THE EFFECT OF THE ANODE OXYGEN CONTENT ON THE ELECTROREFINING OF COPPER

by

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ABSTRACT

Laboratory scale electrorefining tests were carried out to see what effect the oxygen content of a copper anode had on the electrorefining of the copper.

Oxygen in the form of Cu_2O was added to the copper before it was cast into anodes. Some of the copper had added to it certain impurities, which are commonly found in anode copper. The surface appearance of the anode, the current efficiency of both electrodes, and the purity of the cathode deposit were all examined.

At the end of a test run the anodes high in oxygen had a smoother surface appearance than anodes low in oxygen. Anodes high in oxygen also had a higher anode current efficiency. It also appeared that cells operated with a high oxygen anode had a higher cathode current efficiency than cells with low oxygen anode. This cathode efficiency, however, was highly variable and was dependent on which impurity was present.

Because the cathode deposit contained very little impur-

ities, it was impossible to make any correlation between anode oxygen content and impurity level in the cathode. The lack of impurities in the cathode was probably due to the short length of time the cells were run, and so the impurity level of the electrolyte was not built up to a concentration which would lead to deposition on the cathode.

INTRODUCTION

Blister copper contains from 0.5 to 1.5 weight percent impurities. These impurities lower the conductivity, impair the castability, and in general make the copper unsuitable for commercial applications. Some of the impurities, such as Au, Ag, and Pt, also have a great value if they can be recovered from the copper. The copper, therefore, must undergo refining before it is suitable for sale.

There are two general methods of refining. If the blister copper is high in copper and low in precious metals, the whole refining process can be carried out by pyrometallurgical methods. If the blister is low grade and contains a sufficient quantity of precious metals, it is generally more economical to use a combination of fire and electrolytic refining. This latter method is the most widely used and about 85 percent of the world's copper production is so refined.

Blister copper from the converters is transferred molten or is melted in an anode furnace. The molten copper is then agitated with air to oxidize the impurities. A silica flux is added and the high impurity slag is skimmed off. This oxidation step removes most of the Fe, Sn, Zn, and S and partially eliminates the Pb, As, and Sb. Since partial oxidation of the copper also occurs, the metal then must undergo a reduction process called poling. The poling operation consists of plunging large logs into the coke-covered molten copper. The reaction between the molten copper and the wood and reducing gases from the logs gradually lowers the oxygen content of the copper. The poling process is continued until the sample shows that the copper has reached a "level set" - a term used by copper refiners to indicate that the exposed surface of the cast copper is fairly flat and uniform. This set generally occurs at about 0.04 to 0.07 weight percent oxygen. The molten copper is then quickly cast into an anode mold and is now ready for the electrolytic refining step. It is very important to obtain the proper set before casting the copper, for unless the surface of the anode is smooth and uniform it will cause high scrap loss and short-circuiting of the cell.

The impure copper anode and a high purity copper cathode are placed together in a $CuSO_4$-H_2SO_4 electrolyte. A current is passed through the cell and copper is transferred from the anode to the cathode. Although a small amount of impurities may deposit on the cathode, the majority either pass into the electrolyte or fall to the bottom as insoluble slimes.

Thus the blister copper which is about 98+% Cu, is fire refined to anode copper which is about 99% Cu, which is electrolytically refined to about 99.8% Cu. The electrolytic copper is then usually melted and cast into its marketable shapes.

Purpose of Investigation

This study of anode oxygen content was undertaken to determine if the oxygen content had any effect on the electrolytic refining. This investigation was to determine the effect of oxygen on the anode and cathode current efficiencies and on the amount of impurities that are transferred from anode to cathode. The six impurities studied were added singly to the copper. There was no attempt to study the effect of oxygen on any combination of impurities.

Survey of the Literature

Although a great deal of work has been done on electrolytic copper refining, very little research has been done on the role anode oxygen plays in it. The impurities found in anode copper can be separated into metallic and gaseous impurities.

The metallic impurities used in this experiment can be further subdivided into elements that either are highly electropositive to copper or lie between the electrode potential of hydrogen and copper.*

Metallic Impurities. In this experiment the electropositive impurities used were Ni, Fe, and Co. Hayward and Hofman (1924, pp. 351-354) and Butts (1954, pp. 171-174) have reported the following information on these metallic impurities.

Nickel is the chief impurity in most U.S. electrolytic refineries. Nickel is completely soluble in molten copper, regardless of the oxygen content. It can be present either

* These potentials are considered to be the standard oxidation potentials with the hydrogen potential equal to zero. At the anode all elements with an oxidation potential more positive than copper will dissolve at the expense of copper. Elements more negative than copper will not dissolve. At the cathode elements with a positive oxidation potential will not deposit. All elements with an oxidation potential between hydrogen and copper should deposit before it. However, the concentration of the ion in solution determines the exact potential at which the ion will deposit on the cathode, and a metal ion might not deposit if its concentration is very low.

as Ni metal or as an oxide. The nickel metal readily dissolves to form a soluble sulfate in the electrolyte. Nickel oxide is insoluble in dilute H_2SO_4 and this probably accounts for the nickel found in the slimes. Since electrodeposition of nickel in a copper electrolyte is impossible, any nickel found in the cathode is probably due to occluded electrolyte. Hence, the amount of nickel found in the cathode probably depends on the physical nature of the cathode surface.

Iron is also soluble in molten copper but it will combine with any oxygen present to form stable oxides. These oxides are insoluble and separate readily from the molten copper. Iron forms soluble sulfates in the electrolyte but it is a moot point on whether the iron is present as $FeSO_4$ or as $Fe_2(SO_4)_3$. The iron content of the anodes is usually low, however, so iron is generally not a serious problem.

Cobalt is not a major impurity in the U.S. so very little work has been done with it. It is known that cobalt does form a highly soluble sulfate in the electrolyte. Because of its low concentration in the anode, cobalt usually doesn't contaminate the cathode.

The other 3 metallic impurities added in this investigation were Sb, As, and Bi. Their electrode potential lies between hydrogen and copper and they could codeposit with it at low copper concentrations. Luckily the Sb, As, and Bi content of the anode copper in the U. S. is generally low.

Antimony is completely soluble in copper above 700°C but below 700°C partial precipitation of an oxide can occur. Antimony hydrolyzes upon entering the electrolyte and is probably present as antimonious acid or $SbO_3^{\equiv}$ ion. Antimony's limited solubility in the electrolyte, 1.1 gpl (grams per liter), probably prevents it from becoming a serious impurity in the cathode.

Arsenic is completely soluble in molten copper regardless of the oxygen content. Arsenic is hydrolyzed in the electrolyte to arsenic acid or $AsO_4^{\equiv}$ ion. Both of these species are soluble in the electrolyte. At arsenic's theoretical electrode potential it would take a concentration of 18 gpl before it would be codeposited with copper. Regular purification of the electrolyte, however, will hold the arsenic concentration well below this level.

Bismuth is soluble in molten copper but it will combine with any oxygen present to form an oxide that precipitates along the copper grain boundaries. It also hydrolyzes in solution to form a slightly soluble basic sulfate or a bismuth arsenate, $BiAsO_4$. Bismuth's solubility in the electrolyte is about 1.8 gpl and so its presence usually presents no problem.

In most cases the presence of these last three metals in the cathode is probably due to slime inclusions or salting out of a super-saturated solution.

Gaseous Impurities. The three most important gaseous impurities in anode copper are oxygen, sulfur, and hydrogen. These impurities may be present in either elemental form or compounds of these elements.

The oxygen in anode copper is present in the form of Cu_2O. The Cu_2O is not attacked electrochemically (Hayward and Hofman, 1924, p. 352) but reacts with the H_2SO_4 according to Eq. 1.

$$Cu_2O_{(s)} + H_2SO_{4(l)} = Cu_{(s)} + CuSO_{4(l)} + H_2O_{(l)} \qquad (1)$$

The copper metal enters the anode slimes and the $CuSO_4$ becomes part of the electrolyte. Uneven distribution of Cu_2O or other electropositive impurities in the anode will cause the anode to corrode unevenly.

Lange and Schab (1967, p. 63) have found that for anodes low in oxygen the more oxygen in the electrolyte the greater the dissolution rate at the electrodes. They also state that oxygen formed at the anode tends to saturate the electrolyte with oxygen. They found that the high oxygen content of the electrolyte results in a 1.5 to 2.9% loss of cathode current efficiency. For anodes high in oxygen the rate of dissolution of copper depends on how fast oxygen can be formed at the anode-electrolyte interface. They found that impurities decreased the rate at which this oxygen could be formed.

The reaction between oxygen and hydrogen and sulfur is responsible for determining the set of the copper. The main reaction in producing the set copper is given by Eq. 2.

$$\underline{O} + 2\underline{H} = H_2O_{(g)} \qquad (2)$$

The hydrogen and steam come from the fuels and from the combustion of wood in the reduction process. The steam produced is insoluble in the solidified copper. The steam produces the set of the copper by forming enough microscopic bubbles to offset the shrinkage of the copper. Between 1100°C and 1300°C the solubility of hydrogen in pure copper is proportional to the temperature (Bever and Floe, 1944, p. 157). Allen (1930, p. 122) states that with other conditions constant the solubility of hydrogen decreases with increasing oxygen content. Phillips (1947, p. 38) believes that the hydrogen content of the molten copper is relatively unimportant since there will always be enough hydrogen present to produce the minimum amount of steam necessary. He says that any excess hydrogen just starts escaping earlier from the cooling copper. Allen and Hewitt (1933, p. 271) state, however, that the porosity and hence the set are determined by the hydrogen and not by the oxygen content. Thus, hydrogen plays a main role in the production of anode copper but the exact mechanisms of that role are uncertain.

Sulfur is also important in producing anode copper, but like hydrogen the exact function it fulfills is only vaguely understood. The sulfur is present in the copper in the form of Cu_2S. It comes from the fuel used in melting the copper and from the coke used in covering the molten copper during the reduction process. Skowronski (1919a, p. 311) determined that the sulfur was removed from the copper by the following reaction.

$$\underline{S} + 2\underline{O} = SO_{2(g)} \qquad (3)$$

He stated that the sulfur was completely removed in the oxidation process but that it was reabsorbed in the reduction process when the oxygen content became low. He also stated (1919b, p. 317) that the amount of oxygen present to obtain a certain set in the copper is automatically controlled by the sulfur content. Phillips (1947, p. 38), however, felt that the set of the copper was controlled by the oxygen content. The sulfur content was only important when the sulfur approached its commercial maximum.

