

MIT Document Services

Room 14-0551
77 Massachusetts Avenue
Cambridge, MA 02139
ph: 617/253-5668 | fx: 617/253-1690
email: docs@mit.edu
<http://libraries.mit.edu/docs>

DISCLAIMER OF QUALITY

Due to the condition of the original material, there are unavoidable flaws in this reproduction. We have made every effort to provide you with the best copy available. If you are dissatisfied with this product and find it unusable, please contact Document Services as soon as possible.

Thank you.

669.08
Thesis



AN INVESTIGATION OF THE CATALYTIC EFFECT
OF FERRIC OXIDE ON THE SULPHATING OF METALLIC OXIDES.

Submitted by
Adin A. Brown.



AN INVESTIGATION OF THE CATALYTIC ACTION OF FERRIC OXIDE
IN THE SULPHATING OF METALLIC OXIDES

Purpose:

In the sulfating of metallic oxides in an atmosphere of sulfur dioxide and air, the presence of ferric oxide accelerates the oxidation of SO_2 and hence aids in the establishment of a high concentration of SO_3 . The formation of sulfates from the oxides present is increased by this SO_3 concentration. This thesis is an investigation of this effect of ferric oxide when present in varying proportions with the oxide to be sulphated, and a determination of the amounts of oxides rendered soluble in these different mixtures. The effect of varying the time allowed for the ferric oxide to exert its catalytic influence is also investigated.

Previous Work

Because in most roasting operations, it is the object of the roast to eliminate sulfur as completely as possible, and therefore to prevent the formation of sulfates from the oxides formed in the roast and to decompose those which are formed, much has been determined concerning the decomposition of metallic sulfates in roasting, and but very little material is available which concerns their formation. This is due to the fact that only recently has much attention been given to the sulfating and leaching of low grade sulfide copper ores to replace the former methods of concentrating by flotation and subsequent smelting.

Much work of practical interest in the sulfating of copper oxides such as can be found in patented sulfating processes, is available.

M.T. Coolbaugh U.S. Pat. 11315761

This patent covers the process of treating sulfide minerals and concentrates, comprising roasting the ores to convert to oxides and subsequent treating the resultant oxides between 450°C and 800°C in the presence of sulfurous gases to convert the oxides into sulfates. This process begins in a roasting furnace where the sulfide ore or matte is first charged and subjected to an oxidizing roast. The discharge from this furnace may be AgCl, Au, Ag, CuO, PbO, ZnO, FeO, or Fe₂O₃. The next step is the sulfating roast

of these products in presence of SO_2 . The discharge from this furnace consists of Au, Ag, and the sulfates of Cu, Ag, Pb, Zn, and Fe_2O_3 . The sulfates are leached out and the other products are smelted and recovered.

Aarts and Aarts Brit. Pat. 119867

The inventors of this patent process seem to have been the first to include a recognition of the effect of the presence of iron in sulfating. They name three conditions to be decided upon before subjecting an ore to the sulfating treatment. 1.) The proportion of S in the ore. 2.) The proportion of catalyst. 3.) The composition of the ore in general, impurities etc. They also mention the presence of sufficient O in the sulfurous gases, for the oxidation of the SO_2 . The temperature stated is below that at which the sulfate would be decomposed but above that at which the catalytic effect of the iron oxide on the formation of SO_3 from SO_2 and O becomes of practical significance. It is evident that the inventors of this process are familiar at least to some extent with the action of ferric oxide as investigated in this thesis but there seems to be no public record of their work. The process in the main is similar to that of Coolbaugh. They also mention the possibility of differential sulfating, stating that it is possible for the roast to be stopped at such a temperature that sulfates of only certain metals are present.

Other patents of earlier date, while not of as great interest to the investigation carried on in this thesis, give perhaps a good idea of some of the previous attention given to the sulphating process in general.

C.C. Westby U.S. Pat. 1,266,731 and 1,266,732

The first is a process where metalliferous fines which may contain Cu, are freed from fine particles and treated with sulfurous gases in a tower; while the top of the ore column is sprayed with water or spent solvent obtained later in the process. The spray is in such quantities as not to fill the interstices between the particles nor to clog the flow of gases. The liquid leaches values from the ore and absorbs the sulfurous gases.

The other patent is another method for carrying out the same general process. Metalliferous fines, as oxidized Cu, are arranged in series of low heaps in staggered positions upon supports within a closed sulfating chamber. These heaps are vibrated while they are treated with steam SO_2 and air and simultaneously leached with water or other solvent. An apparatus for carrying out this operation is described, but has no place in this discussion.

H.B. Hovland France Pat. 481,815.

This patent covers the treating of minerals under pressure to convert them into sulfates in the dry state.

Another patent of Hovland's is concerned with the sulfating of Cu ores by treating them with an oxidizing agent in the presence of available sulfur. He states the conditions suitable for the dry process to be : a temperature of 500 degrees Centigrade, pressure 100 pounds per square inch. He makes reservation that the pressure at intervals may be reduced to or below atmospheric pressure to facilitate the decomposition of $Fe_2(SO_4)_3$ which he evidently assumes is formed under the above conditions.

Hovland has also designed some very complicated apparatus for the carrying out of this process, among which is a wedge type of furnace into which air mixed with SO_2 is introduced under pressure.

Several German patents closely allied with those of the Aarts and the one of Coolbaugh, give only information of the same type as covered in the patents previously described.

