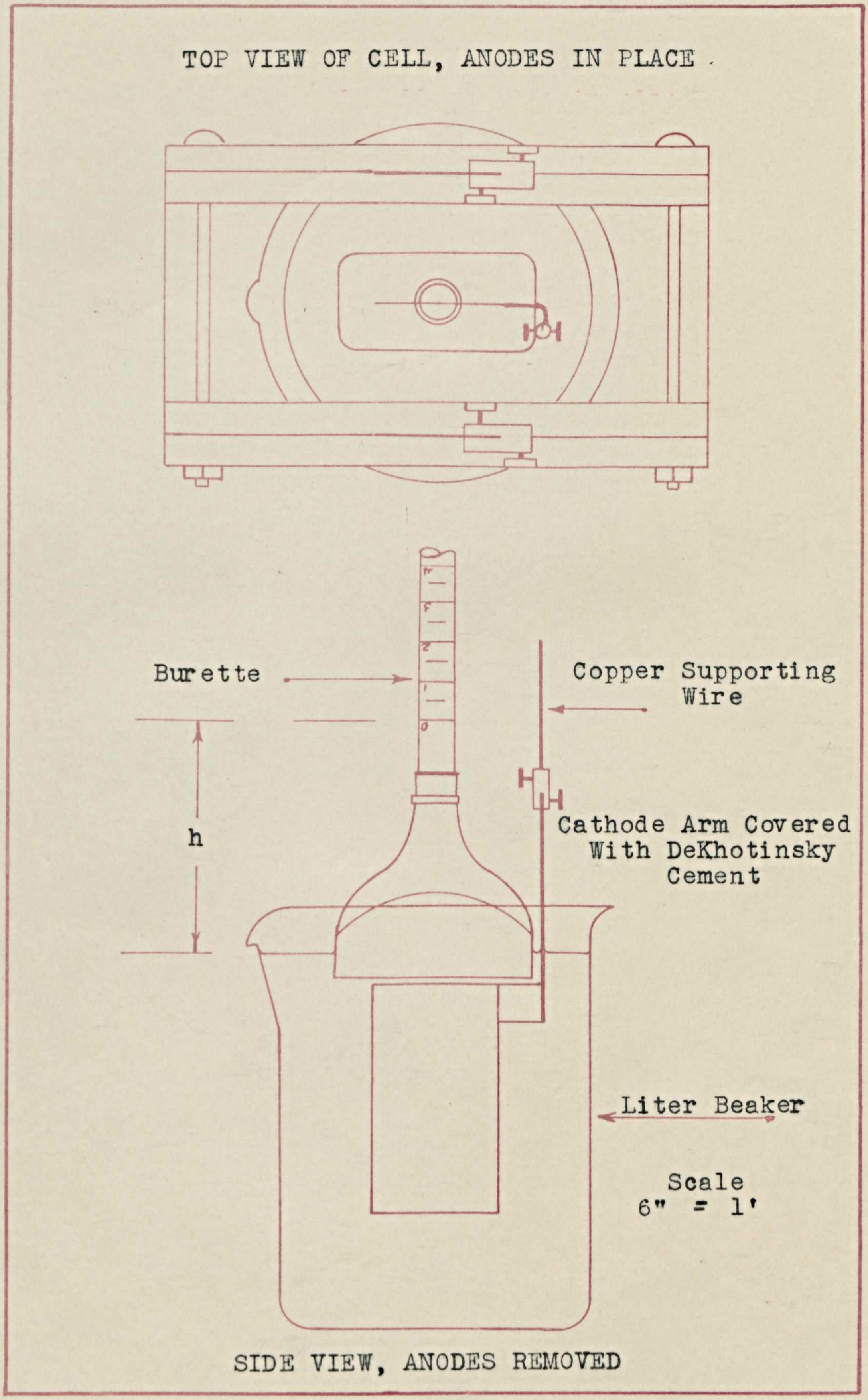
In the early part of this work an attempt was made to find some method other than the conventional weight system for determining current efficiency. This was done with the idea of getting more frequent readings over shorter intervals of time than is possible with the weight method. After several failures, the method of Lee and Busby[1] was adopted.