Carbon has a solubility of 0.0004 wt per cent in copper

(Chipman and Floe, 1942, p. 36). Since its solubility is small, and CO and CO_2 are practically insoluble in solidified copper (Giardi and Siebert, 1950, p. 1170), carbon is not considered a very important impurity in copper anodes.

Thermodynamic calculations were carried out to determine the stability of the different oxides in molten copper. These calculations provided an approximate idea of which oxide could be present in the anode copper. These calculations are shown in Appendix VII.

Therefore, although much is known about impurities in copper, little of this knowledge applies to the effect of these impurities in the electrolytic refining process.

APPARATUS AND EXPERIMENTAL PROCEDURE

The following pages will explain the apparatus used, the preparation of the alloys, and the cell operation during a run.

Apparatus

The electrorefining experiments were carried out in 2 plastic cells. The cells measured 5 in. wide by 5½ in. high by 8 in. long. They were made of 3/8 in. lucite plastic. The electrodes were held in the cell by a piece of plastic with slots in it. The two 1/4 in. slots were 1½ in. long and were spaced 1.35 in. apart. A screw coming in through the outside edge held each electrode in its slot. The holder rested on supports inside the cell. Electrical tape was placed on each end of the holder to help minimize stray current losses. The cells were equipped with a top that had a 1/8 in. deep groove in it the same size as the box. This groove formed a seal with the top of the box that helped reduce heat loss and electrolyte evaporation. The top had slots for the electrodes and

and two 1/2 in. holes for a stirrer and a thermometer.

A cell was also made for the copper coulometer used in these tests. It was of similar construction to the test cells, but it was 2 in. longer and had no top. The coulometer electrodes rested on top edges of the coulometer. These edges were also taped. A 500 ml glass flask was placed in the coulometer during a test. Cold water was circulated through the flask and this helped cool the electrolyte.

A Sargent # S-84805 constant temperature water bath was used to keep the electrolyte in the test cells at a constant temperature during a run. A 5-amp, 135-volt selenium rectifier was used as a power source. A variable resistor and an ammeter were used to regulate the current. The electrolyte in the test cells was agitated with a variable speed electric stirrer. The coulometer electrolyte was agitated with a magnetic stirrer. A thermometer inserted in a rubber stopper was used in the test cells. A plain thermometer was used in the coulometer. The apparatus set up is shown in Figures 1 and 2.

Experimental Procedure

The copper used to make the anodes was supplied by the Anaconda Copper Co. A spectrographic analysis of it is

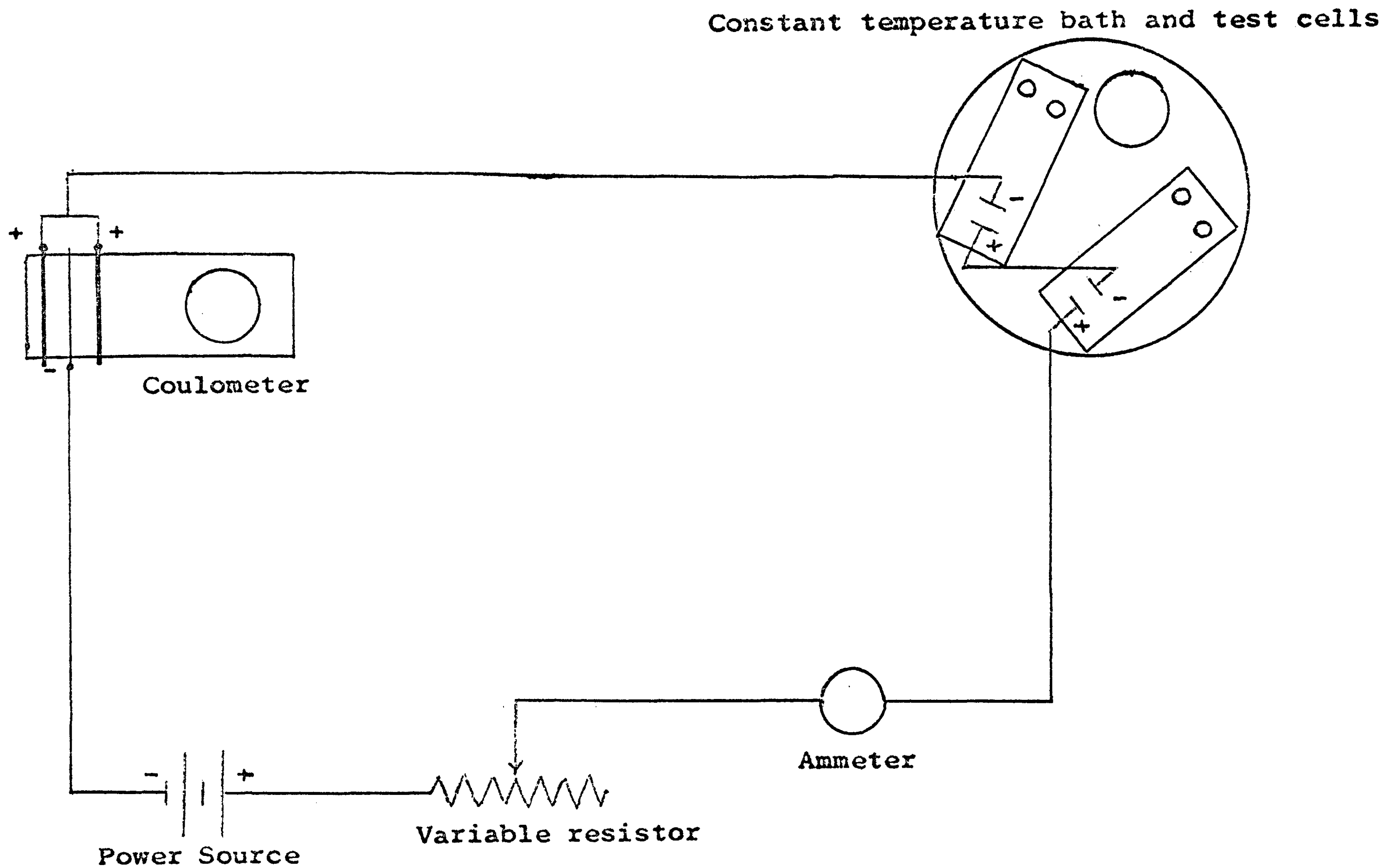


Figure 1. Schematic diagram of electrorefining equipment.

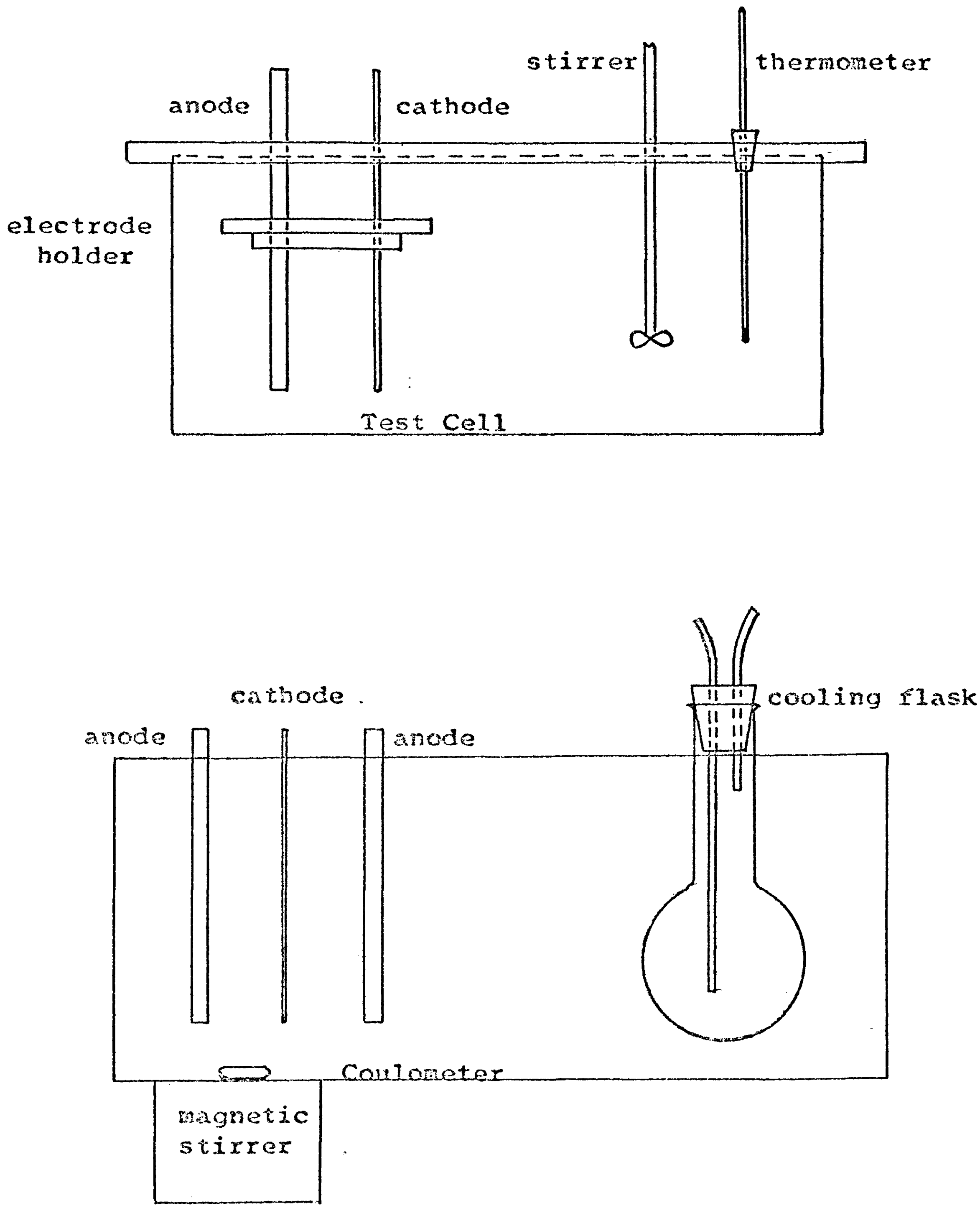


Figure 2. Schematic diagram of cells.

given in Appendix VI. The impurities added in the test were all reagent grade chemicals except for the arsenic and antimony, which were industrial chemicals 98-99% pure. The chemicals used in making the electrolyte were also reagent grade chemicals.

