THE RAPID DIFFERENTIAL REDUCTION AND LEACHING OF CALCINES

CONTAINING COPPER FERRITES

by

Charles Louis Labeka

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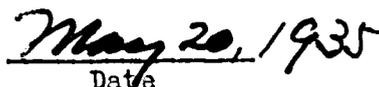
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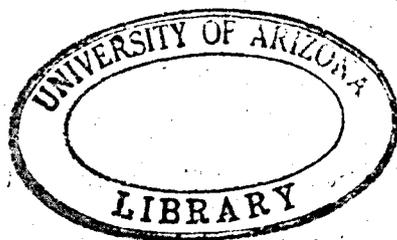
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C O N T E N T S

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CHAPTER I.---INTRODUCTION

It has been demonstrated that the "flash roasting" of
copper concentrates results in the production of considerable
amounts of copper ferrites in the calcine. Although the "flash
roasting" of copper concentrates is still in the experimental
stage, it is believed that the experimental results obtained
justify a further study of copper ferrites with the view of
recovering their contained copper in the event that "flash roasting"
becomes of economic importance.

The results of experimental work undertaken with the view
of preventing the formation of copper ferrites in the "flash
roasting" of copper concentrates indicates that it is almost
impossible to roast a concentrate containing chalcopyrite or bornite
and not produce copper ferrites, since these ferrites are probably
formed below $820^{o}C$.

Thompson[1] states that copper ferrite is known to exist in three
crystalline forms, namely: cubic cupric ferrite, tetragonal cupric
ferrite, and hexagonal cuprous ferrite, and states further that
each of these forms possess certain characteristic properties and
can be converted into one of the other forms by heating. Thompson
also experimented with the solubility of copper ferrites employing
nitric, hydrochloric, and sulfuric acids and found that there was
little hope of recovering the contained copper by the use of solvents

commonly used for leaching copper from its ores.

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[1] Thompson, A. J., A study of the Preparation and Properties of the Ferrites of Copper; Thesis, University of Arizona, 1933; 38 pages.
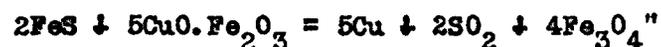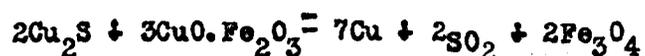
Butler[2] experimented with the formation of metallic copper by heating a copper ferrite, contained in a boat, with a metallic sulfide or sulfide ore and gives the conclusions which follow.

"The results .... demonstrate that cupric ferrite may be caused to undergo several different reactions which effect liberation of the copper content but leave the iron as an oxide. The copper may be subsequently separated from the iron oxide by leaching it out with a dilute, acid solution of ferric sulfate.

".... heating with a metallic sulfide or sulfide ore is a possible method for differential reduction of the copper in copper ferrite, leaving the iron present as an oxide; .. the extent to which the reaction proceeds is directly dependent upon the temperature at which it is allowed to occur, it being more nearly complete, the higher the temperature.

"Reduction occurs even when the mixture of sulfide and ferrite is fused, but the retention of copper, either metallic or combined, in the iron-rich slag prevents adequate separation of the copper and iron by differences in specific gravity alone.

"Typical equations established for the reactions are as follows:

$$2Cu_2S + 3CuO \cdot Fe_2O_3 = 7Cu + 2SO_2 + 2Fe_3O_4$$

$$2CuFeS_2 + 9CuO \cdot Fe_2O_3 = 11Cu + 4SO_2 + 4Fe_3O_4 + 4Fe_2O_3$$

$$2FeS + 5CuO \cdot Fe_2O_3 = 5Cu + 2SO_2 + 4Fe_3O_4"$$

Butler also experimented with the reduction of copper ferrite by carbon monoxide and presented the conclusions which follow.

".... the copper in cupric ferrite may be reduced to metallic copper by passing a gaseous mixture of carbon monoxide and carbon dioxide over the heated material. If the carbon monoxide concentration is less than some figure slightly above 33 per cent, the reaction probably proceeds according to the following equation:

$$3CuO.Fe_2O_3 + 4CO = 3Cu + 4CO_2 + 2Fe_3O_4$$

"If however, the concentration is above this figure but less than a value somewhat below 75 per cent, the iron undergoes a further change in valence, and the reaction is assumed thus:

$$CuO.Fe_2O_3 + 2CO = Cu + 2CO_2 + 2FeO$$

"Concentrations of carbon monoxide above this latter value cause reduction to the metallic state of both copper and iron.

"It is .. apparent that by controlling the composition of the gas mixture, copper may be reduced to the metal while iron remains as an oxide.

The ways for decomposition of copper ferrite herein described suggest methods for treatment on a larger scale; such applications, however, would offer technical difficulties, as to the nature of which this investigation offers only hints."

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[2] Butler, G. M. Jr., Methods For the Decomposition of Copper Ferrite; Thesis, University of Arizona, 1934; 31 pages.

The object of the experimental work described in this paper is to obtain the results of a rapid decomposition of the ferrites produced in "flash roasting" by dropping the calcine in a furnace

similar to a flash roasting furnace while maintaining a reducing atmosphere. A further object of the experimental work presented is to attempt a differential reduction of the copper ferrites so that the copper can be recovered by leaching methods while the iron remains insoluble in the residue.

CHAPTER II.--APPARATUS, MATERIALS USED, AND ANALYTICAL METHODS

<u>APPARATUS</u>

Two furnaces were constructed for the experimental work differing slightly in design.

The first employed a sillimanite tube 30 inches high and $1\frac{3}{4}$ inches internal diameter as the reducing chamber. This furnace was discarded after the initial experimental work showed that a tube at least 60 inches high was necessary for rapid reduction.

The second furnace was then built and proved satisfactory.

Figure 1 presents a diagrammatical drawing of the second furnace including accessory apparatus and figure 2 shows the method of wiring the furnace.