The measurement of current efficiency by hydrogen evolution is based on the assumption that the portion of the current which deposits no zinc will release hydrogen. This assumption is correct for solutions containing no impurities electropositive to zinc.

The apparatus of Lee and Busby consisted of a gas burette placed over the cathode. To the lower end of the burette was fixed an ordinary filter funnel which served as the collecting bell for the hydrogen. The cell was made from an ordinary two liter reagent bottle with the bottom removed. This was inverted and stoppered. A connection to the cathode was made through the stopper. A grid was placed between the anodes and cathode to prevent oxygen formed at the anodes from entering the bell.

Although the apparatus that we used was basically the same as that of Lee and Busby, some improvements in construction were made. The collecting bell was made by cutting off the top portion of an eight ounce druggist's bottle about three inches below the neck. This was fastened to the burette with DeKhotinsky cement. With a cathode 1.6 by 3.0 inches, a clearance of about one inch on all sides of the cathode was obtained. This made it possible to do away with the grids and depend upon the anode to cathode distance to keep oxygen out of the bell. In actual practice it was found that the oxygen tended to rise vertically until it reached the surface, where it turned to follow a horizontal line until it escaped into the air. Since the bottom of the bell was below the surface, it was impossible for the oxygen to enter the bell. Figure 1 gives some idea of the general construction of the apparatus.

Fig. 1


TOP VIEW OF CELL, ANODES IN PLACE
Burette
Copper Supporting Wire
h
Cathode Arm Covered With DeKhotinsky Cement
Liter Beaker
Scale 6" = 1'
SIDE VIEW, ANODES REMOVED

In order that the hydrogen method could be compared with the conventional, a second cell and coulometer were connected in series with the hydrogen cell. Liter beakers were used as cells. Each cell was provided with a thermometer. A thermometer was also fastened to the side of the burette to give the temperature of the hydrogen. Glass cooling coils were used to maintain a temperature of 20 degrees centigrade in the cells. All cathodes were supported on stout copper wires which were fastened to a board on a ring stand. All voltmeter and current connections were made at the upper ends of these wires, the cathodes being suspended on the lower ends by means of small brass clips that were weighed as a part of the cathode. This simplified the removal of the cathodes, as only one connection had to be loosened in order to break the circuit and remove the cathode. In this way the cathode could be quickly removed and washed before the acid clinging to it hadmuch chance to redissolve the zinc. The cathode was dried in alcohol before weighing. A switch was installed on the instrument board to short circuit the weight cell and coulometer so that the hydrogen cell could be kept in operation during the weighing period.

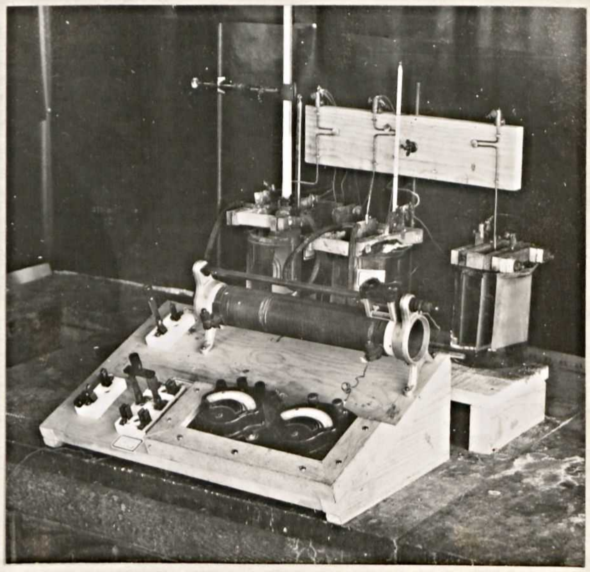


Fig. 2:- Photograph of apparatus showing
instrument board and cells.