In an article for the Metallurgical and Chemical Engineering Journal of April 1915 B. Dudley, Jr. has given the most complete reference obtainable on the formation and decomposition of sulfates during roasting. He states that at a given temperature, a definite concentration of sulfur trioxide must be maintained in the gaseous phase in contact with the metal sulfate and oxide, in order to maintain equilibrium; or in other words, that the dissociation

tension of a sulfate at a given temperature is constant. The dissociation of a sulfate increases with the temperature. From this fact it follows that, if a metal sulfate is held at a constant temperature in a space wherein the sulfur trioxide concentration is less than the equilibrium concentration for that temperature, the sulfate will undergo dissociation. The converse is also true that, if a metal sulfate is held at a constant temperature in a space wherein the sulfur trioxide concentration is greater than the equilibrium concentration that corresponds to the dissociation tension of the sulfate for that temperature, the oxide will be sulfatized.

An important point to be considered in connection with the sulfatizing of a metallic oxide is that of reaction velocity, which determines the length of time required for a mixture of gases to react and produce equilibrium conditions. The time required, of course, depends upon the concentration of the reacting substances and upon the temperature. The effect of temperature is to accelerate the reaction up to the point where decomposition of the product begins. A factor of greater importance than the temperature is the effect of catalysts upon the reaction rate. It has been found that under given conditions of temperature, the reaction will proceed to equilibrium conditions at a greatly accelerated rate in the presence a catalyzer such as ferric oxide. The catalyst does not

alter the conditions of equilibrium, since these are determined by the temperature and the partial pressures of the reacting gases; and in general the catalyst has an equal effect upon the reaction velocity whether the direction of the reaction is toward the formation of sulfur trioxide or toward its decomposition. Owing to the low dissociation tension of ferric sulfate it is natural to believe that this will be the first sulfate to form. Since in the process of sulfating, ferric oxide is usually present in considerable amounts, it is easy to conceive of this being the first sulfate to form. With increasing temperatures the dissociation tension of ferric sulfate increases much more rapidly than that of other sulfates. Consequently although it may be the first to form ferric sulfate will in most cases suffer decomposition at lower temperatures than the other sulfates.

The Effect of the Reaction Velocity

The rate at which a sulfate will be decomposed or formed will increase with increasing temperature, with increasing difference between the partial pressure of the sulfur trioxide present, and the dissociation tension of the sulfate, and with increase in the rate of stirring. The velocity of reaction is also dependent to a large extent upon the nature and depth of the separating surface between the reacting phases.

H.O.Hofman and W.Wanjukow conducted an investigation of the decomposition of metallic sulfates at elevated temperatures in a current of dry air. They determined the decomposition temperatures of some of the common sulfates. Copper sulfate was found to start decomposing at 341 degrees centigrade. It decomposed slowly up to 670 degrees when the action became more vigorous. At this temperature the normal cupric sulfate, CuSO_4 , had been entirely altered to the basic $2\text{CuO} \cdot \text{SO}_3$. At 805 degrees, there remained only a trace of SO_3 in the roasted material.

Previous Theses

In a previous thesis conducted by Turner and Bugbee, the best temperature for the formation of CuSO_4 from the chemically pure CuO in an atmosphere of sulfur dioxide and air was investigated. They found that the maximum amount of CuO was converted into the normal cupric sulfate of copper at a temperature of 500 degrees centigrade.

Nash in a subsequent thesis taking up the work of the study of sulfating, found ~~that~~ the best temperature for the formation of copper sulfate from a mixture of 10% CuO and 90% Fe_2O_3 in an atmosphere of SO_2 and air to be 400 degrees centigrade. At this temperature, he ran a series of tests on varied percentage mixtures of CuO and Fe_2O_3 to study the effect of Fe_2O_3 on the amount of CuO which was converted

into CuSO_4 . His results show that the amount of CuO converted into CuSO_4 is proportional to the percentage of catalyzer, Fe_2O_3 in the charge. It has been the object of this thesis to run a similar test to that run by Nash and to determine whether or not the results obtained by him could be duplicated. The results of this thesis have proven the affirmative.

In both of these theses, tests similar to those on copper oxide, with the exception of the CuO , Fe_2O_3 series have been conducted with ZnO . As this thesis has dealt only with the study of sulfatizing CuO , the results with ZnO have not been included with this report.

INVESTIGATIONS CARRIED ON IN THIS THESIS

In order to study the catalytic effect of Ferric oxide, on the sulfating of copper oxide, roasts were carried on in small silica tube electric resistance furnaces. Ferric oxide mixed in varying proportions with the oxide to be sulfated, was introduced into the furnaces in small porcelain boats and subjected to one hour or two hour roasts in an atmosphere of sulfur dioxide and air. At the end of the specified time, the boats were removed from the furnaces and their contents were leached with hot water. The resultant solution was tested for Cu, Fe, and SO₄.