Preparation of Test Alloys. The various alloys used in this test were made by adding a weighed amount of impurity to a known amount of copper, usually about 1800 gm. The six impurities added were Fe, Ni, Co, Bi, As, and Sb. Besides being common impurities in anode copper, these elements are all capable of combining with oxygen to form stable oxides. They were added in amounts that would be representative of their content in anode copper now processed in the U. S. The copper and impurity was placed in a plumbago crucible (plumbago is a trade name for a crucible that is made of graphite with a small amount of organic binder) and melted in a resistance furnace at 1150°C. A layer of charcoal covered the copper while it was melted. The molten alloy was left in the furnace for two hours during which time it was periodically stirred with a carbon rod. The alloy was then poured into 3 smaller plumbago crucibles to solidify. The alloy was covered with charcoal until it had completely cooled. The alloys were removed from the crucibles and weighed.

Oxygen, in the form of Cu_2O, was added to 2 of the alloys. One alloy had 0.45 weight percent Cu_2O added to it and the other had 0.90 weight percent Cu_2O added. This corresponded approximately to 0.05 and 0.09 weight percent oxygen respectively in the 2 alloys. This oxygen content is representative of the oxygen content of commercial anodes. The 3 crucibles were then placed back in the furnace. The alloy to which no oxygen was added was again covered with charcoal, but the other 2 crucibles were left uncovered. The alloys were stirred twice during the 1½ hours that they remained in the furnace.

The copper was removed from the furnace and cast into a graphite anode mold. The anodes were allowed to cool under charcoal for about 1 minute and then they were quenched in water. Thus 3 anodes were obtained which had the same impurity level but varied in oxygen content. The anodes for the coulometer were made in a similar way except no Cu_2O or impurities were added. This copper was always covered with a layer of charcoal during melting. The dimensions of the anodes are shown in Figure 3. Twenty-two anodes were prepared in this manner, of which four contained no impurities and only varied in oxygen content.

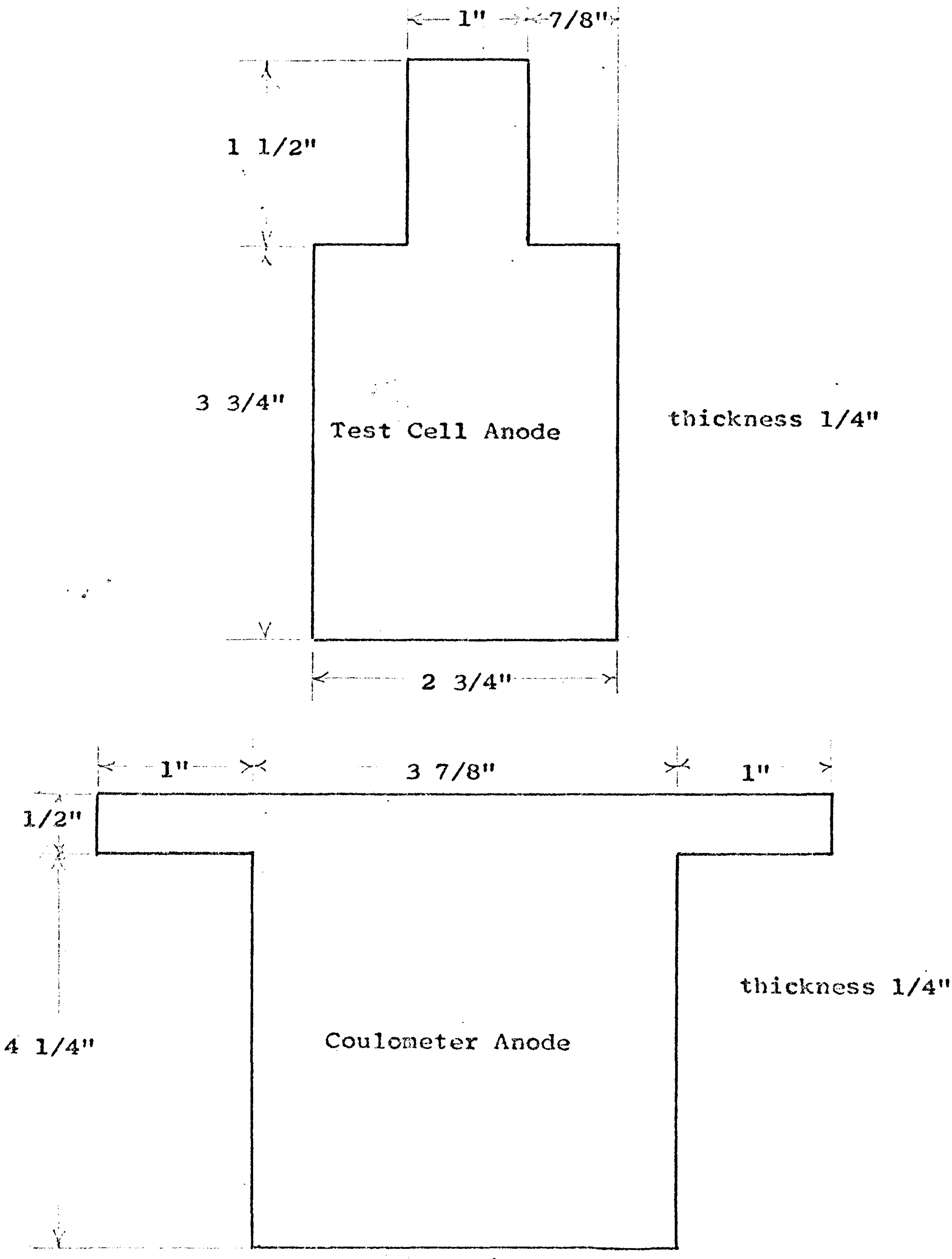


Figure 3. Dimensional diagram of anodes

Operation of Test Runs. The top 0.050 in. on each side of the anode were machined off. This machining was done to remove any differences, such as oxygen content, that might appear in the copper during casting. The anodes were sanded on both sides and edges to remove all imperfections and surface oxidation. They were then cleaned in a 3:1 solution of water and nitric acid. The edges were taped with electroplating tape. One side was sprayed with 3 coats of lacquer. A heavy coating of vacuum grease was spread over the lacquer. The tape, lacquer, and grease were applied so that the anode would corrode from one side only. The anodes for the coulometer were prepared in a similar way. The anodes were weighed and their weights were recorded.

Cathodes for the test cells were cut from 1/16 in. sheet. They were cut to the same dimensions as the anodes. They were also taped, lacquered and greased the same as the anodes. Cathodes for the coulometer were cut from 0.005 in. sheet to the same dimensions as the coulometer anodes. Since the coulometer cathode was to have copper plated on both sides of it, nothing further was done to it. The weights of the finished cathodes were recorded. The anodes and cathodes for the test cells were placed in their holders. Three and one half in. of electrolyte, consisting of 147 gm of $CuSO_4.5H_2O$

(40 gm of Cu) and 104 ml of H_2SO_4 (200 gm of H_2SO_4) made up to a liter with distilled water, was added to the test cells. The electrolyte depth and placement of the anode and cathode in their holder was determined so that the same amount of electrode area was submerged in each cell.

The coulometer electrodes, 2 anodes and 1 cathode, were placed in the coulometer cell. An electrolyte consisting of 125 gm of $CuSO_4 \cdot 5H_2O$, 50 gm of concentrated H_2SO_4, and 50 gm of ethyl alcohol made up to a liter with distilled water was prepared. The alcohol was added to prevent the oxidation of Cu^+ to Cu^{++}. A copper coulometer was used in preference to a silver coulometer, because according to Potter (1961, p. 14) the copper coulometer is more suitable for repeated measurements of moderate accuracy.

The test cells were placed in the water bath. When the electrolyte reached operating temperature, 60°C, the electrodes were placed in the cell, the top was slipped on, and the wiring was hooked up. The coulometer solution was then poured into the coulometer and the wiring and the cooler were hooked up. The rectifier was turned on and the current was adjusted to 1.04 amps. This current setting and submerged cathode area were calculated to produce an 18 asf (amps per square foot) cathode current density, which is about the average current density that is used in commercial operations. The stirrers were turned on and adjusted so they both turned at about 250 rpm. The cells were run like this for 48 hours.

Twice each day while a test was in progress, the current, voltage, temperature of each cell, and the temperature of the water bath were recorded. The temperature of the test cell was kept at $60^{\circ}C \pm 1^{\circ}C$. The coulometer temperature was kept at $21^{\circ}C \pm 2^{\circ}C$. The electrolyte level was also checked at these times and distilled water was added to bring the electrolyte back to its original level.

At the end of 48 hours all electrodes were removed from the solutions and immediately rinsed with distilled water. As soon as the electrodes were free from all copper sulfate crystals, they were rinsed with ethyl alcohol and ignited. They were then placed under heat lamps for 1 hour. At the end of this time the electrodes were completely dry and their weights were recorded.

The electrolyte from the test cells was filtered. The cell was rinsed and this water was also filtered. The rinse water from the electrode washing was also filtered since it contained many particles of copper and flakes of copper oxide. The volume of this filtrate was recorded and the solution was stored in a bottle. The copper on the filter paper was taken into solution. This solution was diluted up to 100 ml in a volumetric flask and stored in small bottles.

After all the alloys had been run, several additional tests were made. In the first test a high oxygen anode and a low oxygen anode prepared in the usual way were placed in a cell with a cathode. A standard electrolytic solution was added until 1/2 in. of the electrodes was covered. The current was adjusted to give an 18 asf cathode current density. After an hour, another 1/2 in. of electrolyte was added and the current readjusted to 18 asf. This was done three more times until there were 5 different sections which varied in electrolysis time from 3 hours to 15 minutes.