OPERATION DETAILS

Before each test electrolysis was allowed to proceed for twenty minutes in order that the flash sheet might form and the cell temperature be regulated. The cathodes of the weight cell and coulometer were then removed, washed, and dried. The burette of the hydrogen cell was filled with electrolyte by means of a rubber bulb to which was attached a splash bottle. Time of filling was recorded. The cathodes of the weight cell and coulometer were then weighed and replaced. After one hour they were again removed for weighing. At the end of the second hour the third weighing was made. This gave two one-hour readings for the weight cell. The hydrogen cell was kept in continuous operation all this time. When the hydrogen had reached the lower part of the burette, say five cc. above the zero mark, the time, reading, and temperature of the hydrogen were recorded, and the burette refilled. The time required for the 50cc. burette to fill with gas was about thirty minutes for the higher current efficiencies and fifteen minutes for an efficiency near 80%. Temperatures were controlled at 20°c plus or minus 1°.

The current density was maintained at 30 amperes per square foot in the zinc cells and at 9.3 amperes per square foot (0.01 amperes / sq. cm.) in the coulometer. Each aluminum cathode had a total area of 9.6 square inches, so that two amperes gave the desired current density. A thin edge of De Khotinsky cement was placed on each cathode to facilitate stripping. The cathodes were stripped at the end of each test and zinc oxide added to each cell in amounts which would replace the zinc removed by electrolysis. This also brought the acidity back to the original figure.

No description of the wiring is necessary other than to state that the two cells and coulometer were connected in series. A double throw switch made it possible to read the voltage across either cell.

ELECTROLYTE

Zinc and acid concentrations of the electrolyte used in the experiments were approximately the same as that used in the zinc plant at Anaconda and contained 92.7 grams of free sulphuric acid and 48.2 grams of zinc as the sulphate per liter. This is the same concentration of acid and zinc that would be obtained by the removal of 30.2 ampere hours of zinc from a neutral solution containing 110 grams of zinc per liter. The removal of four more ampere hours of zinc from this solution will give a spent electrolyte of 10% free acid. Actually this is a higher acid content than the average cell feed in the Anaconda plant. It can be shown that in a cascade of six cells being fed with solution containing 110 grams of zinc per liter and spent electrolyte maintained at 10% acid, the average cell feed is closer to six percent acid. This calculation will be found in the appendix.

CURRENT EFFICIENCY CALCULATION

There are several factors that must be known before the volume of gas collected in the burette can be converted to current efficiency. All of these are easily measured or approximated to the necessary accuracy.

Vapor Pressure Correction

Since the vapor pressure of the electrolyte will differ from that of pure water and is difficult to measure, an approximation must be made. The vapor pressure curve for water was drawn. The boiling point of the electrolyte was measured and found to be 96 degrees centigrade at a barometric pressure of 610 millimeters. The boiling point of water at this pressure is 95° C. It was assumed that the vapor pressure curve for the electrolyte is parallel to that for water, and a line was drawn to comply with this assumption. In the lower regions of the curve, the average difference in the vapor pressures was found to be ten millimeters, the electrolyte having the lower value. In all calculations the vapor pressure used was the vapor pressure of water minus ten millimeters. This was obviously a poor method of approximation, but its best defense is that it worked.

Correction for Electrolyte Left In Burette

The column of electrolyte remaining in the burette when a reading is made tends to reduce the pressure of the gas contained therein. The density of this solution was determined by weighing 100 cc. of it. To do away with the necessity of actually measuring the height of the column each time a reading is taken, the length of each burette division can be measured. It is then necessary to measure only the distance ('h' in Fig. 1) from the surface of the solution in the cell to the zero mark of the burette. This is done at the time the first reading is made and will remain constant until the burette is disturbed. Finally, the barometric pressure must be read for each day's operation.

Some of these factors can be combined to give constants which simplify the work, if a large number of calculations is to be made. Of the two sample calculations which appear in the appendix, the first gives all the steps, and the second the simplified calculation by the use of constants.