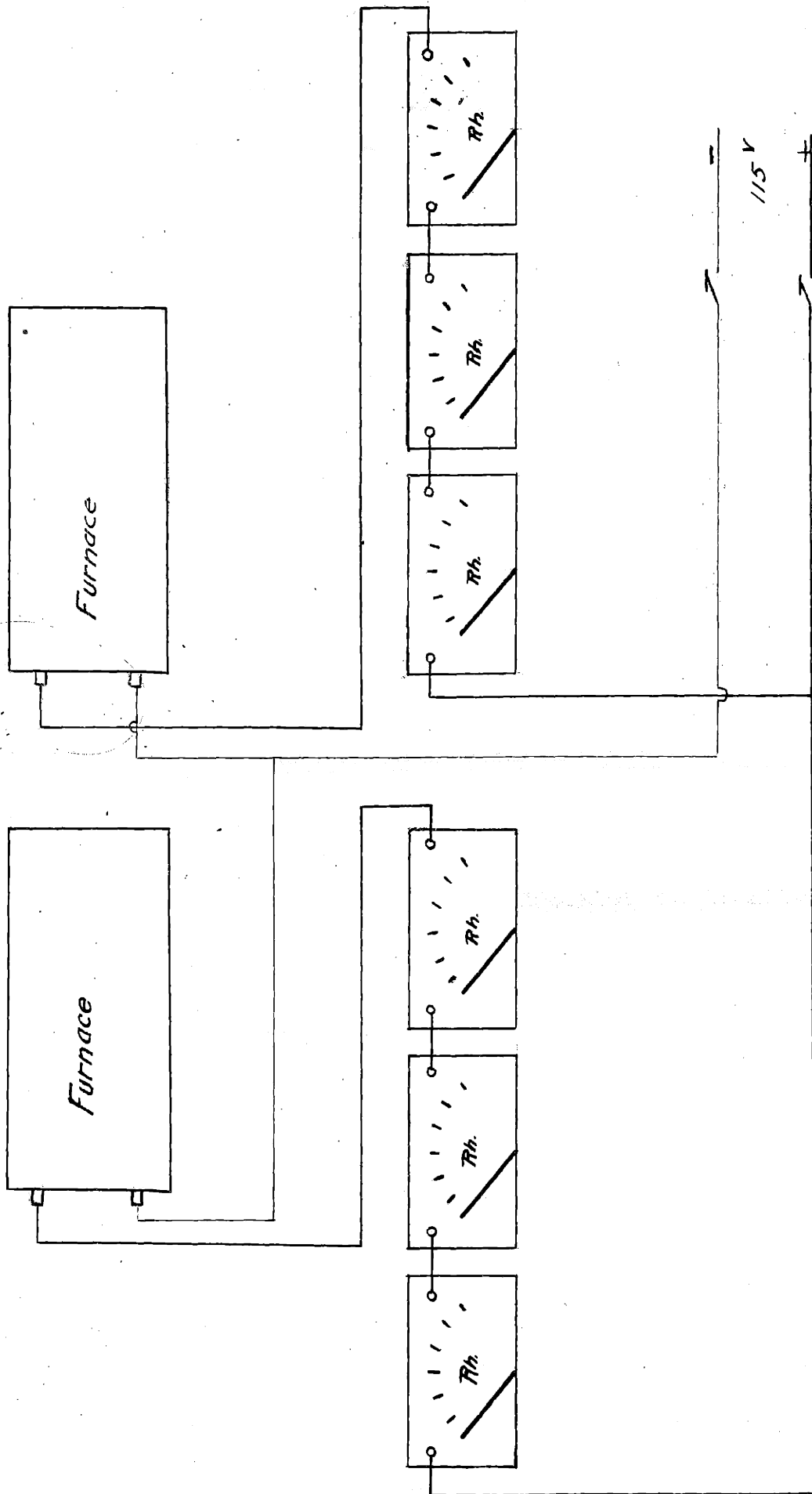
Apparatus

The furnace used for heating was an electric resistance tube-furnace. The heating tube was unglazed quartz material. The diameter of one of the tubes was 1 inch and of the other 1.75 inches. Tubes were wound with wire coils of high resistance wire. The heating tube is enclosed in a fire clay tube surrounded by calcined magnesia which is all inclosed in a galvanized iron cylinder. The whole is bolted on to a heavy piece of asbestos board which forms the foundation. The tube holds a porcelain boat about 2.75 inches long by .37 inches wide by .12 inches deep, which contains the material to be roasted. The ends of the furnace tube are sealed with asbestos with a small hole in each end in which a glass tube is inserted to provide for a steady current of gas over the charge. Thru

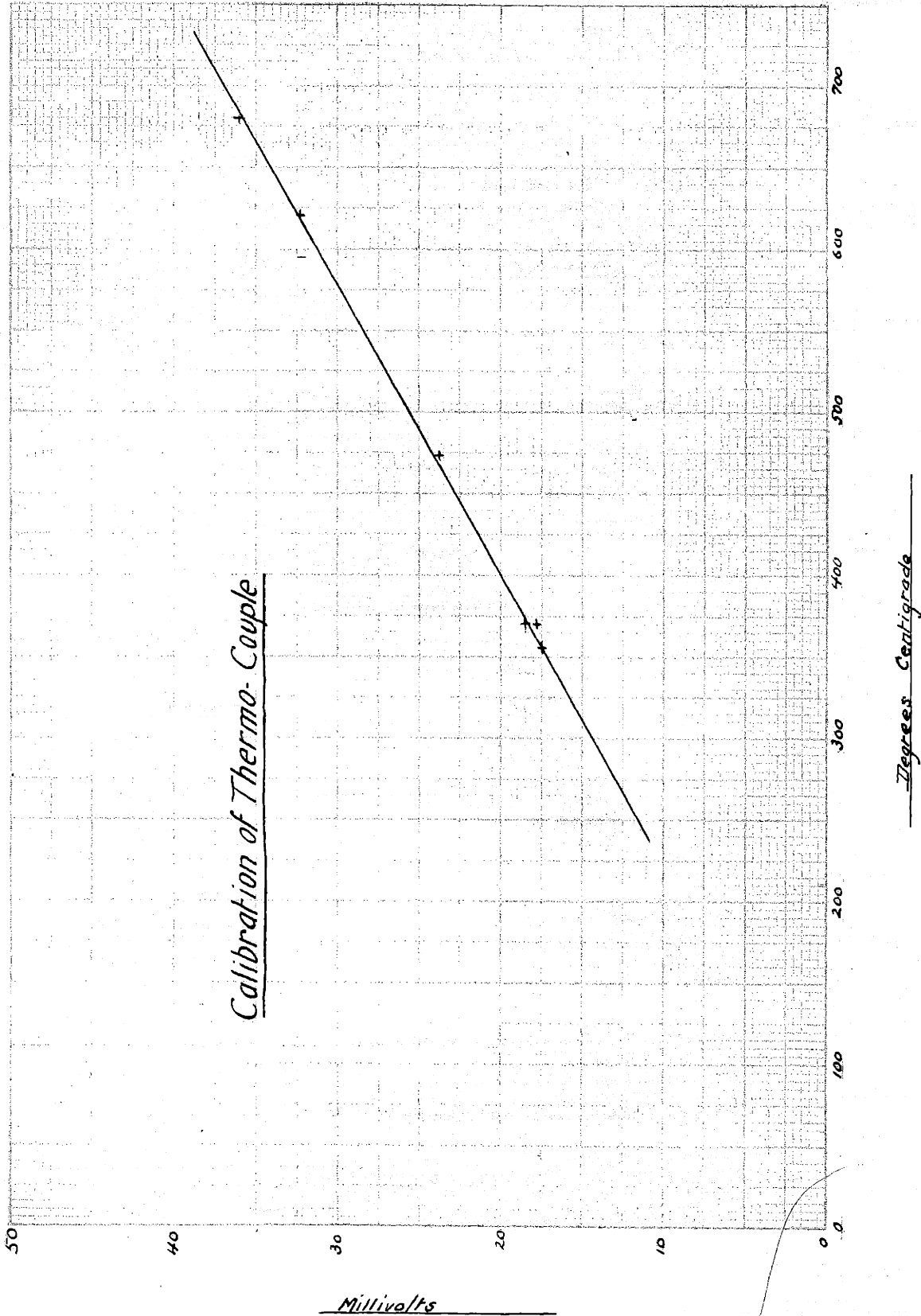
the asbestos plug in one end of the furnace tube, is introduced a small silica tube containing an iron-constantan thermo couple which is held in place directly over the charge. This is connected outside with a potentiometer calibrated by means of a direct reading potentiometer. The resistance coils of the furnace are connected to 115^V d.c. mains thru three rheostats for controlling the heat of the furnace.