The second test was made by placing a high oxygen and a low oxygen anode in the same cell. Electrolyte that contained no $CuSO_4.5H_2O$ was added but no current was passed through the electrodes. The solution was heated and stirred for 48 hours. This test was done to see the effect of H_2SO_4 in the electrolyte on the corrosion of the anode.

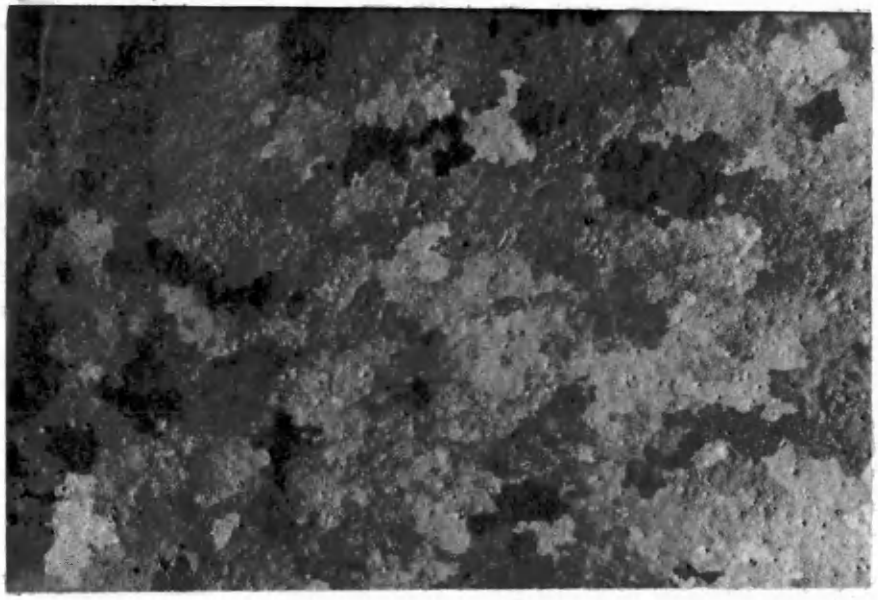
The final test was done by placing a high oxygen anode and a low oxygen anode in a cell with a cathode. Electrolyte containing no H_2SO_4 was added to the cell. The current was adjusted to 18 asf and run for 48 hours. The solution was also heated and stirred. This test was done to see in what way the anodes dissolved when no H_2SO_4 was present.

RESULTS OF EXPERIMENTS

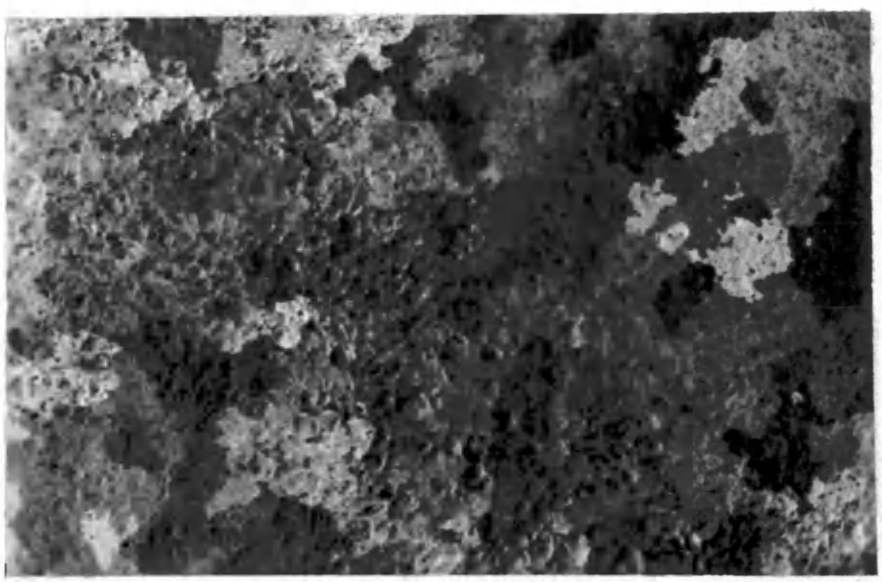
The experimental results obtained during the electrorefining tests can be grouped into three categories. They are corrosion characteristics of the anodes, current efficiency of the anode and of the cathode, and transference of impurities from anode to cathode.

Anode Corrosion

The following description of the anodes applies to observations made under 6X magnification. It was found that anodes low in oxygen had a much rougher surface after electrolysis than anodes that were high in oxygen. This fact was quite apparent in the test that changed the electrolysis time of the anode by small amounts. These anodes are shown in Figures 4, 5, and 6. At the end of 15 minutes electrolysis time the low oxygen anode had small cracks visible in its surface. These cracks were nearly continuous and appeared to be at the grain boundaries of the copper. As time progressed the cracks got wider and deeper while the original surface of the metal appeared relatively untouched. At the

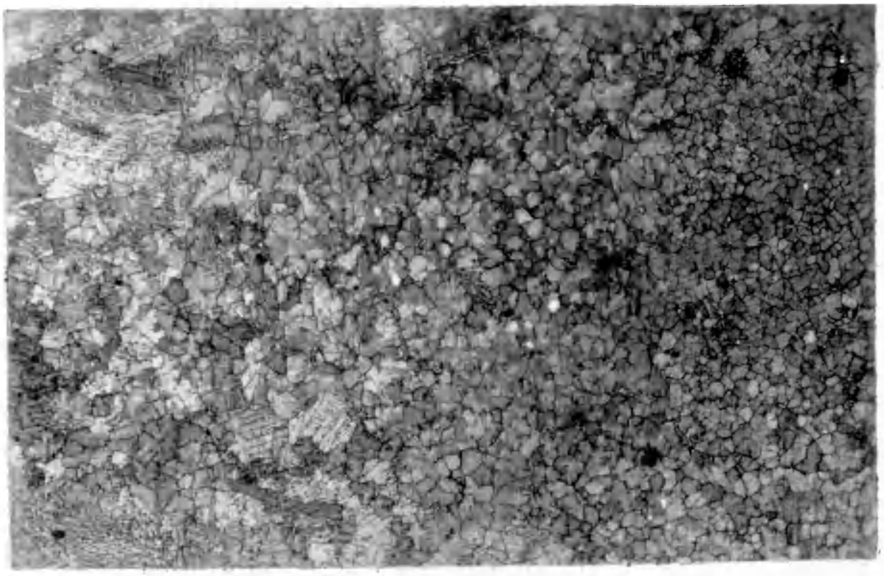


a. Anode surface at 15 minutes. (10X)

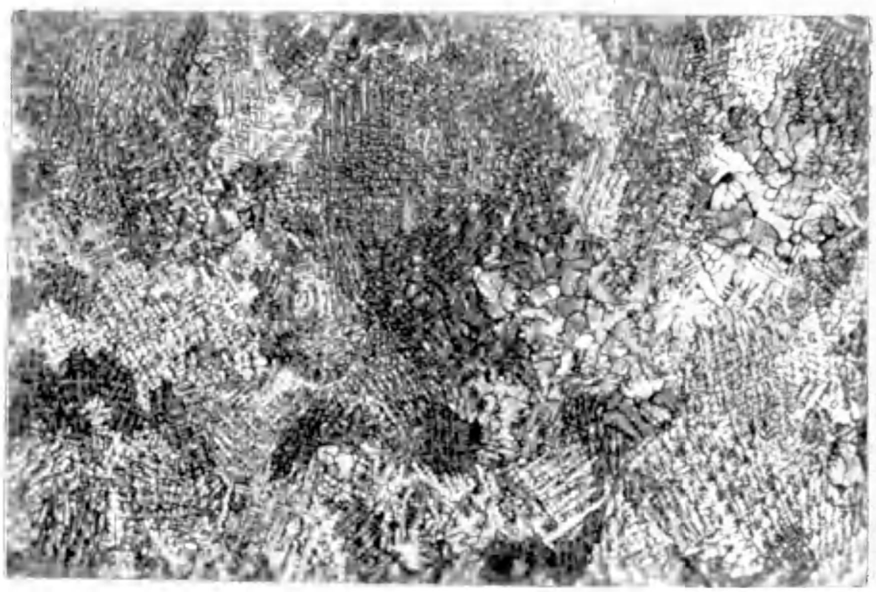


b. Anode surface at 3 hours. (10X)

Figure 4. Early stages of anode corrosion, high oxygen anode. Approximately 0.2 wt % O_2.

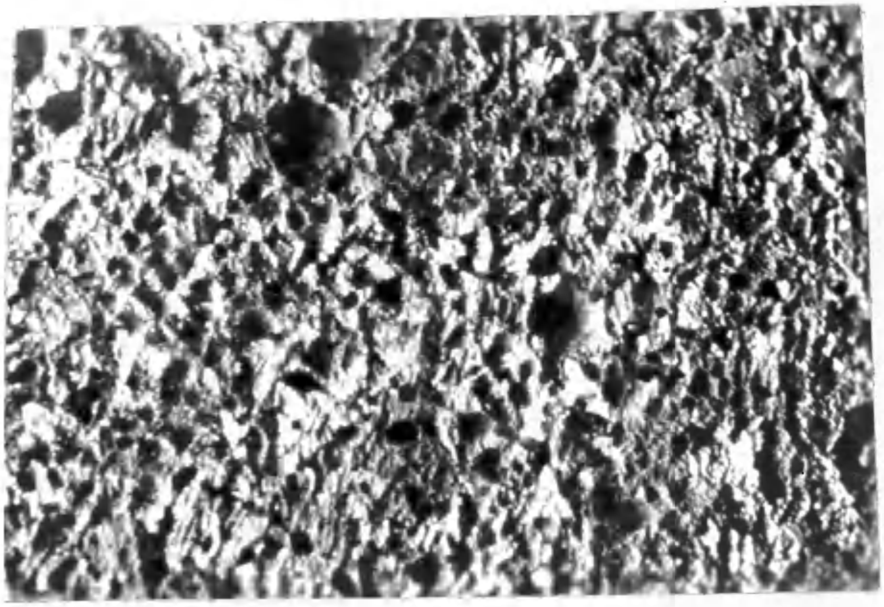


a. Anode surface at 15 minutes. (10X)