In commercial practice it would be possible to arrange the figures on a nomograph so that the calculations would be eliminated. This would make it possible for an unskilled workman to run the tests.

THE EFFECT OF ANTIMONY

A standard solution of antimony sulphate containing 10 milligrams of antimony per liter was made in order to simplify the additions. It was necessary to add 40 cc. of sulphuric acid to dissolve the required amount of the salt. The additions were made with a pipette. Table I gives the results measured both by hydrogen evolution and weight. These data are also presented graphically in Fig. 3.

TABLE I

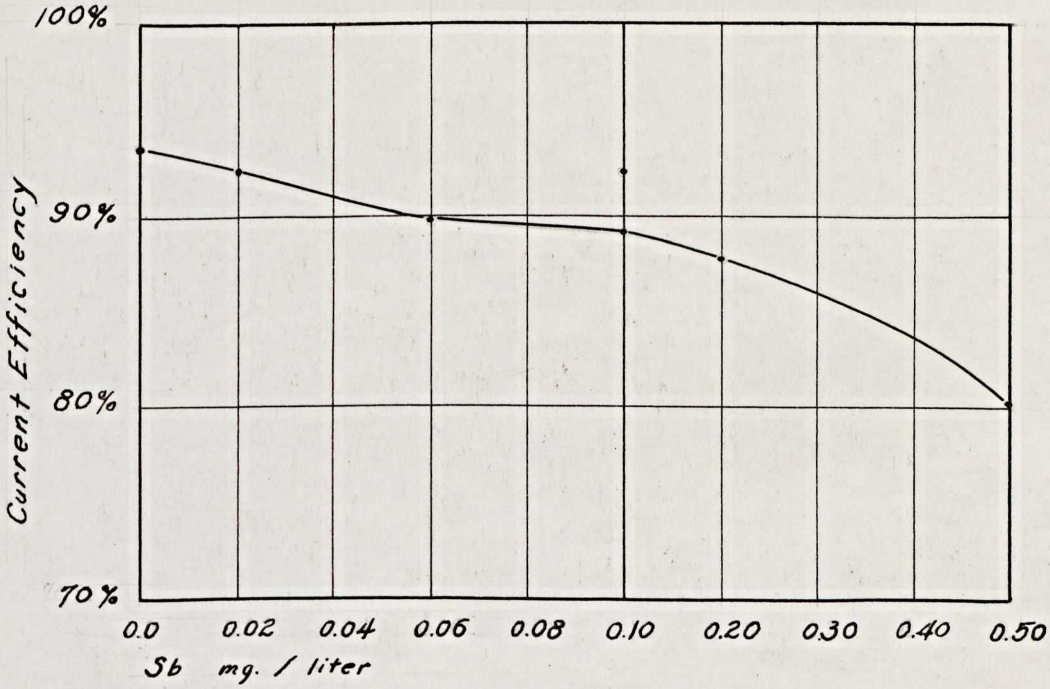
		Current Efficiency		
Test	Sb in mg./l.	By Hydrogen	By Weight	Temperature
1	0.00	93.7	93.6	23°C
2	0.02	92.4	92.3	21°C
3	0.06	88.2	89.7	21°C
4	0.10	89.0	89.1	23°C
5	0.10	92.0	92.2	20°C
6	0.20	*89.4	87.7	20°C
7	0.50	81.1	80.1	20°C

The first four tests were made with no cooling coils in the cells, which accounts for the fluctuation in temperature.

*For this test it was impossible to read the barometer at the laboratory, and the atmospheric pressure was calculated to the elevation of the school from the barometer at the airport. If this reading is excluded, the averages will be 89.37 for the hydrogen, and 89.5 for the conventional method.

Data to supplement the abovewill be found in table IV of the Appendix.

Fig. 3:- Effect of Antimony on Current Efficiency



Samples of Cathode Deposits obtained with varying quantities of Sb in the electrolyte.