A sillimanite tube (A) 60 inches high and 2 inches internal diameter was used as the reducing chamber. The outside of this tube was wound with four sections of chromel wire; each of the two middle sections had three turns per inch and were 15 feet long and the two outside sections were four turns per inch and 11 feet long. The resistance of the wire was 0.25 ohm per foot. Each coil was embedded in alundum cement and a variable resistance in series controlled the amount of current used. To prevent undue heat loss, infusorial earth (B) was packed around the tube approximately four inches thick. The bottom of the sillimanite tube was attached to an iron base plate (C) one inch thick. A hole was cut in the center of the plate just large enough to admit the sillimanite tube which extended through to the bottom. The bottom of this hole was enlarged and threaded for a distance of $\frac{3}{4}$ inch from the bottom to admit a pipe, 2 inches in diameter. The annular space between this
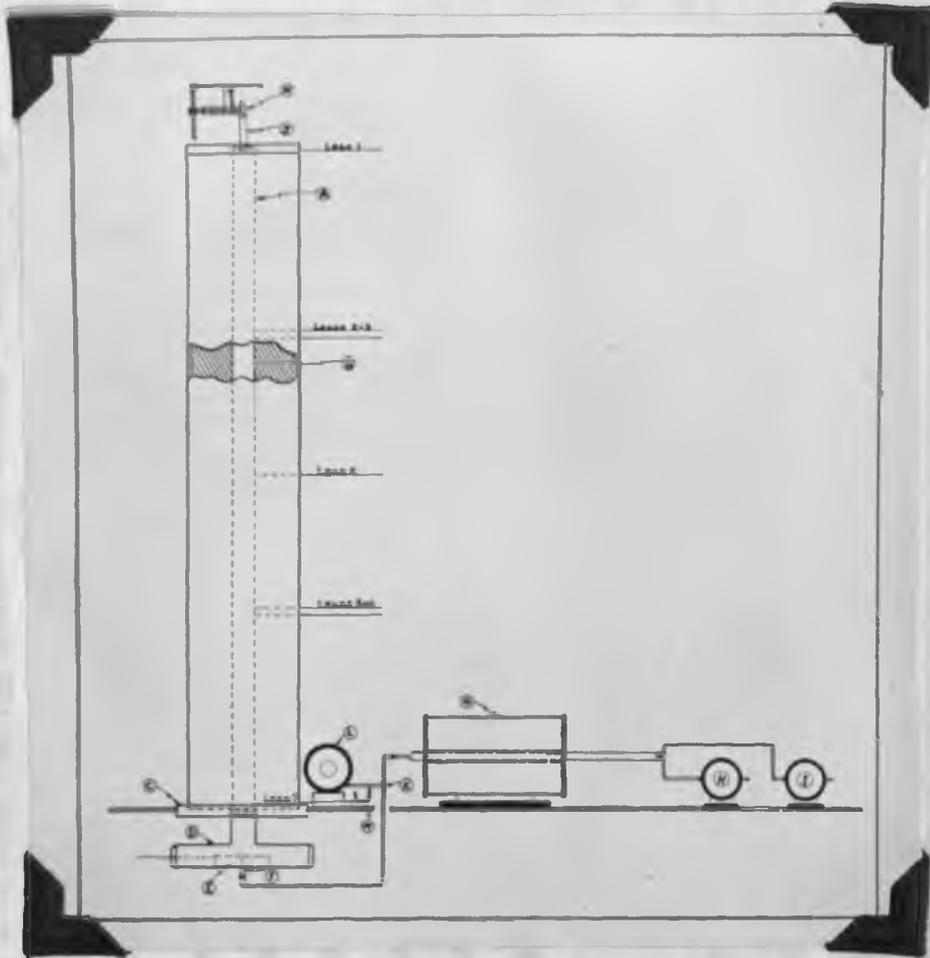
Figure 1.--A Diagrammatical Drawing of the Second
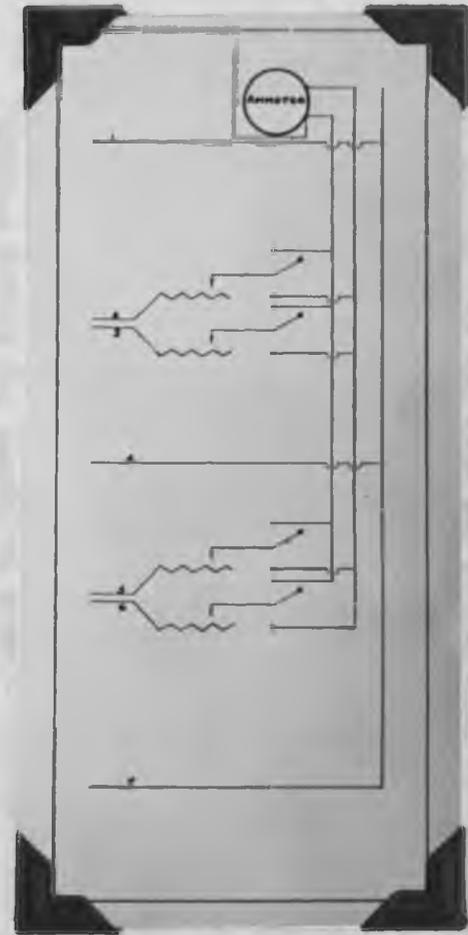Furnace Constructed.

Figure 2.--Wiring Dia-
gram of Second Furnace
Constructed.

enlargement and the tube was filled with asbestos packing. An iron pipe (D) 2 inches in diameter in the shape of an inverted T-tube was screwed up against the packing making the joint gas tight. The two ends of this pipe were closed by caps with rubber gaskets inside; the center of one cap had a small hole through which a wire was extended to push the iron-crucible calcine receiver (E) under the bottom of the sillimanite tube. A small hole was drilled in the center of the inverted T-tube for inserting a small tube which served as the gas port (F).

Two reducing gases were employed; the first containing carbon monoxide and hydrogen was produced by passing natural gas mixed with air over a nickel catalyst in a Multiple-Unit Type 77 combustion-tube furnace (G) heated to 1000° C. The rate of gas and air flow was measured by capillary flowmeters (H) and (I) respectively. This gas was passed updraft or countercurrent to the direction of the fall of the particles of feed and entered the bottom of the reducing chamber through gas port (F). The catalyst was prepared by dissolving nickel nitrate in water, adding alundum to the solution and evaporating to dryness. The second reducing gas employed was produced from coke and air, the coke being added directly to the feed. Air was passed both updraft and downdraft. When updraft was employed the air passed through a capillary flowmeter and entered the bottom of the reducing chamber through gas port (F). When downdraft was employed the air entered at the top of the reducing chamber through gas port (J) and flowed downward in the same direction as the fall of the feed particles. In each case a T-tube connection (K) was made to a gas analysis

apparatus (L) so that a representative sample could be obtained. A

U-tube connection (M) containing water, opened on one arm of the gas

flow so that a sample could be drawn off at atmospheric pressure.

To obtain a gas analysis a sample of 100 c.c. of gas was passed through

potassium hydroxide to determine the carbon dioxide content, and then

through potassium pyrogallate for oxygen content. The standard com-

bustion method was used for the determination of carbon monoxide,

hydrogen, methane (CH_4), and ethane (C_2H_4).