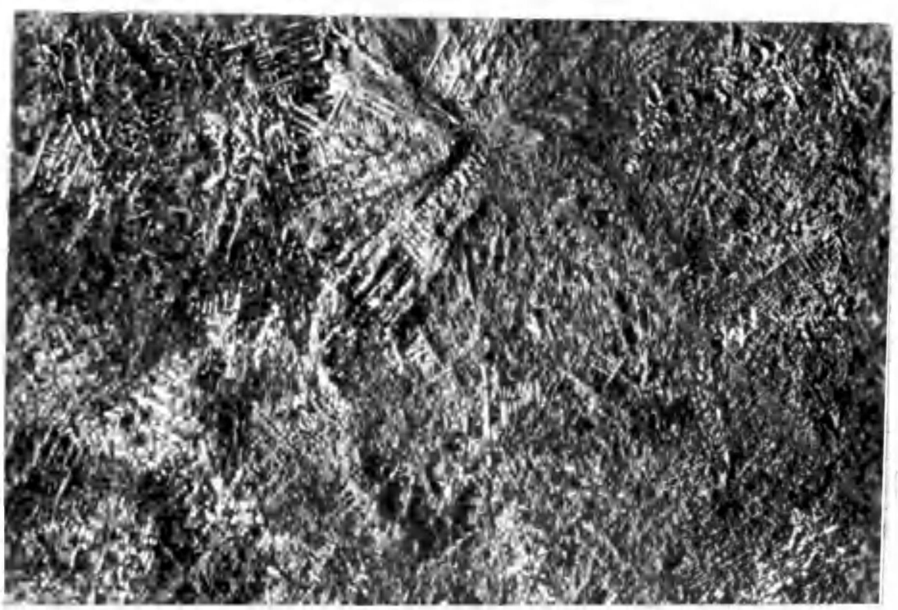


b. Anode surface at 3 hours. (10X)

Figure 5. Early stages of anode corrosion, low oxygen anode. Approximately 0.03 wt % O_2



a. Low oxygen anode, 0.058 wt % O_2. (10X)



b. High oxygen anode, 0.298 wt % O_2. (10X)

Figure 6. Anode surface after 48 hours of electrolysis.

end of two hours the surface appeared to be about half cracks and half original surface. At the end of three hours almost all of the original surface was gone. A specimen that had been run 48 hours looked similar to a specimen that had been run 3 hours.

In high oxygen anodes a different type of corrosion was observed. At the end of 15 minutes the surface appeared slightly rough but had no visible cracks. As the electrolysis continued, slight depressions on the anode surface became visible. After 3 hours the only apparent surface features were these slight depressions. At the bottom of many of these depressions were small holes. In test specimens run 48 hours the depressions were no longer present but were replaced by an irregular notchy surface. Some impurities tended to lessen the effect of oxygen on the surface corrosion but others increased it.

The two copper anodes without impurities that were electrolyzed in a solution containing no acid showed a difference in surface appearance, but the anodes that were left in the solution that contained just H_2SO_4 and water and were not electrolyzed did not. These specimens showed very little corrosion and each one only lost 0.60 gm during the 48 hours that they were in the solution. Thus the presence of oxygen in the anode tends to give the anode a more uniform corrosion characteristic.

Current Efficiency

Current efficiency is defined as the ratio of the amount of copper that was lost or gained by an electrode over that amount which theoretically should have been lost or gained. The theoretical amount that should have been lost or gained was taken as the weight of copper that was deposited on the coulometer cathode. This was done because it was felt that the coulometer cathode deposit was the closest representation of the amount of current that had actually passed through the cell. Since two samples were run at a time, the efficiencies listed in Table I are grouped in the same way. Table II lists the efficiencies grouped by impurities addition.

Transference of Impurities

Table III lists the impurities found in the anodes. In samples 2 through 18 the sulfur was determined by the induction furnace technique explained in Appendix I. Also in these same samples the oxygen content was determined by hydrogen reduction, weight loss method described in Appendix II. Because samples 19-24 contained volatile impurities,

Table I. Current efficiency of anodes and cathodes

Run #	Sample #	Impurity Added Wt.%	Impurity Present Wt.%	Oxygen in Anode Wt.%	Sulfur in Anode Wt.%	Amount of Copper Deposited on Coulometer Cathode(g)	Wt.Gain Cathode	Cathode Current Eff.	Wt. Loss Anode	Anode Current Eff.
2	3	None	None	0.058	0.015	61.33	59.91	97.7	64.74	105.6
	4	None	None	0.298	0.0008		60.39	98.5	67.39	109.9
3	5	None	None	0.180	0.005	62.44	60.25	96.5	65.44	104.8
	6	None	None	0.479	0.0002		60.71	97.2	67.00	107.3
4	7	Fe-0.05	0.009	0.093	0.002	64.93	62.25	95.9	67.56	104.1
	8	Fe-0.05	0.008	0.138	0.001		61.59	94.9	68.83	106.0
5	10	Ni-0.20	0.125	0.019	0.002	64.90	63.00	97.1	67.51	104.0
	12	Ni-0.20	0.150	0.043	0.002		63.34	97.6	67.01	103.3
6	9	Fe-0.05	0.009	0.060	0.002	64.62	62.90	97.3	67.03	103.7
	11	Ni-0.20	0.140	0.040	0.002		62.52	96.8	67.05	103.8
7	13	Co-0.01	0.010	0.038	0.002	65.14	63.02	96.8	67.09	103.0
	15	Co-0.01	0.010	0.052	0.002		63.34	97.2	67.15	103.1
8	16	Bi-0.01	0.0057	0.036	0.004	66.88	65.19	97.5	68.18	101.9
	18	Bi-0.01	0.0061	0.072	0.003		64.83	96.9	68.90	103.0
9	14	Co-0.01	0.011	0.040	0.002	66.16	64.62	97.7	67.91	102.7
	17	Bi-0.01	0.059	0.063	0.003		64.02	96.8	68.20	103.1
10	19	As-0.05	0.031	0.022	0.003	66.12	64.35	97.3	67.40	101.9
	21	As-0.05	0.027	0.066	0.003		63.98	96.8	67.97	102.8

Table I. (contd)

Run #	Sample #	Impurity Added Wt.%	Impurity Present Wt.%	Oxygen in Anode Wt.%	Sulfur in Anode Wt.%	Amount of Copper Deposited on Coulometer Cathode(g)	Wt.Gain Cathode	Cathode Current Eff.	Wt. Loss Anode	Anode Current Eff.
11	22	Sb-0.010	0.065	0.051	0.003	66.26	65.07	98.2	67.97	102.6
	24	Sb-0.010	0.067	0.088	0.003		64.38	97.2	68.14	102.8
12	20	As-0.05	0.029	0.044	0.003	65.21	62.70	96.2	67.05	102.6
	23	Sb-0.10	0.059	0.023	0.002		62.63	96.0	67.98	104.2

Table II. Anode and cathode current efficiencies as a function of impurity addition and anode oxygen content.

Sample #	Impurity Present Wt.%	Anode % O	Anode Current Eff.	Cathode Current Eff.
3	None	0.058	105.6	97.7
5	None	0.180	104.8	96.5
4	None	0.298	109.8	98.5
6	None	0.479	107.3	97.2
9	Fe=0.009	0.060	103.7	97.3
7	Fe=0.008	0.093	104.1	95.9
8	Fe=0.009	0.138	106.0	94.9
10	Ni=0.125	0.019	104.0	97.1
11	Ni=0.150	0.040	103.8	96.8
12	Ni=0.140	0.043	103.2	97.6
13	Co=0.010	0.038	103.0	96.8
14	Co=0.011	0.040	102.7	97.7
15	Co=0.010	0.052	103.1	97.2
16	Bi=0.006	0.036	102.0	97.5
17	Bi=0.006	0.063	103.1	96.8
18	Bi=0.006	0.072	103.0	96.9
19	As=0.031	0.022	101.9	97.3
20	As=0.029	0.044	102.6	96.2
21	As=0.027	0.066	102.8	96.8
23	Sb=0.059	0.023	104.2	96.0
22	Sb=0.065	0.051	102.6	98.2
24	Sb=0.067	0.088	102.8	97.2

Table III. Spectrographic analysis of anodes.

Sample #	Wt.% Fe	Wt.% Ni	Wt.% Co	Wt.% Bi	Wt.% As	Wt.% Sb	Wt.% Pb
3	0.0075	N.D.	N.D.	N.D.	N.D.	N.D.	0.019
4	0.0049	N.D.	N.D.	N.D.	N.D.	N.D.	0.002
5	0.0052	N.D.	N.D.	N.D.	N.D.	N.D.	0.009
6	<0.003	N.D.	N.D.	N.D.	N.D.	N.D.	0.0058
7	0.009	N.D.	N.D.	N.D.	N.D.	N.D.	0.031
8	0.0081	N.D.	N.D.	N.D.	N.D.	N.D.	0.012
9	0.009	N.D.	N.D.	N.D.	N.D.	N.D.	0.027
10	0.0071	0.125	N.D.	N.D.	N.D.	N.D.	0.011
11	0.0055	0.150	N.D.	N.D.	N.D.	N.D.	0.019
12	0.0053	0.140	N.D.	N.D.	N.D.	N.D.	0.010
13	0.0042	N.D.	0.010	N.D.	N.D.	N.D.	0.014
14	0.0042	N.D.	0.011	N.D.	N.D.	N.D.	0.012
15	0.0040	N.D.	0.010	N.D.	N.D.	N.D.	0.013
16	0.0040	N.D.	N.D.	0.0057	N.D.	N.D.	0.002
17	0.0035	N.D.	N.D.	0.0061	N.D.	N.D.	0.002
18	<0.003	N.D.	N.D.	0.0059	N.D.	N.D.	0.0056
19	0.0039	N.D.	N.D.	N.D.	0.031	N.D.	0.037
20	<0.003	N.D.	N.D.	N.D.	0.029	N.D.	0.032
21	<0.003	N.D.	N.D.	N.D.	0.027	N.D.	0.031
22	0.0041	N.D.	N.D.	N.D.	N.D.	0.065	0.034
23	0.0040	N.D.	N.D.	N.D.	N.D.	0.059	0.013
24	<0.003	N.D.	N.D.	N.D.	N.D.	0.067	0.018

the oxygen and sulfur content was determined by a variation of the hydrogen reduction method. This method is described in Appendix III. The metallic impurities were determined by the spectrographic method outlined in Appendix IV.