0.00 mg. Sb

0.02 mg. Sb

0.06 mg. Sb

0.10 mg Sb

0.20 mg. Sb

0.50 mg. Sb

THE EFFECT OF COBALT

The additions of antimony were terminated at 0.50 milligrams per liter to test the effect of the addition of cobalt to an electrolyte containing this concentration of antimony. The standard cobalt solution contained 100 milligrams of cobalt per liter and was prepared from cobalt sulphate and distilled water. The additions were made in the same manner as the antimony additions. Table II gives the results measured by hydrogen evolution and weight. All cell temperatures in these tests were maintained at 20°C plus and minus 1°C.

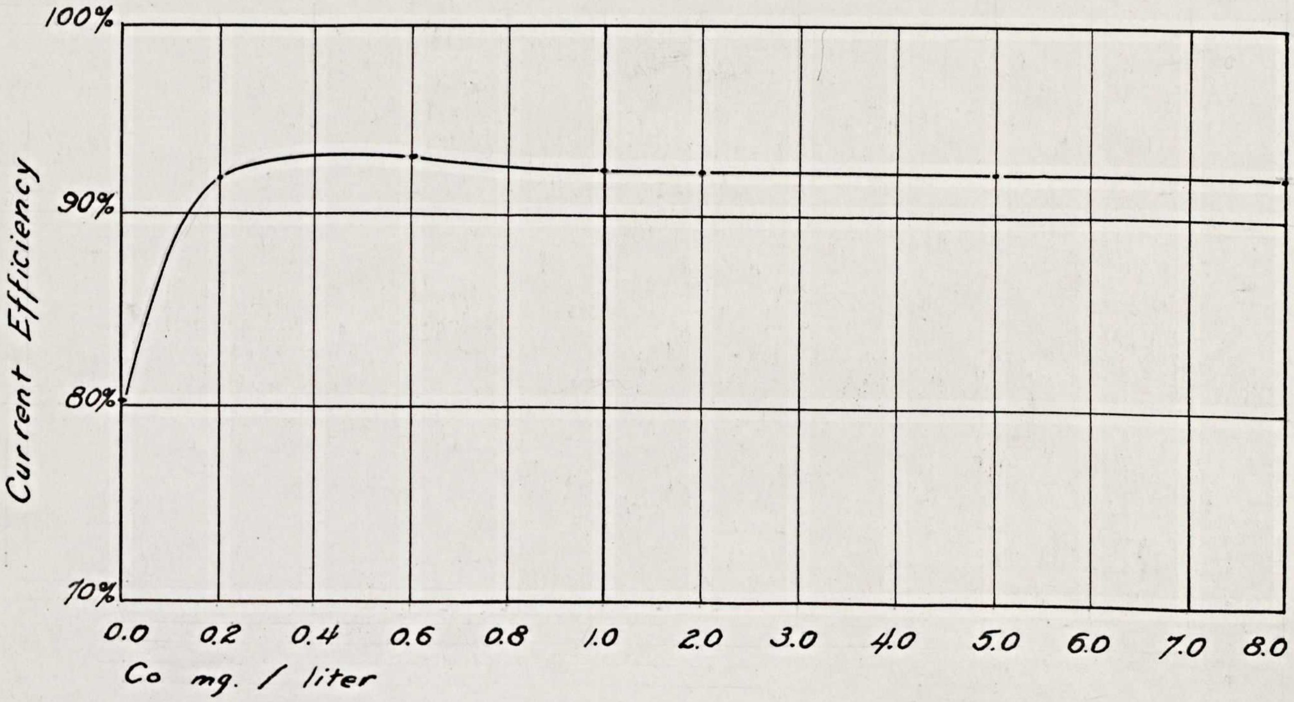
TABLE II

Test	Sb mg./l.	Co mg./l.	Current Efficiency	
			By Hydrogen	By Weight
7	0.50	0.00	81.1	80.1
8	0.50	0.20	*	91.9
9	0.50	0.60	93.3	93.0
10	0.50	1.00	92.3	92.3
11	0.50	2.00	91.7	92.3
12	0.50	5.00	91.2	92.3
13	0.50	8.00	92.3	92.5