Feed was introduced at the top of the reducing chamber by means

of a variable-speed screw (N) operated by an electric motor with a

speed reducer attachment.

Temperatures of both furnaces were measured by platinum-rhodium

thermocouples connected to a double-throw switch which lead to a

millivoltmeter. In this way the temperatures of the combustion-tube

furnace and the reducing furnace could be read from the same milli-

voltmeter.

MATERIALS USED

The analyses of calcines used are given in table 1.

Table 1.--Analyses of Calcines

No.		Copper	Iron	Sulfur	Insoluble
		Per cent			
1.	Calcine produced from flash roasting Hayden concentrate contain- ing chalcocite and pyrite.	16.01	45.04	0.50	12.13
2.	Calcine produced from flash roasting United Verde chalcopyrite No. 1.	37.14	36.59	0.75	2.35
3.	Calcine mixture obtained from the walls of a furnace which flash roasted United Verde Chalcopyrite No. 2.	32.38	32.52	0.40	---

Calcine No. 3 contained a considerable amount of copper ferrite since it was necessary to leave the accretions on the walls of the furnace until the furnace cooled sufficiently to permit its removal.

ANALYTICAL METHODS

Copper analyses were made in most cases by the electrolytic method. To save time in later work the copper content was determined by the standard short iodide method. Iron was in all cases determined by the standard potassium dichromate method and sulfur by the barium sulfate method.

The acid leaching technique was the same in all experiments and consisted of boiling a 0.5-gram sample for 15 minutes in 100 c.c. of a dilute, acid ferric sulfate solution containing 47.9 grams of the salt and 5.7 c.c. of sulfuric acid per liter. The solution was filtered and the residue washed twice with cold water. The filter paper was then burned in an electric muffle and the residue dissolved and analysed by the standard methods mentioned.

Two ammonia leaches were made; the first was accomplished by rotating a 0.5-gram sample in 100 c.c. of a solution made up by adding 200 grams of ammonium chloride and 500 c.c. of ammonium hydroxide to 700 c.c. of water. The second leach contained 6 per cent of NH_3 and 4 per cent of CO_2 per liter. Ammonium carbonate was used instead of ammonium chloride. The filtering and analyzing was done in the same manner as described for the acid leach. The leaching with heated solutions was done in a thermostat controlled chamber, the pulp being agitated by means of revolving rolls.

CHAPTER III.--REDUCTION OF COPPER FERRITES BY CARBON MONOXIDE AND
HYDROGEN FOLLOWED BY LEACHING OF REDUCED PRODUCTS

The object of the experimental work described in this chapter
was to attempt to reduce copper ferrites in calcines by dropping the
latter down a heated tube while suspended in a rising stream of hot
reducing gas.

The first experimental work consisted, as previously mentioned,
in dropping flash-roasted calcine through a 30-inch vertical-tube
furnace heated to various temperatures, the gas stream passing counter-
current to the direction of fall of the feed.

A calcine mixture containing 50 per cent minus 150 plus 200 mesh
and 50 per cent minus 100 plus 150 mesh was used to facilitate feeding.
The rate of feeding in all experiments was maintained as close to
1/3 gram per minute as the accuracy of the screw feeder would permit.

The reducing gas was obtained by passing 37 c.c. of natural gas
and 89 c.c. of air per minute over the nickel catalyst. This gas-air
ratio was calculated using the formula:

$$(1) \quad CH_4 + \tfrac{1}{2}O_2 = CO + 2H_2$$
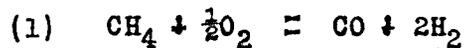
Since natural gas consists mainly of methane (CH_4), this formula was
believed to be within a reasonable degree of accuracy. An analysis
of reducing gas issuing from the combustion-tube furnace showed the
following composition:

Table 2.--Analysis of Reducing Gas

		Per Cent, by Volume
CO_2	:	0.1
O_2	:	0.2
H_2	:	41.0
CO	:	18.3

Referring to equation (1) the hydrogen and carbon monoxide contents should be 2 and 1 molecules respectively. The analysis of the reducing gas as given in table 2, however, indicates a higher hydrogen content than the calculated value but no reason could be found for the discrepancy.

The prepared gas was passed through the reducing furnace without introduction of calcine and an analysis of the gas leaving the top yielded the following composition:

Table 3.--Analysis of Gas After Passing Through Reducing Furnace without Introduction of Calcine.

	:	Per Cent. by Volume
CO_2	:	1.8
O_2	:	0.1
H_2	:	27.9
CO	:	15.7

Referring to table 3, there is an apparent absorption of hydrogen or a diffusion of hydrogen through the walls of the furnace tube, but the reason for the loss of hydrogen could not be determined.

The preliminary experimental work in the reduction of ferrites in calcines was, as previously mentioned, done in a furnace which proved to be too short for efficient reduction. Six tests were made with this furnace and although the tests were quantitative the results are not given since no reduction occurred as shown by analyses of the copper and iron contents. At the conclusion of these tests the second furnace described was constructed and it is considered that the quantitative experimental work started with this furnace.

The method of conducting tests 1 to 12 inclusive was the same in

each case except for the kind of calcine used. Calcine 1 (see table 1) was used for tests 1 to 3 inclusive and calcine 2 for tests 4 to 12 inclusive.

In the latter series of tests the reduced calcine obtained after the first treatment was weighed, and a sample removed for analysis. The remainder of the calcine was sized and passed through the furnace a second time with the same conditions as in the first treatment. This operation was again repeated for a third treatment. These repeated treatments are designated in table 5 as furnace treatments 1, 2 and 3.

The quantities of air and gas used were 177 c.c. air and 75 c.c. natural gas per minute respectively. This gas stream was passed counter-current to the fall of calcine particles. An analysis of the gas leaving the top of the reducing chamber of the furnace without intro-duction of feed was as follows:

Table 4.—Analysis of Reducing Gas
Used in Tests 1-12 inclusive.

	:	Per Cent, by Volume
CO_2	:	2.3
O_2	:	0.0
H_2	:	36.2
CO	:	18.1

The data of the reducing operations are given in table 5.

The results of the reducing operations of tests 1 to 12 inclusive were determined by leaching the reduced products with sulfuric acid-ferric sulfate, ammonium chloride-ammonia and ammonium carbonate-ammonia solvents. A summary of these leaching results are given in table 6 and additional data with respect to variables in leaching are given in table 7.

Table 5.--Reduction of Copper Ferrites by Hydrogen and Carbon Monoxide.