Table IV lists the impurities found in the cathode deposit. These impurities were determined by the spectrographic method described in Appendix V. The statement in this table<0.000X means that 0.000X was the lowest standard available and that the impurity was less than this but still present. Usually there was no difference discernible between samples at this level. The notation N.D. (not detectable) means that the spectrographic lines for that element were not visible.

Table V lists the amount of copper found in the slimes at the end of a run. The copper in the slimes was taken into solution with a mixture of nitric and sulfuric acids. The copper in solution was then titrated, using the short iodide method of copper determination.

Table IV. Spectrographic analysis of cathodes.

Sample #	Wt.% Fe	Wt.% Ni	Wt.% Co	Wt.% Bi	Wt.% As	Wt.% Sb	Wt.% Pb
3	0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0001
4	0.001	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0001
5	0.0005	0.0004	N.D.	0.00002	<0.0003	<0.0003	0.0002
6	0.001	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	<0.0001
7	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0005
8	0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0005
9	0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
10	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	<0.0001
11	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	<0.0001
12	0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
13	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0001
14	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
15	0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
16	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
17	0.001	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
18	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0002
19	<0.0005	<0.0002	N.D.	<0.00002	0.0003	0.0003	0.0002
20	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	0.0003	0.0001
21	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	<0.0003	0.0001
22	<0.0005	<0.0002	N.D.	<0.00002	0.0003	0.0005	0.0002
23	<0.0005	<0.0002	N.D.	<0.00002	0.0003	0.0006	0.0002
24	<0.0005	<0.0002	N.D.	<0.00002	<0.0003	0.00055	0.0002

Table V. Amount of copper found in slimes as a function of oxygen content in the anode.

Sample #	Wt.% O_2	Impurity Present	Cu in Slimes(g)
3	0.058	None	0.80
5	0.180	None	0.57
4	0.298	None	2.12
6	0.479	None	0.09
9	0.060	Fe	0.29
7	0.093	Fe	0.29
8	0.138	Fe	0.26
10	0.019	Ni	0.52
11	0.040	Ni	0.20
12	0.043	Ni	0.27
13	0.038	Co	0.25
14	0.040	Co	0.06
15	0.052	Co	0.32
16	0.036	Bi	0.03
17	0.063	Bi	0.06
18	0.072	Bi	0.19
19	0.022	As	0.03
20	0.044	As	0.02
21	0.066	As	0.02
23	0.023	Sb	0.10
22	0.051	Sb	0.43
24	0.088	Sb	0.01

INTERPRETATION OF RESULTS

The oxygen content of the anode seems to play an important role in the way that the anode corrodes. Hayward and Hofman (1924, p. 378) stated that the purer the anode the more even the corrosion. This was not true for the anodes electrolyzed in this experiment. Figures 4, 5, and 6 show the difference in corrosion behavior between anodes of low oxygen and high oxygen content. One possible explanation for the corrosion is the presence of Cu_2O in the metal. Most pure metals when placed in an etching solution, first begin etching in the grain boundaries. This attack at the grain boundaries is attributed to the fact that the atoms in the grain boundaries are in a higher energy state because of their location between the grains. These atoms of high energy dissolve and go into solution before atoms of average energy. It seems reasonable to suppose that if Cu_2O is present in the solidified structure, areas of higher energy would be produced around the Cu_2O sites.

Some of the oxygen present will react with the hydrogen and sulfur present to form steam and SO_2. If the copper is quickly quenched, these gases will not have time to escape from the copper and they will form many microscopic bubbles in it. These bubbles would tend to strain the lattice and produce areas of higher strain immediately around each bubble. Hence, the corrosion should be faster around these bubbles. This method of corrosion is evident in Figure 4.

Another possible explanation for the difference in corrosion between low and high oxygen anodes is the formation of a eutectic mixture. At low oxygen concentrations the eutectic would be interspersed between the grains of pure copper. If the eutectic corroded at a faster rate than the pure copper, it could produce the rough appearance observed in the low oxygen anodes. As the oxygen content and hence the amount of eutectic present increased, the surface would become smoother because more of it would be corroding at the same rate.

Thus the presence of oxygen in anode copper tended to increase the smoothness of the corroded surface although the mechanism by which it does is uncertain.

The impurities played a less definite role in the corrosion of the anode. Iron did not seem to have any effect at all. Nickel, Co, and Sb seemed to increase the smoothness of the anode. These samples all had a fairly smooth surface with very little difference between samples. Arsenic and bismuth had a roughing effect on the anode surface and all samples with arsenic and bismuth in them had a rough and irregular surface. This was especially true of bismuth. Since bismuth is known to form an oxide which precipitates in the grain boundaries, this oxide may further increase the strain at the boundaries and lead to rougher anode surfaces. It may be that the impurity phase and the location of this phase in the copper lattice determines how it will affect the corrosion characteristics of the anode.

Table V shows the amount of copper found in the slimes.

As pointed out earlier, Cu_2O reacts with H_2SO_4 to form $Cu_{(s)}$ and $CuSO_{4(1)}$. Thus anodes higher in oxygen should have more copper in the slimes. There appears to be in Table V no general relationship between oxygen content and copper in the slimes. Anodes containing bismuth were the only ones that showed a steady increase of copper in the slimes with increasing oxygen in the anode. It is interesting to note that the arsenic bearing anodes had very little copper in their slimes. These 3 anodes all had a heavy black coating on them at the end of their run. This coating may have prevented any loose copper particles from falling off of the anode.

Thus it appears that the copper content of the slimes does not necessarily increase with increasing oxygen content of the anodes. It may be that the smoother surface corrosion nullifies the effect of the Cu_2O dissolutions.

Table II shows some interesting correspondence between oxygen content in the anode and current efficiency. In general the anode current efficiency was affected more than the cathode current efficiency.

Besides the passage of current, the anode current efficiency also depends on the dissolution of Cu and Cu_2O and the loss of any pieces of copper which become loose when the surrounding matrix is corroded away. Because the Cu_2O will go into solution under the attack of acid, the anodes high in oxygen should lose more weight and have a higher anode current efficiency. This is exactly what was found. In all but one of the eight sets of samples, the high oxygen anode had a greater current efficiency. Nickel containing anodes were the only ones that did not show this trend. It may have been that because the nickel content was so high, it had more of an influence on the corrosion rate than the oxygen did. Table II also shows that although the oxygen content of the other anode fell between the oxygen content of the high and low anode, the current efficiency didn't always fall between the other two current efficiencies. It could be that operating conditions changed just enough between runs to make any correlation between runs impossible, or it might be that slight changes in the coulometer operating conditions cause the coulometer to operated with a slightly different efficiency. Even a slightly different efficiency would make it hard to correlate between runs. Whatever the cause for the differences, it seems reasonable to place more emphasis on differences in a run than differences between runs.

The cathode current efficiency depends on the amount of Cu^{++} reduced to copper metal, the reduction of any other ions at the cathode to a lower valence state, and on any chemical dissolution of the cathode. Chemical dissolution of the cathode is thought to be controlled by the oxygen content of the electrolyte. Since all runs were open to the air, the oxygen content in the electrolyte should be constant throughout the experiment. The presence of Fe^{+3} in the solution is thought to lower the cathode current efficiency because of the reduction of Fe^{+3} to Fe^{+2}. Butts (1954, p. 194) states that this reduction usually does not occur until the Fe^{+3} concentration reaches 3 gpl. He further states that even if the Fe^{+3} reaches this concentration it is very controversial as to how much influence this has on the current efficiency.

When no impurities were present in the anode or when these impurities were nickel or cobalt, the cathode current efficiency increased with increasing oxygen content in the anode. The experiments with four other anode impurities all showed a loss in cathode current efficiency with increase in oxygen content. Anodes with iron were especially notable as the cathode current efficiency dropped almost 3% between the lowest and highest oxygen content. Although both the impurity level and the oxygen content of the anode may play a part in determining the cathode current efficiency, it is hard to imagine what this role is. It has to be involved with either the reduction of different ions or the dissolution of the cathode. None of the data obtained, however, indicate in what way this happens.

Table IV, which shows the cathode impurity analysis, indicates that only very small amounts of impurities were transferred to the cathode during the test runs. No set of cathodes showed any significant difference in impurity level that could be attributed to the composition of the anode. It was hoped that some of the oxygen that was added to the anodes would combine with some of the impurities present to form stable oxides. If these oxides were insoluble in dilute H_2SO_4 then there would be a lesser amount of impurities in the electrolyte. Less impurities in the electrolyte should produce less chance for deposition of impurities in the cathode. It appears that the tests must be run for longer intervals of time, so that the impurity level in the electrolyte can reach a significant enough level to be detected if it's deposited in the cathode.

SUMMARY

Oxygen plays an important part in the electrorefining of copper. Although the main reason oxygen is added to copper is to produce a level surface on the cast anodes, it has many side effects.

An increase in oxygen content in the anode tends to make the anode corrode more evenly. This is thought to be due to the effect of the Cu_2O in the copper lattice. The strain in the lattice caused by the presence of Cu_2O and possibly small gas holes makes the surface corrode at the same rate as the normally high strain areas like the grain boundaries. Some of the impurities present in the anode nullified this effect, some increased it, and one had no effect on it.

An increase in the anode oxygen content also seems to increase the dissolution rate of the anode. This is thought to be the result of the dissolving of the Cu_2O by H_2SO_4. Nickel was the only impurity added which changed this relationship. The cathode current efficiency was increased by higher oxygen content when no impurities were present.

Nickel and cobalt did not change this relationship, but Fe, As, Bi, and Sb reversed it. No mechanism is known to explain the relationship between anode composition and cathode current efficiency.