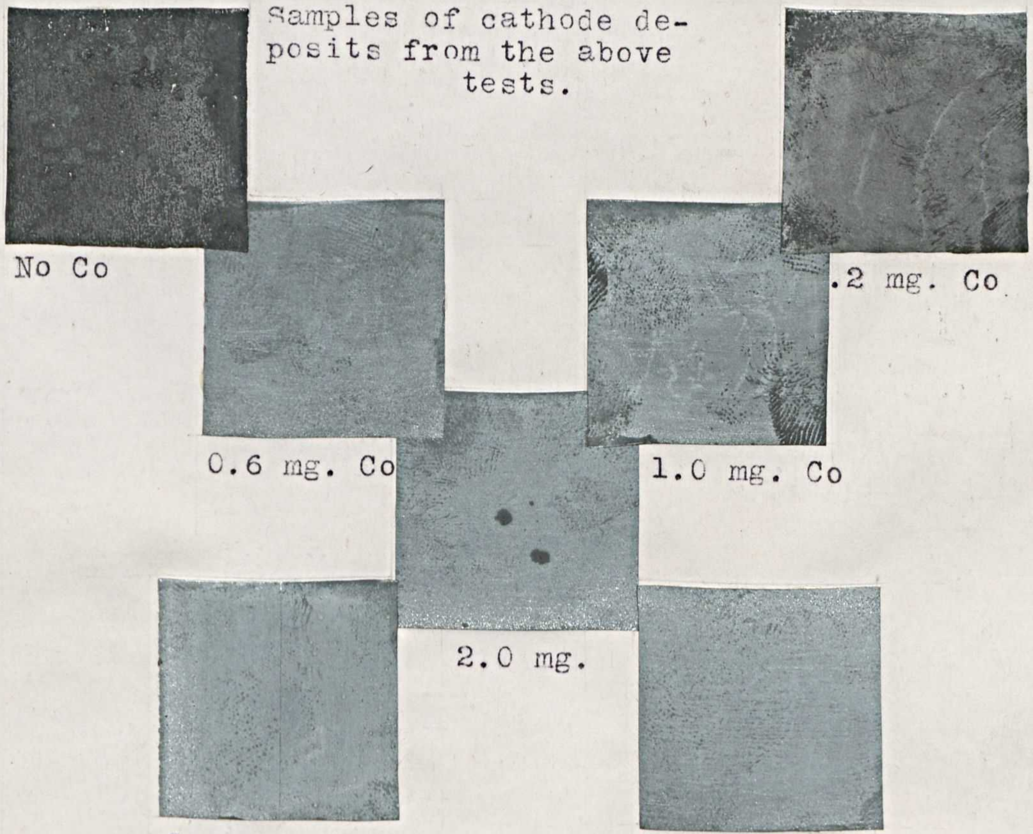
*On this occasion the burette was leaking and the readings had no value.

Data to supplement the above will be found in table IV of the Appendix.

Fig. 4:- Effect of cobalt additions on the current efficiency of a solution containing 0.50 mg. antimony.



Samples of cathode deposits from the above tests.



No Co

.2 mg. Co

0.6 mg. Co

1.0 mg. Co

2.0 mg.

5.0 mg. Co

8.0 mg. Co

SUMMARY

1. The hydrogen method was investigated by determining current efficiencies for a number of solutions containing antimony and cobalt. The method was found to give an average discrepancy of 0.57 when compared with the weight method. The greatest difference was 1.5 per cent. Part of this discrepancy is due to the fact that the hydrogen cell was kept in continuous operation, and the weight cell was stopped in order that the cathode could be weighed. This resulted in a higher acidity in the spent electrolyte of the hydrogen cell.

2. The effects of antimony in concentrations up to 0.50 milligrams per liter were determined. Investigations above this concentration have been made by Rontgen and Buchkremer[2] and by Ellsworth[3].