Furnace Reduction of Flash Roasted Calcines

Test No.	Calcine No. (See table 1)	No. of Furnace Treatments	Calcine Feed		Temp. °C.	Loss in wt. of Calcine, Grams	Calcine Feed Analyses, Per Cent				Reduced Calcine Analyses, Per Cent				C.c. Air per Min.	C.c. Natural Gas per Min.
			Grams per Min.	Total Calcine Fed, Grams			Cu	Fe	S	Insol.	Cu	Fe	S	Insol.		
1	1	1	0.33	22.0	900	2.1	16.01	45.04	0.50	12.13	17.43	49.89	0.44	18.03	177	75
2	1	1	0.33	21.0	1000	1.7	16.01	45.04	0.50	12.13	17.74	49.32	0.55	17.97	177	75
3	1	1	0.33	22.0	1100	2.4	16.01	45.04	0.50	12.13	18.16	50.33	0.62	17.50	177	75
4	2	1	0.33	34.0	900	3.7	37.14	36.59	0.75	2.35	41.60	39.60	0.81	1.64	177	75
5	2	2	0.33	21.0	900	1.7	41.60	39.60	0.81	1.64	44.00	41.10	0.82	1.74	177	75
6	2	3	0.33	10.5	900	0.7	44.00	41.10	0.86	1.74	46.05	42.80	0.92	1.74	177	75
7	2	1	0.33	34.5	1000	3.7	37.14	36.59	0.75	2.35	41.46	39.55	1.28	2.50	177	75
8	2	2	0.33	20.0	1000	1.2	41.46	39.55	1.28	2.50	43.12	40.80	1.37	2.68	177	75
9	2	3	0.33	9.5	1000	0.4	43.12	40.80	1.37	2.68	44.30	43.10	1.34	2.94	177	75
10	2	1	0.33	34.0	1100	4.8	37.14	36.59	0.75	2.35	40.40	39.09	1.23	2.23	177	75
11	2	2	0.33	21.0	1100	0.5	40.40	39.09	1.23	2.23	41.40	39.60	1.33	2.26	177	75
12	2	3	0.33	11.0	1100	0.3	41.40	39.60	1.33	2.26	41.30	40.02	1.41	2.14	177	75

Table 6.--Leaching of Reduced Products of Table 5.

Test No.	Calcine No. (See Table 1)	Sulfuric Acid, Ferric Sulfate [3]				Ammonium Chloride, Ammonia [3]				Ammonium Carbonate, Ammonia [3]			
		Leached Residue Per Cent		Per Cent of Tot. Dissolved		Leached Residue, Per Cent		Per Cent of Tot. Dissolved		Leached Residue, Per Cent		Per Cent of Total Dissolved	
		Cu	Fe	Cu	Fe	Cu	Fe	Cu	Fe	Cu	Fe	Cu	Fe
	A[1]	9.42	42.10	41.1	6.5	13.12	44.32	18.1	1.6	12.00	45.50	25.0	0.0
1	1	3.56	37.80	79.5	24.2					4.70	49.70	73.0	0.38
2	1	2.19	23.00	87.6	53.3								
3	1	1.98	23.10	89.0	54.1	5.33	50.20	70.8	0.26	5.27	48.40	70.7	3.08
	A[2]	15.77	32.20	58.0	12.0	25.30	35.60	31.9	2.7	23.30	37.20	37.3	0.0
4	2	4.98	11.83	88.0	72.0								
5	2	0.84	2.70	98.0	93.5								
6	2	0.72	1.90	98.5	95.6					1.55	38.40	97.5	10.25
7	2	1.78	10.70	96.0	73.0					6.20	40.00	84.9	0.00
8	2	1.06	6.01	97.5	85.0								
9	2	0.54	3.41	98.8	92.0	25.10	42.20	43.3	2.1	32.90	40.20	25.7	6.75
10	2	2.44	11.13	94.0	71.5								
11	2	1.48	6.32	96.5	84.0								
12	2	0.86	6.22	98.0	84.5	3.97	40.00	90.3	0.05	1.76	37.80	95.6	5.55

(1) Original flash roasted calcine number 1 leached as described.
(2) Original flash roasted calcine number 2 leached as described.
(3) See Chapter V for quantities and strength.

DISCUSSION OF RESULTS

Although the loss in weight of each reduced calcine was given in table 5, results on the reduction could not be obtained from these figures since an accurate determination of the per cent of copper ferrite in the calcines was not made. However, since the solvents employed should effectively dissolve the metallic copper, a fairly accurate determination of the degree of reduction could be made by comparing the per cent of copper dissolved in the reduced products to the original calcine feed.

Referring to table 5 it can be noted that there was an increase in per cent of both the copper and iron contents in the reduced products as compared to the feed showing that the iron, copper, or both iron and copper were reduced. Repeated furnace treatments had a slight effect in increasing the per cent of copper, iron or both, reduced. At 900° C. the amount of reduction was approximately the same as at the higher temperatures showing that an increase in temperature did not effectively increase the rate of reduction.

From table 6 it should be noted that in tests 1 to 3 inclusive, employing the acid solvents, both the copper and iron were rendered soluble and that at the highest temperature, 1100° C., the leached residue of the reduced calcine contained 11.0 per cent of the total copper which still remained insoluble, whereas the leached residue of the original calcine contained 59.9 per cent of the total copper which was insoluble. The chalcocite and pyrite used in the calcine mixture for tests 1 to 3 inclusive appeared to be differentially reduced to a greater degree than the chalcopyrite of the number 2 mixture employed

in tests 4 to 12 inclusive, although the copper was not rendered as soluble in the former tests as compared to the latter.

In test 12, 98 per cent of the copper was rendered soluble in the acid solvent but 84.5 per cent of the iron was also dissolved. When employing the ammonium chloride-ammonia solvent, however, it should be noted that 90.3 per cent of the copper was rendered soluble leaving all but 0.5 per cent of the iron insoluble.

In test 9 employing both ammonia leaches, an insoluble ferric hydrate was formed which filtered with difficulty, and probably accounted for the high percentage of copper in the residue since thorough washing was not obtained.

Conclusions from the results of the data obtained in the reduction of copper ferrites in calcines using carbon monoxide and hydrogen gases as the reducing agents can be summarized as follows:

1. A drop of five feet was not sufficient for complete reduction of copper ferrites.

2. The reducing gases employed were too active to yield a differential reduction of the copper and iron oxides contained in the copper ferrites.

3. Although both of the ammonia leaches effectively kept the iron insoluble the copper was not dissolved as completely as when the acid solvent was used.

4. When iron was in the metallic state and ammonia solvents employed, a ferric hydrate was formed which made filtering inefficient.