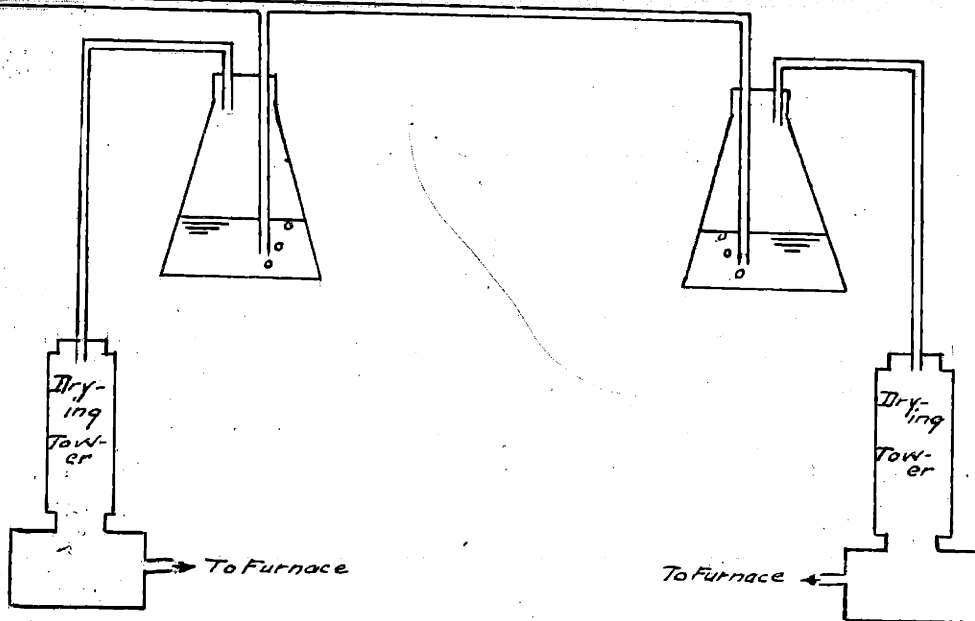
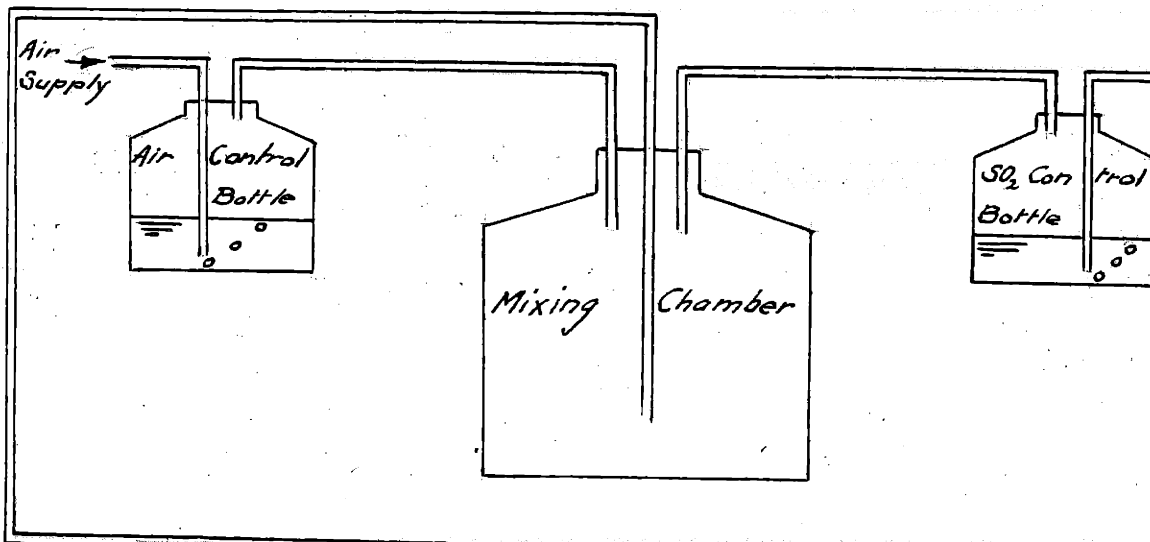
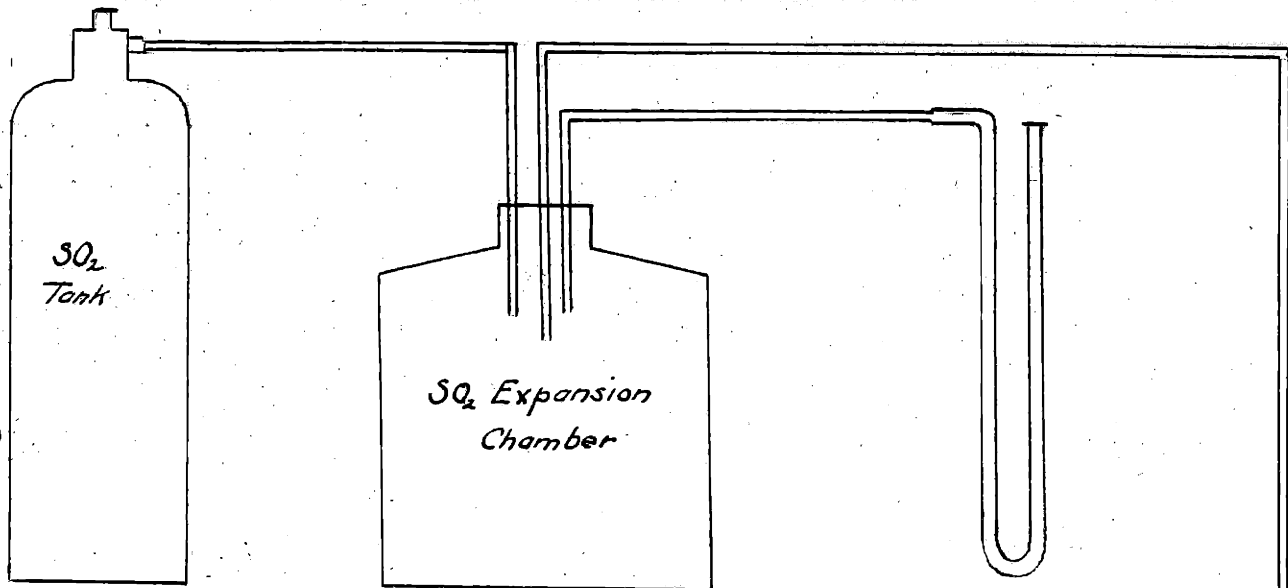
The gases for the roast were SO₂ and air. The SO₂ was led from an ordinary gas storage tank into an expansion chamber consisting of a large empty acid bottle leading from which are two glass tubes. One of the tubes leads to a barometer tube in which the height of the water column was kept constant during the entire roasting operation. The other, leads to a control bottle into which the SO₂ supply is regulated by a stop-cock. The SO₂ is measured by bubbling it under an inch head of water. Sixty bubbles per minute passed thru this bottle to each of the furnaces. Sixty bubbles per minute equal 1.4 liters per hour. From this bottle the SO₂ is led to a mixing chamber where a measured amount of air is introduced and mixed with it. The mixture passes out of the mixing bottle thru a tube containing a T-joint the opposite ends of which lead to control bottles for the two furnaces. The same number of gas bubbles are led to each furnace every hour. From these bottles the gas mixture passes thru calcium chloride drying towers and