It can be seen from table IV of the appendix that the current efficiency declines rapidly with time in the impure solutions, but is fairly constant for the pure electrolyte. The figures for test numbers one and two demonstrate the fact that longer readings are much more accurate than the fifteen minute readings.

3. The beneficial effect of cobalt additions to an electrolyte is shown in tables II and IV. Although the current efficiency was raised from 80% to 93% by the addition of 0.60 milligrams, the efficiency showed a marked tendency to decline with time, as shown by the hydrogen readings in test 12 of table IV.

SUGGESTIONS FOR FUTURE STUDY

1. Part three of the summary at once suggests that a study of the decay of efficiency in solutions containing one impurity which has been neutralized by another would be of interest and that the hydrogen method is adaptable to an investigation of this kind.

2. As little information on the effect of germanium is available, a complete investigation of this impurity would be of value. This should include the single effect and the effect of other impurities as well as the time consideration.

3. The effect of temperature of impure solutions would be interesting from a theoretical standpoint in order that the existing laboratory data could be better correlated with plant practice.

APPENDIX

CALCULATION OF AVERAGE TANK HOUSE FEED

In commercial practice at the Anaconda Zinc Plant the cells are operated in cascades of six. Fresh solution containing 110 grams of zinc per liter and no free acid is fed into the head cell of each cascade. The spent electrolyte from this cell flows to the next, where more fresh solution is added to keep the acidity from building up too high. This means that except for the first cell the feed is made up of fresh electrolyte plus the discharge of the previous cell. The amount of new feed entering the cascade is regulated to give a spent electrolyte of about ten percent acid at the last cell.

Assume that a cascade is so adjusted that the discharge of each cell is ten percent acid. The amount of fresh feed entering each tank will then be one liter for a given period of time. From these assumptions the data on page nineteen may be assembled.

CALCULATION OF AVERAGE FEED IN A CASCADE

CELL	FEED ACID grams/liter	VOLUME FEED liters	% Acid in Feed
#1	0	1	0
#2	100	2	5.0%
#3	200	3	6.6
#4	300	4	7.5
#5	400	5	8.0
#6	500	6	8.3
	Average feed for entire cascade		5.9%
	Average discharge		10.0%
	Average in tanks		8.0%

Since each gram of zinc deposited results in the generation of 1.5 grams of acid, the average feed will contain 110- $(59 \times \frac{2}{3})$ = 70.7 grams zinc.

In the above calculation it is assumed that the fresh feed entering each cell is one liter for a given unit of time.

In calculations made on actual plant data with corrections applied for the volume of fresh feed entering each tank, the following figures were obtained.

TABLE III

Cascade	Discharge Acidity Being Maintained		Average Feed	Average in Tanks
	Desired	Actual		
Av. of 23 & 24 Unit 4	12.5%	12.2%	7.0	9.6
23 Unit 1	10.5	11.0	5.0	8.0
Theoretical	10.0		5.9	8.0

CURRENT EFFICIENCY CALCULATIONS

The following data were obtained from test10:

Time	Burnette Reading	Volume	Temperature
15	1.4	52.7cc	21.6°c
15	1.8	52.5cc	21.5°c

Barometric pressure: 615.0 mm. Current - 2 amps.
Zero to surface of electrolyte ('h' in Fig. 1.) 6.4 cm.
Each division on Burette is 1.1 centimeter.

The volume is found by subtracting the reading from 54.1, since the burette was inverted, and there was a volume of 4.1 cc. between the top reading and the pet cock.

Temperatures refer to hydrogen and not to that of the electrolyte.

Other data necessary:

Density of electrolyte........................1.169
Density of mercury..........................13.54

CALCULATIONS

1. Convert height of solution in burette to millimeters of mercury:

$$(1.4 \times 1.1 + 6.4) \times \frac{1.169 \times 10}{13.54} = 6.9 \text{ mm.}$$

Vapor pressure of water at 21.6° C..19.3mm.
Vapor pressure of solution 21.6° C.. 9.3mm.