5. Of the two ammonia leaches the ammonium carbonate-ammonia mixture was more effective than the ammonium chloride-ammonia mixture in dissolving copper.

CHAPTER IV.—VARIABLES IN LEACHING OF REDUCED CALCINES

The method of conducting the sulfuric acid-ferric sulfate leaching tests was the same in all experiments and consisted in boiling a 0.5-gram sample in 100 c.c. of the solvent solution for 15 minutes as described in Chapter I. The strengths of the sulfuric acid and ferric sulfate were 0.5 grams and 1.0 gram of iron as ferric sulfate respectively, or expressed in terms of a liter of solution were 5.7 c.c. and 47.9 grams respectively.

The first alkaline leach employed an ammonium chloride-ammonia solvent made up to the strength which follows: ammonium chloride, 200 grams, was dissolved in 500 c.c. of ammonium hydroxide, and 750 c.c. of water.

In the second leach an ammonium carbonate—ammonia solvent was used (6 per cent ammonia and 4 per cent carbon dioxide). Expressed in terms of a liter the amounts used were as follows: ammonium carbonate, 100 grams, was dissolved in 120 c.c. of ammonium hydroxide, and the resulting solution was made up to a liter.

A series of leaches was made to determine the best conditions as to time and temperature of treatment. The method of conducting these tests was as follows:

A 0.5-gram sample of the reduced calcine was placed in a revolving bottle containing 100 c.c. of the alkaline leach. The solution was filtered and the residue treated in the same manner as described for all tests in Chapter I. The results of these tests are given in table 7.

DISCUSSION OF RESULTS

Referring to table 7, the leaching tests made at temperatures between 55 and 60° C. for two hours yielded approximately the same

Table 7.--Effect of Time and Temperature on the Solubility of Copper and Iron in Alkaline Solvents.

Solvent	Calcine	Calcine Analyses Per Cent		Time, Min.	Temp. °C.	Leached Residue Per Cent		Per Cent of Total Dissolved	
		Cu	Fe			Cu	Fe	Cu	Fe
Ammonium Carbonate -Ammonia	A[1]	35.64	33.60	15	Room	13.79	33.6	61.3	0.0
				30	Room	12.37	33.6	65.3	0.0
				60	Room	7.34	33.6	79.3	0.0
				120	Room	7.12	33.0	80.0	1.78
				180	Room	7.00	32.6	80.4	2.97
				300	Room	7.00	32.3	80.4	3.87
				420	Room	6.84	32.7	80.8	2.68
				900	Room	6.35	33.8	82.2	0.0
				60	55-60	6.68	32.6	81.3	2.97
				120	55-60	6.35	32.7	82.2	0.0
				240	55-60	6.25	32.5	82.4	3.27
	Calcine Feed	37.14	36.59	420	Room	26.50	35.3	28.7	3.53
				900	Room	25.40	36.2	31.6	1.07
				120	55-60	25.30	35.6	31.9	2.71
C. P. Ammonia	A[1]	35.64	33.60	120	55-60	8.33	32.8	76.6	2.38

(1) Reduced calcine from test 22.

amounts of dissolved copper as the leaches run at room temperature for 900 minutes. For expediency, all the alkaline leaches described in this paper were made between 55 and 60° C. for 2 hours. The ammonia solvent was not as effective as the ammonium carbonate-ammonia solvent in dissolving the copper.

CHAPTER V.--THE DIFFERENTIAL REDUCTION OF COPPER FERRITES
WITH COKE.

Since the $CO-H_2$ gas mixture used in the series of experiments
described in Chapter III proved to be too active for differential
reduction, a series of tests using a gas of less reducing potential
was tried.

If a $CO-CO_2$ mixture could be obtained of such a composition that
the value of the ratio in the relation $PCO_2/PCO = K$ would be less
than that of the equilibrium constant K at a definite temperature
and if the concentration of the CO could be such so as to be above
the critical concentration for cupric oxide and still be below the
critical concentration for ferric oxide, reduction of cupric oxide
would take place with the iron remaining unaffected or nearly so.

Butler[2] showed that a concentration of CO in a $CO-CO_2$ mixture
less than some composition slightly above 33 per cent would reduce
the cupric oxide in copper ferrite and leave the iron unattacked or
nearly so.

An attempt was then made to produce a CO_2 concentration of
approximately twice that of CO by the partial combustion of methane
by passing oxygen and natural gas over the nickel catalyst in the
combustion-tube furnace.

It was found that a variation in flow of the oxygen as low as
5 c.c. per minute would cause an error of 3 per cent in the concen-
tration of carbon dioxide and carbon monoxide. Since the maintaining
of a constant composition required much closer control than the
apparatus would permit, this method was abandoned. Passing CO_2 over
hot carbon to obtain a CO_2-CO mixture could not be attempted because

a tube-furnace large enough to hold sufficient carbon for a run could not be obtained.

An attempt was then made to produce a CO_2-CO mixture by dropping coke through the reducing furnace with air passed both updraft and downdraft. The amount of air was varied from 50 c.c. to 250 c.c. per minute and the coke from 1/3 gram to 2 grams per minute. In all cases an analysis of the resulting gas showed the CO_2 content to vary between 17.5 and 20 per cent by volume, and the CO content between 1.1 and 3.4 per cent. This fact showed that oxygen in the air formed CO_2 and that the rate of formation of CO from the coke was too slow to take place under the conditions given. It was believed that the complete combustion (formation of CO_2) was due to leaks or to occluded oxygen in the coke. The coke was burned in an atmosphere of nitrogen and an analysis showed that 0.6 per cent oxygen was present. The furnace was tested for leaks by drawing air out at the bottom of the reducing furnace at a rate equivalent to the flow of gases when making the runs in the experimental work. Nitrogen at the rate of 350 c.c. per minute was introduced by means of a tube which was placed at different heights inside the sillimanite tube of the reducing furnace. In this manner air was prevented from entering at the upper end of the tube since the nitrogen flowed up and around the tube. An analysis of the gas drawn off at the bottom would show whether any air was entering the furnace at points below the nitrogen tube. After passing the nitrogen tube from the top to the bottom of the reducing furnace no leakage of air was found. All the rubber tubing in the apparatus was then replaced by glass tubing and it was found

that a slight leakage of air took place due to the rubber tubing.

Although a gas mixture containing a CO_2 content twice that of CO could not be produced, a series of tests was made under varying conditions to attempt to differentially reduce copper and iron oxides contained in the ferrites of the calcines.