The impurity level in the cathodes was not high enough to determine if there was any relationship between the amount of impurity in the cathode and the oxygen content of the anode. The low level of impurities in the cathode was probably caused by the shortness of the test runs.

SUGGESTIONS FOR FURTHER WORK

Because very little has been published on work of this type, the author feels it would be beneficial to offer the following remarks and suggestions to anyone interested in doing any similar work.

The first thing to do before undertaking a project similar to this would be to visit a refinery and talk to their engineers. A knowledge of recent operating conditions and problems could produce more valuable results. They also might be able to indicate an optimum size for the anodes and an idea of how long to run them.

Another important thing to do would be to use the highest purity copper possible. The removal of any gases present could be done in a vacuum furnace. Crucibles made out of a non-reactive material are also another necessity. Silica and alumina were tried but they both reacted with the Cu_2O. Magnesium oxide did not react with the Cu_2O and although it did crack a little, it was the best of those tried.

The use of bigger anodes and of a longer run time would probably also produce better results. The current efficiency and the buildup of impurities in the electrolyte would both be more meaningful if longer run times were used. If the anodes were too heavy, however, their weight could be measured less accurately.

More valuable information would be obtained if all samples containing the same impurity were run at the same time. This might be possible by redesigning the cells so that each had its own heater. These heaters might be similar to the ones used to heat aquariums. It might also be a good idea to use 2 different impurity levels. If one level used was about the average and the other close to the maximum, it might be easier to determine if there is a correlation between oxygen content and transference of impurities. An analysis of the electrolyte and of the slimes to determine where the impurity goes might also aid in making the above correlation.

Finally, another interesting idea would be to remelt some actual anode copper and vary the oxygen content of it.

APPENDICES

Appendix I. Analytical procedure for the sulfur analysis in copper. (Technique used by Kennecott Copper Refinery)

DETERMINATION OF SULFUR IN COPPER USING THE INDUCTION FURNACE

Principle of Method:

The determination of the sulfur content is based on the following 2 equations:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$
$$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$$

Oxygen reacts with the sulfur in the molten copper to produce SO_2. The SO_2 reacts with the HCl and starch solution to form HI. This is then back titrated with the KIO_3 solution to the original color.

Reagents and Apparatus:

Potassium Iodate Solution	0.0444 gm of KIO_3 per liter of distilled water. Standardize against refined copper standard.
Starch Solution	Dissolve 4 gm of arrowroot starch and 40 mg of phenylmercuric acetate in 50 ml of distilled water. Add this solution while stirring constantly, to 350 ml of boiling distilled water. Continue to boil for 1 minute. Cool and add 12 g of KI.
Silica	Free of sulfur
HCl Solution	15 ml per liter of distilled water
Oxygen and 2 stage regulator	
Low sulfur crucibles	Leco # 528-120
Crucible covers	For above crucibles

Appendix I (contd.)

Induction furnace	Leco Model 521
Automatic timer	Leco # 551
Automatic sulfur titrator	Leco Model 532
Starch dispenser	Leco # 533-100
Purifying train	Leco # 516

Procedure:

Turn on titrator and induction furnace. Titrator should be on 15 minutes before use. The grid circuit tap switch on the furnace should be kept on the lowest setting.

Adjust oxygen flow to 1 liter per minute. Fill bubbler with HCl solution to about 1/2 in. to 3/4 in. above oxygen inlet. Add one measure of starch from starch dispenser, about 5 ml, to bubbler.

Adjust end point to use about to the 0.030 buret reading of the titrating solution. Refill buret and turn switch to titrate position.

Add a small porcelain spoonful of silica, about 1/2 g, to the crucible. Weigh a 2 g sample of copper turnings and place in the crucible. Place cover on top.

Place crucible on pedestal, lift into the combustion tube and close.

Press the button on the automatic timer, preset for 4 minutes. After combustion, lower the pedestal and remove the crucible with tongs. Continue with other samples as above.

The samples will titrate automatically. Read the buret after each combustion and refill as necessary.

Appendix I (contd.)

Calculation:

Multiply buret reading by 0.05 to give percentage of sulfur in a 2 g sample.

Appendix II. Analytical procedure for the determination of oxygen in copper. (Technique used by Kennecott Copper Refinery)

DETERMINATION OF OXYGEN IN COPPER

Principle of Method:

Hydrogen is passed over heated copper drillings. The oxygen in the copper combines with hydrogen to form water vapor. The weight loss of the sample can then be converted to weight percent oxygen.

Reagents and Apparatus:

Hydrogen gas	Commercial grade
Tube furnace	
Alundum boats	5 in. by 3/4 in. by 7/16 in.
Collecting flask	500 ml round distilling flask with flat bottom
Rubber tubing and rubber stoppers	Amber latex tubing is used

Procedure:

Weigh carefully a sample of copper drillings of 20.02xx g. The drillings must be unoxidized and clean, about 1 mm maximum thickness. Carefully transfer the drillings to an alundum boat and place the boat in a combustion tube of a tube furnace. With rubber tubing connections, pass hydrogen through the tube and through a glass tube dipping into a flask of water. Pass 3 to 5 bubbles of hydrogen per second and allow a few minutes passage to sweep the air from the tube. Turn on heat and heat the sample to 850°C. Hold at this heat for about 1½ hours.

Cool to about 650°C and then remove tube from furnace and place in a cooling rack. Cooling may be speeded up by using a fan on the tube. It is advisable to reconnect the tube to the flask during cooling to make sure hydrogen continues to be passed over the sample.

Appendix II (contd.)

When the tube is cooled to room temperature, shut off the hydrogen and remove the boat from the tube. Carefully transfer the copper back to the balance pan and reweigh. By taking the 20.02xx original sample the deoxidized copper should weigh about 20.01+ making for convenience in weighing. Since sulfur is usually present in copper, the difference is taken to be sulfur plus oxygen.

Calculation:

Weight loss divided by initial weight is weight of sulfur and oxygen lost. Subtract weight percent of sulfur to get oxygen percent.

Appendix III. Analytical procedure for the determination of sulfur and oxygen in copper. (Technique used by Kennecott Copper Refinery)

DETERMINATION OF OXYGEN AND SULFUR IN ANODE COPPER

Principle of Method:

The principle is similar to the procedure given in Appendix II except any volatile impurities present in the copper would be volatilized and make the percentages wrong. The volatile impurities are contained in a combustion vessel and the sulfur is precipitated as CdS in a $CdCl_2$ solution.

Reagents and Apparatus:

Hydrogen gas	Commercial grade
Cadmium chloride solution	22 g $CdCl_2$, 480 ml NH_4OH made up to a liter with distilled water. 10 ml of this solution is diluted to 50 ml with water.
Iodine solution	1.4 g I_2 and 4 g KI per liter of water. Standardize against AsO_3. Arsenic value of iodine solution times 0.4278 equals sulfur value.
Sodium Thiosulfate solution	2.2 gpl
Hydrochloric Acid solution	One part HCl to 3 parts water.
Starch solution	Triturate 2.5 g starch with 10 ml of cold water. Pour gradually with constant stirring into 1 liter of boiling water. Boil 15 minutes with stirring. Cool and add 1.25 g of salicylic acid and stir until dissolved.

Appendix III (contd.)

Special quartz bulb	Available from Amersil Co., Hillside, New Jersey.
Collecting flask	Round 500 ml distilling flask with flat bottom.
Amber latex tubing	

Procedure:

A 10 g sample of copper drillings is placed in the quartz tube. This bulb consists of a sphere about 1 3/4 in. diam with a tube opening out from diametrically opposite sides. These tubes taper out slightly to about 3/4 in. and the total length of the bulb is about 8 in. A small pad of glass wool is placed in each end of the tube. The bulb is then carefully weighed. The bulb must not be charged with static electricity as this will affect the weight. It is a good idea to go over the tube with a grounded stranded wire before weighing.

The bulb is then clamped in a horizontal position and a hydrogen tube connected at one end and a tube leading to a sulfur flask connected to the other end. A small piece of cloth is wound around the discharge end of the bulb at the position of the glass wool and a small drip of water is used on the cloth. After sweeping any oxygen out of the flask a gas flame is lighted under the bulb and the bottom of the flask heated so that the copper is heated in the range of 750°-850°C. By means of baffling around the bulb the top is protected from the heat and the volatile impurities collect as a mirror on the top of the bulb and in the tube and glass wool.

The bulb is heated for about 2½ hours and then allowed to cool. When the bulb cools to room temp, disconnect and by means of a vacuum sweep the hydrogen out with air. Then reweigh, making sure that the bulb is not statically charged.

Appendix III (contd)

To the flask containing the CdS add the following: 120 ml of previously mixed and cooled 1:3 HCl to which 10 ml of accurately measured standard iodine solution has been added. Stir flask to make sure all sulfide is in solution. Titrate the excess iodine with the thiosulfate solution, using starch indicator. Standardize the thiosulfate against 10 ml iodine solution in the same volumes of reagents.

Calculation:

Establish ml thiosulfate soln equivalent to 10 ml iodine soln.
(ml thiosulfate for 10 ml iodine) - (ml thiosulfate for sample) = (ml thiosulfate equivalent to iodine consumed by sulfur in sample).

ml thiosulfate difference X 10/(ml thiosulfate for 10 ml iodine soln) X sulfur factor of iodine soln X 10 = percent sulfur.

Total weight loss X 10 - %S = %oxygen

Note:

Reactions of the CdS precipitate in preparation for titration are the following:

$CdS + 2HCl = H_2S + CdCl_2$

$H_2S + I_2 + 2HI + S$

Appendix IV. Analytical procedure for the determination of impurities in anode copper. (Technique used by Kennecott Copper Refinery)

DETERMINATION OF IMPURITIES IN ANODE COPPER USING THE SPECTROGRAPH

Principle of Method:

A sample of copper is burned in the spectrograph. All elements present in the sample give off light of certain wavelength when they are burned. These lines of light are recorded on film and the position and intensity of the lines compared to standard lines indicates the amount of each element present.

Equipment and Supplies:

Copper standards	Samples of anode in which the impurity level has been carefully determined by standard chemical methods. Range of impurities in standard should cover the range of impurities expected in sample.