thence to the furnaces. The amount of air used was measured by a gas meter and due to the bellows in the meter was fed in pulsations to the air control bottle. Although the number of bubbles per minute were kept at approximately the same as those Nash allowed to go to each furnace per minute, the meter only indicated .1 cu. ft. per hour or 2.83 liters which is about one half of that calculated by Nash from the calibration of Turner and Bugbee. It may be that the amount of air allowed to pass the control bottle during the two runs that the meter was connected was less than that which was allowed to pass in the other runs, due to the difficulty of measuring or estimating the number of bubbles when they were fed in pulsations. However, the amount in the other runs was very close to the same as used by Nash as the same bubbling effect was observed as was used by him.



REPRODUCTION OF THIS DOCUMENT IS PROHIBITED





Procedure

Three gram charges of varying percentages of the chemically pure oxides CuO and Fe_2O_3 in porcelain boats were inserted in the furnace tubes under the thermo couples after the furnaces had been brought up to a temperature of 400 degrees centigrade. A current of SO_2 and air measured and cleaned and dried was passed over the charge continually during the roast. The roast was continued for one hour intervals and two hour intervals. At the end of the specified time, the the boat was removed from the furnace immediately and allowed to cool. When cool it was placed in a beaker containing 400 c.c. of water and then boiled for ten minutes when it was removed from the hot plate and filtered. The solution was made up to 500 c.c. and tested for Cu, Fe, and SO_4 .

Analysis for Cu

50 c.c. of the solution was measured in a pipette. 3c.c. of sulfuric acid was added to the solution in a beaker, and the beaker transferred to a hot plate. 12c.c. of saturated hypo was added after the solution became hot. The n it was boiled until the solution cleared up; when it was filtered. The precipitate was placed with the filter paper in a porcelain crucible and the paper burned off. The residue was taken up in nitric acid, neutralized with ammonia, and the ammonia boiled off. Then 6 c.c. of acetic acid were added

and the solution boiled again to dissolve all the copper. Then the solution was diluted to about 200 c.c. and titrated with standardized hypo solution (1c.c. equals 1% for 1/2 gm. sample) using iodo-starch indicator.