Tests 13 to 16 inclusive were made feeding coke with the calcine and passing CO_2 very slowly updraft. The CO_2 was made in a generator containing marble and 1 to 1 hydrochloric acid. Accurate control of this gas was not possible. The calcine used was number 2 (see table 1) sized 50 per cent minus 150 plus 200 mesh and 50 per cent minus 100 plus 150 mesh to facilitate feeding. The coke, sized in the same manner as the calcine, was added in the following proportion: assuming the calcine to be Fe_2O_3 and CuO, calculations were made to determine the amount of coke necessary to completely reduce the calcine to metallic copper and metallic iron. Hereafter coke additions were designated as factors of the theoretical amount. In test 13 the theoretical amount of coke was added to the calcine feed, whereas in tests 14 to 16 inclusive twice the theoretical amount of coke was added. The results of these tests are given in table 8.

DISCUSSION OF RESULTS

From table 8 it should be noted that the per cents of the copper and iron of the reduced products of tests 13 to 16 inclusive in a few cases were lower than the per cents of the copper and iron in the calcine feeds. This condition was due to the fact that additions of coke to the calcine feeds caused a dilution of the copper and iron in the reduced furnace products so that when a 0.5-gram sample was taken for analysis some coke was included in the sample. How-

Table 8.--Reduction of Copper Ferrites by Coke

| | | | Furnace Reduction of Flash Roasted Calcine | | | | | | | | | | | | Leaching of Reduced Products | | | |
Test No.	Calcine No. (See table 1)	No. of Furnace Treatments	Calcine Feed Grams per Min.	Total Calcine Fed, Grams	Temp. °C.	Coke Feed, Grams	Loss in wt. of Calcine, Grams	C.c. Air per Min.	Draft	Size of Calcine, Mesh	Calcine Feed Analysis Per Cent Copper	Iron	Reduced Calcine Analysis Per Cent Copper	Iron	Sulfuric Acid Leached Residue Per Cent Copper	Iron	Ferric Sulfate[2] Per Cent of Total Dissolved Copper	Iron
A[3]											37.14	36.59			15.77	32.20	58.0	12.0
13	2	3	0.33	10	1000	1.87	0.39	5-15[1][1]	Up				29.70	32.88	11.76	26.26	60.5	20.5
14	2	1	0.33	20	1000	3.75	1.03	5-15[1]	Up	50 per cent minus 150 plus 200 and 50 per cent minus 100 plus 150	37.14	36.59	30.36	31.08	10.36	25.36	65.9	18.4
15	2	2	0.33	15	1000	2.80	0.52	5-15[1]	Up		30.36	31.08	31.00	32.38	8.78	25.36	71.6	21.7
16	2	3	0.33	10	1000	1.87	0.39	5-15	Up		31.00	32.38	31.14	33.08	9.90	26.47	68.3	19.9
17	2	1	0.33	20	1000	3.75	1.40	100	Down		37.14	36.59	33.30	31.14	15.67	25.90	52.9	16.8
18	2	2	0.33	15	1000	2.80	0.90	100	Down		33.30	31.14	30.21	28.21	14.02	23.13	53.5	18.0
19	2	3	0.33	10	1000	1.87	1.35	100	Down		30.21	28.21	27.20	24.93	11.30	20.20	58.4	19.0
20	2	1	0.33	20	1100	1.87	1.96	100	Down		37.14	36.59	37.78	35.31	11.51	28.54	69.7	19.2
21	2	2	0.33	15	1100	1.40	0.68	100	Down		37.78	35.31	36.24	34.00	5.03	25.61	86.0	24.7
22	2	3	0.33	10	1100	0.98	0.48	100	Down		36.24	34.00	35.64	33.60	3.83	22.00	89.3	34.5
A[4]											32.38	32.52			15.82	30.60	51.1	5.9
23	3	1	0.33	20	1100	1.69	2.21	100	Down	Minus 200 plus 270	32.38	32.52	29.60	33.63	10.56	30.12	64.4	10.4
24	3	2	0.33	15	1100	1.27	0.64	100	Down		29.60	33.63	31.00	31.62	9.10	26.74	70.7	15.4
25	3	3	0.33	10	1100	0.85	0.44	100	Down		31.00	31.62	30.12	31.46	9.08	27.23	70.0	13.4
26	3	1	0.33	20	1100	1.69	1.93	100	Up		32.38	32.52	31.60	32.81	13.12	28.71	58.4	12.5
27	3	2	0.33	15	1100	1.27	0.70	100	Up		31.60	32.81	30.84	31.53	11.20	26.90	63.7	14.7
28	3	3	0.33	10	1100	0.85	0.43	100	Up		30.84	31.53	30.23	30.31	9.60	25.70	68.3	15.2
29	3	1	0.33	20	1100	1.69	1.86	100	Down	Minus 150 plus 200	32.38	32.52	30.30	32.63	15.56	29.32	48.7	10.1
30	3	2	0.33	15	1100	1.27	0.83	100	Down		30.30	32.63	28.51	30.86	13.04	27.30	54.3	11.5
31	3	3	0.33	10	1100	0.85	0.57	100	Down		28.51	30.86	27.00	30.51	8.90	22.46	67.0	26.4
32	3	1	0.33	20	1100	1.69	2.32	100	Down	Minus 270	32.38	32.52	31.34	34.71	9.54	29.73	69.5	14.4
33	3	2	0.33	15	1100	1.27	1.25	100	Down		31.34	34.71	30.02	35.31	5.44	27.21	81.8	22.9
34	3	3	0.33	10	1100	0.85	0.60	100	Down		30.02	35.31	28.91	35.53	4.24	26.90	85.4	24.3
35	3	1	0.33	20	1100	1.69	2.48	15	Down		32.38	32.52	32.92	36.00	8.25	27.20	75.2	24.4
36	3	2	0.33	15	1100	1.27	1.31	15	Down		32.92	36.00	30.92	34.21	4.80	26.24	84.5	23.3
37	3	3	0.33	10	1100	0.85	0.95	15	Down		30.92	34.21	30.02	33.64	2.82	24.61	90.6	26.8
38	3	1	0.33	20	1100	3.38	2.52	15	Down		32.38	32.52	28.58	32.13	3.72	26.00	87.2	19.1
39	3	2	0.33	15	1100	2.54	1.50	15	Down		28.58	32.13	28.00	31.51	3.34	24.41	88.1	22.5
40	3	3	0.33	10	1100	1.70	1.01	15	Down		28.00	31.51	26.82	31.00	2.46	21.16	90.7	31.7

(1) CO_2 used instead of air.

(2) See Chapter V for strengths and amounts.

(3) Original flash roasted calcine No. 2.