1½ meter spectrograph

Procedure:

The samples of drillings or similar sized particles are weighed in triplicate. The samples are weighed to the nearest 0.05 g. Each sample is briquetted in a 1/2 in. mold at 16,000 pounds pressure. Standards are prepared in a similar manner. A 1/4 in. graphite rod with a flat end is mounted in the lower electrode holder and the pellet is laid on this rod. A graphite rod with a hemispherically shaped tip is placed in the upper electrode holder and the two electrodes set against the gap spacer. The gap spacer is then swung out of the way and the spark stand door is closed. The sample is then burned and additional samples are mounted and burned until the film is completed. The film is then placed in the densitometer-comparator unit and the transmission readings recorded for each line in each sample and standard. The

Appendix IV (contd.)

amount of impurity present is determined by finding the amount of transmittance on a transmittance versus impurity level curve. An average assay is determined by using the duplicate samples.

Details of the excitation conditions and film development are as follows:

Spectrograph	
Slit width	50 microns
Filter	No. 6 (17% transmission)
Electrodes	
Upper	Special high purity graphite nominal 1/4 in. with hemispherical tip.
Lower	One-half in. copper sample pellet supported by 1/4 in. graphite rod.
Electrode gap	3 mm
Electrical	
Initiator	Continuous
Discharge	Interrupted
Voltage	940 v
Amperage	2 amps
Inductance	Residual
Resistance	25 ohms
Capacitance	42 microfarads
Rotary gap pointer	90
Discharge type	Modified spark
Exposure time	45 seconds
Photographic	
Film type	Spectrum Analysis #1
Development	Two minutes in D-19
Stop bath	Fifteen seconds in 5% acetic acid.
Fixing	One minute in Kodak X-ray fixer.
Drying	Two minutes on infrared dryer.

Appendix V. Analytical procedure for determination of impurities in cathode copper. (technique used by Kennecott Copper Refinery)

DETERMINATION OF IMPURITIES IN CATHODE COPPER BY THE SPECTROGRAPH

Principle of Method:

Same as Appendix IV.

Equipment and Supplies:

Copper standards	Same requirement as Appendix IV.
1½ meter spectrograph	
Lathe	Small metal working lathe to prepare electrode rods.
Graphite cups	One in. diam of commercial graphite rod. Fifteen degree slope and approximately 1/2 in. thick.

Procedure:

A 1/2 g sample of drillings is roughly weighed and briquetted in a 1/4 in. mold at 8,000 pounds pressure. A high purity copper rod, 3 in. long and 0.220 in. diam, is machined on the lathe to a 45° tip. The rod is placed in the upper electrode holder and the briquetted sample is placed in graphite cup which is supported on a platform in the lower electrode holder. Each electrode is moved to the gap spacer and the pellet is centered to the rod. The gap spacer is swung out of the way and the spark stand door is closed. The sample is then arced. A standard is also arced on each film. The amount of impurities present is determined in the same way as Appendix IV.

Details of excitation and film development are as follows:

Appendix V. (contd)

<u>Spectrograph</u>

Slit width	50 microns
Filter	200 mesh screen #7 filter (12% transmission)

<u>Electrodes</u>

Upper	1/4 in. high purity copper rod with 45° tip.
Lower	Positive polarity. 1/2 g sample as 1/4 in. pellet on graphite cup.
Electrode gap	3 mm - maintained by manual adjustment.

<u>Electrical</u>

Initiator	Strike
Discharge	Continuous
Voltage	300 v
Amperage	10 amps
Inductance	Residual
Resistance	25 ohms
Capacitance	57 microfarads
Rotary gap pointer	90
Discharge type	Multisource d-c arc

<u>Exposure</u>

Pre-arc	45 seconds
Total time	100 seconds

<u>Photographic</u>

All conditions same as Appendix IV, except stop bath is 10 seconds longer.

Appendix VI. Spectrographic analysis of initial cathode copper.

Element	Concentration (parts per million)
O_2	60
Zn	10
Pb	7
Bi	1
Ni	10
Sn	10
Fe	14
S	17
As	1
Sb	3
Se	1
Te	1
Total impurities	134
Purity of copper	99.9866 %

Appendix VII. Calculation of the standard free energy of formation at 1400°K for the various oxides studied in this experiment.

The following calculations are intended to provide an approximate idea of which oxides could be present in copper at a temperature slightly above melting point of copper. These calculations were to give an indication of which elements could be removed from copper by oxidizing it. The calculations can be classified into three sections.

First, the basic equation for which the data were obtained from the Handbook of Chemistry and Physics.

Second, the equation which calculates the change in free energy in going from oxygen gas to 1 wt% oxygen dissolved in molten copper. This value was obtained from a paper by T. C. Wilder.

Finally the calculation of change in free energy from pure metal to 1 wt% of metal dissolved in molten copper. This calculation was carried out as follows:

$$M_{(s)} = \underline{M} \ (1 \text{ wt\% in Cu})$$

$$\Delta G^{\circ} = RT \ln \frac{(\gamma^{\circ} m)\ (M.W.\ Cu)}{(M.W._M)\ (100)}$$

Substituting in known values at 1400°K this equation becomes:

$$\Delta G^{\circ} = 6410 \log \frac{(\gamma^{\circ} m)\ (.635)}{(M.W._M)}$$

It was assumed that γ° was equal to 1. This would only be true for ideal solutions but it was used to provide a useful approximation of ΔG°.

Appendix VII (contd.)

Antimony

	1.	$2Sb_{(l)} + 3/2\ O_{2(g)} = Sb_2O_{3(l)}$	$\Delta G^o = -85{,}900$ cal.
	2.	$3\underline{O} = 3/2\ O_{2(g)}$	$\Delta G^o = +54{,}300$ cal.
	3.	$2\underline{Sb} = 2Sb_{(s)}$	$\Delta G^o = +36{,}200$ cal.
Eqs. 1+2+3		$2\underline{Sb} + 3\underline{O} = Sb_2O_{3(l)}$	$\Delta G^o = +\ 4{,}600$ cal.

Arsenic

	1.	$\frac{1}{2}As_{4(g)} + 3/2\ O_{2(g)} = \frac{1}{2}As_4O_{6(g)}$	$\Delta G^o = -90{,}300$ cal.
	2.	$3\underline{O} = 3/2\ O_{2(g)}$	$\Delta G^o = +54{,}300$ cal.
	3.	$2\underline{As} = \frac{1}{2}As_{4(g)}$	$\Delta G^o = +26{,}200$ cal.
Eqs. 1+2+3		$2\underline{As} + 3\underline{O} = \frac{1}{2}As_4O_{6(g)}$	$\Delta G^o = -\ 9{,}900$ cal.

Bismuth

	1.	$2Bi_{(l)} + 3/2\ O_{2(g)} = Bi_2O_{3(l)}$	$\Delta G^o = -48{,}300$ cal.
	2.	$3\underline{O} = 3/2\ O_{2(g)}$	$\Delta G^o = +54{,}300$ cal.
	3.	$2\underline{Bi} = 2Bi_{(l)}$	$\Delta G^o = +32{,}200$ cal.
Eqs. 1+2+3		$2\underline{Bi} + 3\underline{O} = Bi_2O_{3(l)}$	$\Delta G^o = +38{,}200$ cal.

Nickel

1.	$Ni_{(s)} + \frac{1}{2}O_{2(g)} = NiO_{(s)}$	$\Delta G^o = -26,500$ cal.
2.	$\underline{O} = \frac{1}{2}O_{2(g)}$	$\Delta G^o = +18,100$ cal.
3.	$\underline{Ni} = Ni_{(s)}$	$\Delta G^o = +12,600$ cal.
Eqs. 1+2+3	$\underline{Ni} + \underline{O} = NiO_{(s)}$	$\Delta G^o = +\ 4,200$ cal.

Cobalt

1.	$Co_{(s)} + \frac{1}{2}O_{2(g)} = CoO_{(s)}$	$\Delta G^o = -37,250$ cal.
2.	$\underline{O} = \frac{1}{2}O_{2(g)}$	$\Delta G^o = +18,100$ cal.
3.	$\underline{Co} = Co_{(s)}$	$\Delta G^o = +12,600$ cal.
Eqs. 1+2+3	$\underline{Co} + \underline{O} = CoO_{(s)}$	$\Delta G^o = -\ 6,550$ cal.

Iron

1.	$Fe_{(s)} + \frac{1}{2}O_{2(g)} = FeO_{(s)}$	$\Delta G^o = -41,150$ cal.
2.	$\underline{O} = \frac{1}{2}O_{2(g)}$	$\Delta G^o = +18,100$ cal.
3.	$\underline{Fe} = Fe_{(s)}$	$\Delta G^o = +12,400$ cal.
Eqs. 1+2+3	$\underline{Fe} + \underline{O} = FeO_{(s)}$	$\Delta G^o = -10,650$ cal.

Copper

1.	$2Cu_{(l)} + \frac{1}{2}O_{2(g)} = Cu_2O_{(s)}$	$\Delta G^o = -16,600$ cal.
2.	$\underline{O} = \frac{1}{2}O_{2(g)}$	$\Delta G^o = +18,100$ cal.
Eqs. 1+2	$2Cu_{(l)} + \underline{O} = Cu_2O_{(s)}$	$\Delta G^o = +\ 1,500$ cal.

Appendix VII (contd.)

Hence the order of stability of the oxides in molten copper at 1400°K is as follows:

		ΔG^o (cal.)
Most Stable	FeO	-10,650
	As_2O_3	- 9,900
	CoO	- 6,550
	Cu_2O	+ 1,500
	NiO	+ 4,200
	Sb_2O_3	+ 4,600
Least Stable	Bi_2O_3	+38,200

These calculations show that the three elements (Fe, As, Co) with a ΔG^o more positive than copper form oxides easily in copper. The three elements below copper do not form as stable an oxide as copper. Thus, these calculations show that Fe, As, and Co should form oxides in oxidized copper while Ni, Sb, and Bi probably do not form oxides in oxidized copper. These calculations, however, do not show whether the element will be removed from the oxidized copper as this depends on the solubility of the oxide in the molten copper.

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