Analysis for Fe

50 c.c. of the of the solution to be tested was measured by a pipette into a beaker. To the beaker was added 3 c.c. of HCl and about 2 gms. of pure granulated Pb. The solution was then boiled until all the copper was precipitated and all the iron was reduced. Then the solution was titrated with standard Bi-chromate solution (1c.c. equals 1% for 1/2 gm. sample) with potassium ferri-cyanide as indicator.

Analysis for SO₄

50c.c. of the solution ~~were~~ measured into a beaker to which 3c.c. of HCl ~~were~~ added. The solution was placed on the hot plate and when hot, 10 c.c. of BaCl₂ solution ~~were~~ added. The solution was boiled until the precipitate settled. Then it was filtered, the precipitate on the filter was ignited and weighed as BaSO₄. The SO₄ was calculated from the relation 1 gm. BaSO₄ gives .412 gms. SO₄.

TABLE OF RESULTS

1-Hour Series

Furnace	% CuO	% Fe ₂ O ₃	% Cu ext.	% Fe ext.	Cu/SO ₄
#1	10	90	60	0.00	.386
* #2	10	90	90.6	2.4	.238
#2	20	80	62.5	0.00	.552
* #2	20	80	75.5	0.00	.362
* #2	30	70	50.1	0.00	.474
#1	30	70	21.9	0.00	.620
* #2	40	60	21.4	0.00	.686
#2	40	60	16.8	0.00	.710
* #2	50	50	16.2	0.00	.530
* #2	60	40	14.8	0.00	.560
#2	60	40	5.45	0.00	.720
* #2	70	30	9.68	0.00	.557
#2	80	20	5.50	0.00	.580
* #2	80	20	7.05	0.00	.695
#1	90	10	3.65	0.00	1.000
* #2	90	10	9.2	0.00	.790

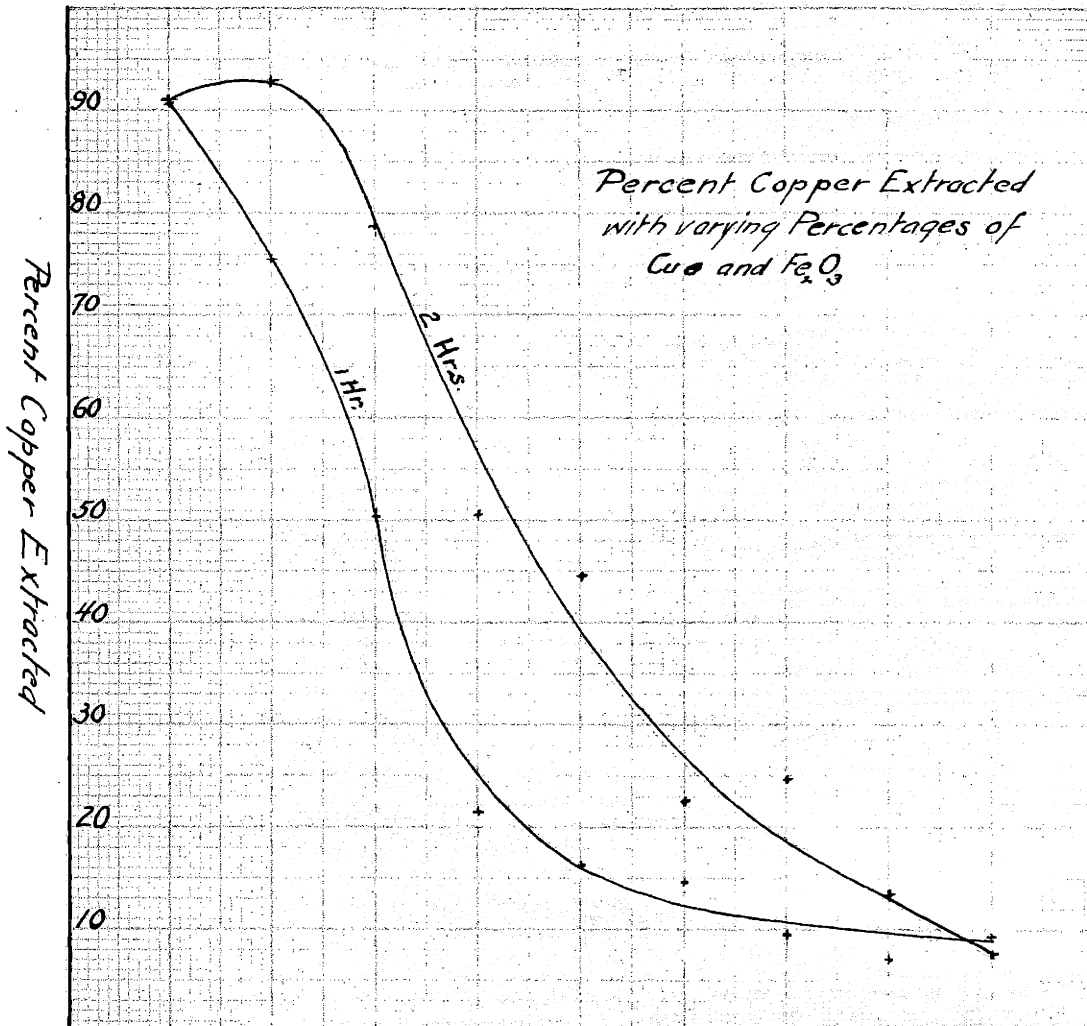
The lines marked with(*) are used on plot as most representative.