(4) Original flash roasted calcine No. 3.

ever, the leaching tests showed that reduction did occur. The reduction was slow in all cases but especially in the tests to which the theoretical amount of coke was added as compared to larger additions of coke. Although 80.1 per cent of the total iron remained insoluble in the product of test 16, only 68.3 per cent of the copper was rendered soluble. Most of the coke evidently burned completely to CO_2 and the reduction of the CO_2 to CO by the coke was not rapid.

VARIABLES EMPLOYED IN THE DIFFERENTIAL REDUCTION OF COPPER FERRITES IN CALCINES EFFECT OF TEMPERATURE

In tests 17 to 22 inclusive the calcine feeds comprised chalcopyrite number 2 sized 50 per cent minus 150 plus 200 mesh and 50 per cent minus 100 plus 150 mesh. Coke, sized in the same manner, was fed directly with the calcine. Twice the theoretical amount was added in tests 17 to 19 inclusive, whereas the theoretical amount was added in tests 20 to 22 inclusive. Air was passed downdraft at the rate of 100 c.c. per minute. The temperature of the reducing furnace was 1000° C. for tests 17 to 19 inclusive and 1100° C. for tests 20 to 22 inclusive. Results of these tests are given in table 8.

DISCUSSION OF RESULTS

Increasing the temperature from 1000° to 1100° C. and decreasing the coke feed from twice the theoretical to the theoretical amount had a decided effect on increasing the solubility of the copper as was shown by the acid leaching of the reduced products of table 8. However, 19.2 to 34.5 per cents of the iron in the residues of the reduced calcines were rendered soluble as compared to 12.0 per cent soluble iron in the original calcine.

EFFECT OF DRAFT

In tests 23 to 28 inclusive the temperature and rate of air were kept constant being 1100° C. and 100 c.c. per minute respectively. The feed, sized minus 200 plus 270 mesh, was chalcopyrite number 3 mixed with the theoretical amount of coke. The direction of air draft was varied, passing air updraft in tests 26 to 28 inclusive, and downdraft in tests 23 to 25 inclusive. Results of these tests are given in table 8.

DISCUSSION OF RESULTS

The acid leaching of the reduced products from tests 23 to 28 inclusive indicated that downdraft was more effective than updraft in reducing the copper oxide contained in the copper ferrites. When downdraft was employed, as in test 25, 70 per cent of the copper was rendered soluble with 86.6 per cent of the iron remaining insoluble, whereas in test 28, employing updraft, 68.3 per cent of the copper was soluble and 84.8 per cent of the iron was made insoluble.

EFFECT OF PARTICLE SIZE

In tests 23 to 25 inclusive and in tests 29 to 34 inclusive the temperature, the direction of draft and air flow remained constant. The size of the calcine feed was varied, employing minus 150 plus 200 mesh in tests 29 to 31 inclusive, minus 200 plus 270 mesh in tests 23 to 25 inclusive and minus 270 mesh in tests 32 to 34 inclusive. The theoretical amount of coke was employed and sized in the same manner as the calcine feeds.

DISCUSSION OF RESULTS

Variations in particle size of the calcine feed produced a considerable

effect on the solubilities of the reduced copper and iron. In test
31 with the calcine feed minus 150 plus 200 mesh, 67 per cent of the
copper and 26.4 per cent of the iron were rendered soluble. In test
25, minus 200 plus 270 mesh calcine indicated that 70 per cent of the
copper and 13.4 per cent of the iron were rendered soluble. In test
34 the use of minus 270 mesh sizes indicated that 85.4 per cent of the
copper and 24.3 per cent of the iron were dissolved by the acid solvent.
Although a greater per cent of the iron remained insoluble in the
leached residue of the calcine in test 25 sized minus 200 plus 270 mesh,
the copper was not as effectively dissolved as in the minus 270 mesh
calcine of test 34.

EFFECT OF VARYING QUANTITIES OF AIR

In tests 32 to 37 inclusive the temperature, draft, size of feed
and proportion of coke feed were maintained constant. The rate of
air flow was varied, being 100 c.c. per minute in tests 32 to 34
inclusive and 15 c.c. per minute in tests 35 to 37 inclusive.

DISCUSSION OF RESULTS

A considerable effect on the reduction of copper ferrites was
obtained in lowering the rate of air flow from 100 c.c. to 15 c.c.
per minute. In test 34, employing the higher rate of air flow,
85.4 per cent of the copper and 24.3 per cent of the iron were dis-
solved, whereas in test 37, utilizing an air flow of 15 c.c. per
minute, 90.6 per cent of the copper and 26.8 per cent of the iron
were rendered soluble. Although the solubility of the iron was
slightly increased, the solubility of the copper was increased to a
greater degree in the latter tests as compared to the former.

EFFECT OF VARYING THE PROPORTION OF COKE

In tests 35 to 40 inclusive the amount of coke added to the calcine feed was the only variable.

DISCUSSION OF RESULTS

From table 8 it should be noted that increasing the proportion of coke from the theoretical to twice the theoretical amount had a slight effect on increasing the solubility of the copper. However from test 37, employing the theoretical amount of coke, it should be noted that the iron was rendered insoluble to a greater degree than in test 40 which contained twice the theoretical amount of coke.

Conclusions from the results of the data obtained in the reduction of copper ferrites in calcines using coke as the reducing agent can be summarized as follows:

1. A differential reduction of the copper and iron oxides contained in copper ferrites was obtained although all the iron in no case remained insoluble.

2. The speed of the reduction varied directly with the temperature.

3. Downdraft produced somewhat more effective results than updraft.

4. The smaller the particle size, the greater the degree of reduction of both copper and iron oxides.

5. The theoretical amount of coke employed with small amounts of air were the best conditions for differential reduction.

CHAPTER VI--THE EFFECT OF ADDITION OF SODIUM CHLORIDE ON
THE DIFFERENTIAL REDUCTION OF COPPER FERRITES

In view of the results obtained from the data on the differential
reduction of copper ferrites using coke as the reducing agent, it was
believed that the addition of sodium chloride forming chlorides with
the copper and iron would increase the recovery of copper by leaching
methods.

The method of conducting the tests described in this chapter was
the same as in the tests employing coke as the reducing agent except
that sodium chloride was added.

In tests 41 to 49 inclusive the calcine number 3 was employed.
The temperature, coke feed, air flow, direction of draft and size of
feed were maintained constant. The sodium chloride, screened minus
270 mesh, was added in varying amounts to the coke and calcine feeds.
In tests 41 to 43 inclusive, the sodium chloride added was 5.0 per cent
of the calcine weight, in tests 44 to 46 inclusive, 3.0 per cent of the
calcine weight and in tests 47 to 49 inclusive 1.0 per cent. The
results of these tests are given in table 9.