Pressure inside burette:
615.0 - 6.9 - 9.3 = 598.8mm.

2. Volume of hydrogen per ampere hour:, S.T.P. :

$$\text{Vol.} = 52.7 \times \frac{30}{15} \times \frac{598.8}{760} \times \frac{273}{294.6} = 77.0 \text{ cc}$$

One ampere hour of hydrogen is equal to 417.5 cc.

3. Loss of current efficiency $= \frac{77.0}{417.5} \times 100 = 18.4\%$

Current efficiency = 100 - 18.4 = 81.6%

Simplified calculation of second reading:

$(1.8 \times 1.1^{*} + 6.4) \times 0.861^{*} = 7.2$ mm of Hg

Vapor pressure correction 9.2 " " "

615.0 minus 16.4 = 598.6 mm Hg

$$C. E. = 100 - (52.5 \times 598.6 \times 30 \times 0.0861^{*})$$

$$C. E. = 81.7\%$$

Constants in above calculation are marked with an asterick.

CURRENT EFFICIENCY BY WEIGHT METHOD

(Simplified Calculation)

Since the valence numbers of copper and zinc are both two, faradays of current should deposit 63.57 grams of copper and 65.37 grams of zinc.

From test ten:

Wt. Copper deposited = 2.7594 grams
Wt. Zinc deposited = 2.2373 grams

$$C. E. = \frac{2.237}{2.759} \times 97.23 = 79.0\%$$

The factor 97.23 is obtained by dividing the molecular weight of copper by that of zinc and multiplying by 100%.

TABLE IV

The data in tables I and II are the averages of several readings. In order that the complete data may be available, these readings are presented in the following table.

TABLE IV

Test	Mg. Sb Per Liter	Mg. Co Per Liter	HYDROGEN METHOD		WEIGHT	
			Time in Min.	C. E. %	Time in Min.	C. E. %
1g	0	0	15	88.7	60	89.3
			15	89.5	60	91.2
			15	89.5		
			15	92.0		
			15	91.2		
			15	91.5		
			30	93.5		
2	0	0	33	93.8	60	93.3
			39	93.6	60	94.0
			31	93.5		
			30	93.1		
3	0	0			65	94.0
4	0.02	0			60	92.8
5	0.02	0	33	93.0	60	92.3
			29	91.8		
6	0.06	0	24	89.2	54	89.4
			23	88.5	48	89.9
			22	87.9		
			21	87.0		
7	0.10	0	23	89.1	61	89.1
			26	89.1		
			23	89.0		
			22	88.9		
8	0.10	0	35	92.8	60	91.6
			31	89.1	63	93.7
			31	92.9		
			30-	92.8		
			26	92.7		

TABLE IV (Cont'd)

Test	Mg. Sb per liter	Mg Co per liter	HYDROGEN METHOD		WEIGHT	
			Time in Min.	C. E. %	Time in Min.	C. E. %
9	0.20	0	26	90.4	45	87.8
			23	88.9	45	87.5
			22	90.0		
			23	88.3		
10	0.50	0	15	81.6	30	79.0
			15	81.7	30	80.6
			15	81.2		
			15	80.9		
11	0.50	0.20			80	92.0
					46	91.8
12	0.50	0.60	25	94.3	61	93.6
			35	94.3	52	92.5
			47	94.2		
			19	92.5		
			34	92.7		
			29	92.2		
13	0.50	1.00	37	92.6	50	93.5
			37	93.0	53	91.1
			35	92.4		
			29	91.3		
14	0.50	2.00	30	93.3	63	93.6
			30	92.6	60	91.0
			28	91.0		
			26	90.1		
			24	89.3		
15	0.50	5.00	28	92.5	74	93.5
			27	92.3		
			30	91.5		
			27	90.1		
			28	89.9		
16	0.50	8.00	43	93.0	74	94.0
			37	92.2	67	90.9
			34	92.3		
			31	91.6		

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