The runs made in furnace number one give poorer extractions as shown. Also the runs in number two when connected and run together with number one are lower than those runs in which number two was run alone. This may be accounted for by better gas and temperature control when only one furnace was used and a new and better potentiometer connected.

2-Hour Series

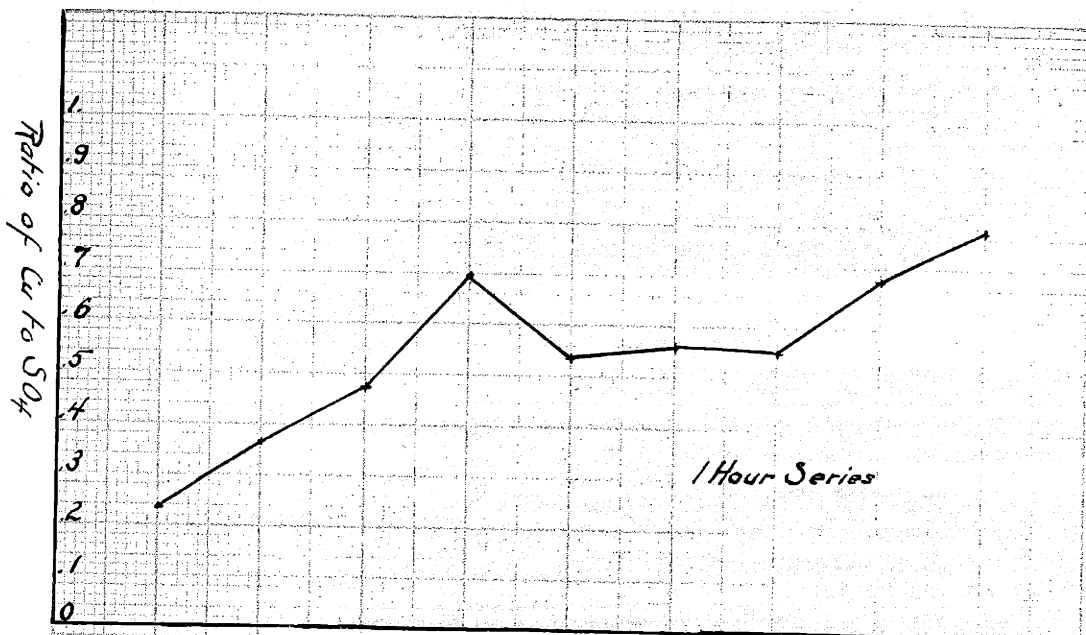
Furnace	% CuO	% Fe ₂ O ₃	% Cu ext.	% Fe ext.	Cu/SO ₄
#2	10	90	90.9	1.3	.320
#2	20	80	93	.5	.470
#2	30	70	78.8	0.00	.582
#2	40	60	50.5	0.00	.690
#2	50	50	44.3	0.00	.730
#2	60	40	22.4	0.00	.740
#2	70	30	24.8	0.00	.750
#2	80	20	13.3	0.00	.660
#2	90	10	7.5%	0.00	.700

Theoretical ratio of Cu/SO₄ equals .663



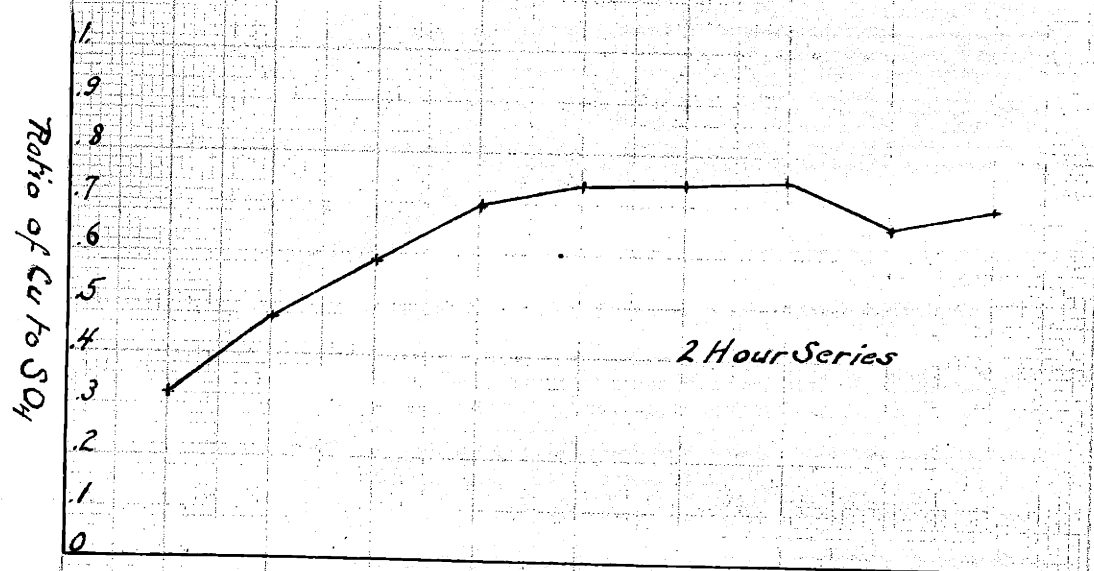
CuO	10	20	30	40	50	60	70	80	90
Fe ₂ O ₃	90	80	70	60	50	40	30	20	10