DISCUSSION OF RESULTS

Accurate determinations of the copper and iron contents in the
residues of the reduced calcines were complicated by the fact that
coke and chlorides of copper and iron were present. However, in the
series of tests employing coke and salt the results should be accurate
with relation to each other.

From table 9 it should be noted that in tests 41 to 49 inclusive,
employing quantity of salt as the only variable, there was not a great
difference in the per cents of copper dissolved by the acid solvent.

Table 9.--Reduction of Copper Ferrites by Coke with the Addition of Sodium Chloride.

Test No.	Calcine No. (See table 1)	No. of Furnace Treatments	Calcine Feed Grams per Min.	Total Calcine Fed, Grams	Temp. °C.	Coke Feed, Grams	Sodium Chloride Feed, Grams	C.c. Air per Min.	Draft	Size of Calcine, Mesh	Calcine Feed Analysis Per Cent Copper	Iron	Reduced Calcine Analysis Per Cent Copper	Iron	Sulfuric Acid, Leached Residue Per Cent Copper	Iron	Ferric Sulfate[1] Per Cent. of Tot. Dissolved Copper	Iron
	A (2)										32.38	32.52			15.82	30.60	51.1	5.9
41	3	1	0.33	20	1100	1.69	1.0	15	Down	Minus 270	32.38	32.52	27.21	37.22	7.86	32.50	71.0	12.6
42	3	2	0.33	15	1100	1.27	0.75	15	Down	Minus 270	27.21	37.22	27.60	35.20	4.98	30.50	81.9	13.4
43	3	3	0.33	10	1100	0.85	0.50	15	Down	Minus 270	27.60	35.20	29.73	31.41	1.14	27.20	96.3	13.4
44	3	1	0.33	20	1100	1.69	0.60	15	Down	Minus 270	32.38	32.52	27.92	33.39	9.44	32.28	66.3	3.3
45	3	2	0.33	15	1100	1.27	0.45	15	Down	Minus 270	27.92	33.39	28.41	33.30	4.94	30.81	82.8	7.5
46	3	3	0.33	10	1100	0.85	0.30	15	Down	Minus 270	28.41	33.30	28.69	31.28	3.37	26.60	88.2	5.4
47	3	1	0.33	20	1100	1.69	0.20	15	Down	Minus 270	32.38	32.52	33.19	28.93	9.00	30.09	72.9	0.0
48	3	2	0.33	15	1100	1.27	0.15	15	Down	Minus 270	33.19	28.93	32.30	28.50	4.28	25.69	86.7	9.8
49	3	3	0.33	10	1100	0.85	0.10	15	Down	Minus 270	32.30	28.50	30.79	29.60	2.86	25.90	90.7	1.3
50	3	1	0.33	20	1100	1.27	1.0	15	Down	Minus 270	32.38	32.52	26.29	34.28	9.35	31.10	64.7	9.3
51	3	2	0.33	15	1100	0.95	0.75	15	Down	Minus 270	26.29	34.28	25.00	34.40	5.74	32.90	77.2	4.4
52	3	3	0.33	10	1100	0.64	0.50	15	Down	Minus 270	25.00	34.40	27.50	31.58	4.20	31.11	84.7	1.6
	A (3)										37.14	36.59			15.77	32.20	58.0	12.0
53	2	1	0.33	20	1100	1.87	0.20	15	Down	Minus 270	37.14	36.59	33.51	38.41	7.50	29.81	77.7	22.4
54	2	2	0.33	15	1100	1.40	0.15	15	Down	Minus 270	33.51	38.41	35.40	36.90	3.70	31.31	89.7	15.2
55	2	3	0.33	10	1100	0.94	0.10	15	Down	Minus 270	35.40	36.90	35.31	33.42	2.90	27.80	92.0	16.8

(1) See Chapter V for strengths and amounts.

(2) Original flash roasted calcine number 3.

(3) Original flash roasted calcine number 2.

This was thought to be due to the fact that the action occurred when the salt was in the vapor state and that only a small amount of sodium chloride vapor was necessary to increase the amount of copper rendered soluble. However, in the tests employing 1.0 per cent sodium chloride, a greater per cent of iron remained insoluble than in the tests employing 5.0 per cent or 3.0 per cent salt.

It should be noted that in the tests employing 3.0 per cent and 1.0 per cent sodium chloride the per cent of iron dissolved in most cases was lower than the per cent of iron dissolved when the original calcine was leached. This indicated that not only the iron which originally existed as a copper ferrite was insoluble but also some iron existing originally in a soluble form was rendered insoluble after the furnace reduction treatments with sodium chloride.

The inconsistency of some of the results can be partly attributed to the fact that no data could be obtained as to the degree of the vapor loss of the chlorides of copper and iron.

Tests 50 to 52 inclusive were conducted in the same manner as the tests 41 to 49 inclusive. The amount of coke used was three fourths the theoretical amount and the sodium chloride used amounted to 5 per cent of the calcine feed.

From table 9 it should be noted that the copper was not rendered as soluble as in tests 41 to 43 inclusive employing the theoretical coke.

In tests 53 to 55 inclusive calcine number 2 was used with 1.0 per cent of salt and three fourths the theoretical coke amount. Results obtained from the data of test 55 in table 9 indicated that

almost all the iron of the copper ferrite remained insoluble with 92

per cent of the copper being rendered soluble by the acid leach.

CONCLUSIONS

From the data obtained in table 9 it should be noted that although

the iron appeared to be insoluble to a greater degree than in the

tests employing the coke without sodium chloride additions as described

in Chapter V, the copper solubility was not increased to any great

extent.

CHAPTER VII--SUMMARY OF CONCLUSIONS

1. Reductions amounting to as high as 97.2 per cent of the copper oxide and 95.0 per cent of the iron oxide contained in copper ferrites have been obtained in this experimental work.

2. The copper and iron oxides of the copper ferrites may undergo differential reductions when coke is used as the reducing agent. The solubility of the copper did not exceed 90.7 per cent of the total copper at any time and all the iron in no case remained insoluble.

3. The reduction of the copper and iron oxides of the copper ferrites varied directly with temperature and reduction of the copper oxide proceeded at a more rapid rate than that of the iron oxide.

4. When the flow of air was passed in the same direction as the fall of particles of feed the reduction was more rapid than when the air flow was counter current to the fall of feed particles.

5. The rate of reduction varied inversely with feed particle size.

6. When sodium chloride was added directly to the calcine and coke feed it was found that although the recovery of copper by leaching methods was not substantially improved, the solubility of the iron was materially reduced.