ANALYTICAL CHEMISTRY SOCIETY, CAMBRIDGE



CuO	10	20	30	40	50	60	70	80	90
Fe_2O_3	90	80	70	60	50	40	30	20	10

Ratio of Cu to SO_4 with varying percentages of CuO and Fe_2O_3



CuO	10	20	30	40	50	60	70	80	90
Fe_2O_3	90	80	70	60	50	40	30	20	10

RESEARCH COOPERATIVE SOCIETY, CAMBRIDGE

Discussion, Conclusions, and Suggestions

From the observed data, it is seen that the extractions of copper from the material roasted in furnace number 1 are in every case poorer than those obtained by the roasting of the same mixture in furnace number two. The temperatures were the same and the amount of gas led to each during the roasts were also the same. Attention was first called to this when in not securing as high an extraction of the copper from the mixture of 10% CuO and 90% Fe₂O₃, as was obtained in the previous thesis, the mixture was re-run, by accident more than design, in the other furnace. The increase in extraction from 60% in furnace 1, to 90% in furnace 2, was supplemented by the increase in extraction of the 30% CuO, 70% Fe₂O₃, run from 21.9% in furnace 1 to 50.1% in furnace number 2. Number 1 furnace was then abandoned for the remainder of the tests and the series was completed by making the rest of the runs in the second furnace.

The poorer extraction in furnace #1 may or may not be accounted for by the fact that the diameter of its tube was one inch while that of furnace number 2 was one and three quarter inches. The velocity of the same volume of gases thru these furnaces would be inversely as the square of their diameters which would be $V_1 : V_2$ as 49 : 16 or approximately 3 : 1. Suppose that 1/3 of the amount of

the SO_3 which is formed in furnace number 2 is formed in furnace number 1. For every unit volume of SO_3 that is formed there is a contraction of $\frac{3}{2}$ units of volume to one unit volume or in other words the final product has $\frac{2}{3}$ the volume of the original factors due to the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$. This reaction will cause a retardation of the velocity. And if the amount of SO_3 formed depends to even a small extent upon the time of contact the furnace having the larger diameter has not only a longer time of contact due to its greater cross section, but the advantage also of the contraction and hence velocity retardation due to the formation of SO_3 in excess of that formed in the smaller furnace.

Some of the runs in the one hour series which took place in the same furnace, are variable in the amount of the copper extracted. In every case the poorer extraction was when the two furnaces were run in conjunction and the temperature was controlled by a potentiometer which was very unsatisfactory. The runs marked with (*) show those runs which are the most representative and which were conducted with #2 furnace alone and with a reasonably sensitive potentiometer.

The plot of the one hour series bears out the principle which was determined by Nash; that the amount of Cu

converted into sulfate by the roast is proportional to the amount of catalyst (Fe_2O_3) in the charge.

It may be observed from the results that there is sulfate present in excess of that necessary to form the normal or basic sulfates with the Cu and Fe found in the solutions. This excess sulfate may be considered present as free acid. This was not tested for as the acid was not present in sufficient amounts to be determined by ordinary methods. The average weight of BaSO_4 precipitated from the whole solution in any of these runs would be about 2 gms. The SO_4 from this would equal $2 \times .412$ or .824 gms. of SO_4 . The normality of a sulfuric acid solution containing this amount of SO_4 in 500 c.c. of solution would be .034 normal. This could be tested for by distilling after the addition of NaCl and catching the distillate in standard .1 normal NaOH which could be titrated back with standard acid. However, this was not considered in this thesis, as the time was too limited.

From the curve showing the ratio of Cu/SO_4 , it can be seen that the amount of free acid present is greatest in the cases where the amount of Fe_2O_3 of the charge was also high. This is what one would naturally expect in view of the catalytic effect of ferric oxide on the formation of sulfur trioxide from sulfur dioxide and air.

The two-hour curve of copper extractions shows that the advantage of increasing the time of roast from one to two hours is of significant value only with mixtures of over 70% ferric oxide. The extractions increase with high percentage of ferric oxide in the mixtures but where the ferric oxide is present in amounts of less than 30% the increase in extraction by prolonging the roast is negligible.

The Cu/SO_4 curve for the two hour roast is much smoother than that for the one hour roast. This may be due to the fact that there was a longer time allowed for the reacting gases to attain their equilibrium values for the temperature of 400 degrees centigrade.

From the references on the subject of sulfating, it seems evident that the effect of temperature on the amount of copper sulfate formed by this roast is of less significance than the concentration of the SO_3 and the dissociation tension of the sulfate formed. If the concentration of the SO_3 is great enough, it seems very probable that the sulfate can be formed at any temperature below 670 degrees centigrade which was shown by Hofman to be the temperature at which the decomposition of CuSO_4 is very rapid. This SO_3 concentration can be increased by allowing only a very small amount of air to enter the furnace in excess of that which is necessary to react with

the SO_2 present to form SO_3 , and by decreasing the velocity of the gases thru the furnace so that the Fe_2O_3 will have more time to get in its catalytic effect. Another way would be to generate the SO_3 in a separate apparatus and to lead it into the roasting chamber as SO_3 at lower temperatures than 400 degrees centigrade since the dissociation tension of the sulfate is lower at lower temperatures.

At the first part of the roast, both in this investigation and in practice, there is very little sulfate, (at the beginning of the roast) so that at the first part of the roast it will require only a small amount of SO_3 to overcome the tendency of the sulfate to dissociate. Toward the end of the roast, the sulfate is present in much larger quantities and if the SO_3 concentration is increased at this point, it is possible that more of the sulfate will be formed than if it were kept at the same low figure during the entire roast as it is at the beginning.

INDEX TO PAGES

1. Purpose of the thesis.
2. Previous work in sulfating.
10. Investigations carried on in this thesis.
13. Diagram of electrical connections.
14. Calibration curve of thermo couple.
15. Diagram showing gas connections.
16. Procedure.
18. Table of results for one hour series.
19. Table of results for two hour series.
20. Curve of copper extraction. One hour and two hour series.
21. Curve showing ratios of Cu/SO_4 .
22. Discussion, conclusions and suggestions.