

THE EFFECT OF LEACH CONCENTRATION
ON THE
ROASTING AND LEACHING
ON A
COMPLEX SULFIDE ORE

by

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INTRODUCTION

At the beginning of the industrial development of heavy non-ferrous metallurgy, the raw materials used were rich nonmetallic oxide ores from which the metal was easily recovered by thermal reduction with carbon. With the gradual exhaustion of these ores reserves, the problem of utilizing sulfide ores instead of the oxides arose. The standard practice was to prepare the ores chemically for melting by calcination, and thereby convert the sulfides to oxides. Furthermore, exhaustion of the rich nonmetallic sulfide ores led to the processing of poorer polymetallic sulfide ores. This required an additional physical treatment known as mineral dressing. Toward the end of the 19th century systematic investigations were started on calcination of Fe, Cu, Zn, and Pb among others.

Research work at the beginning of the 20th century covered some reactions in the Me-S-O system, both in a state of equilibrium and a state of nonequilibrium. Reactions of the zinc-sulfur-oxygen and copper-sulfur-oxygen systems were studied in detail since the reactions of sulfides with sulfates and of sulfides with oxides of metals were found to be of decisive importance in zinc and copper systems.

The main economic sulfide minerals in the bulk sulfide flotation and in the table concentrate of the Gossan Lead Ore are pyrrhotite (Fe_9S_9) or ($\text{Fe}_x\text{S}_{x+1}$) marmatite (Zn, Mn) S , pyrite (FeS_2),

chalcopyrite (Fe,Cu)S and galena (PbS) in the order of their decreasing importance. The objective of the research effort in this paper was to separate selectively the important constituents of iron, copper, and zinc from each other.

The roasting technique applied in the present research consists of heating the complex sulfide ore in the presence of air below the fusion point of the constituent minerals. The oxygen then reacts with the complex sulfide ore at a high temperature converting the sulfides into soluble oxides. The significant factors affecting roasting were bed temperature, air flow rate, feed rate, and roasting time.

Next the ore was leached by putting the oxidized solute minerals into solution with the addition of an appropriate solvent of sulfuric acid and under the specific conditions of high temperatures and pressures. This oxidation resulted in the loss of electrons to the oxidizing agents such as oxygen, chlorine, and nitric oxide, which requires electrons to achieve their most stable state. As a result these reactants actively remove electrons from the minerals, forming charged metallic ions in solution. In this process, leaching time, temperature, pressure and concentration of H_2SO_4 must be considered.

Combinations of roasting and leaching of the ores proved successful in previous works, and the present paper is chiefly concerned with the feasibility of these procedures with high

temperatures and pressures for a complex sulfide ore from the Great Gossan Lead, Carroll County, Virginia.

The ore is rich in iron units, and before it can meet market specifications, the removal of critical impurities is necessary. Therefore the objective is to selectively separate the important constituents of iron, copper, and zinc from each other. Special attention will be paid to the removal of zinc in the calcine, since zinc in iron ores vigorously attacks the refractory lining of steel furnaces.

LITERATURE REVIEW

Location of The Great Gossan Lead Ore

The location of the Great Gossan Lead ore body is in Carroll County, Virginia, near the North Carolina-Virginia state line (Fig. 1). Mineralization can be traced for about 17 miles, more or less continuously with the exception of only a few unexplored areas near Galax, Virginia.

The airline distances from the principal cities of commercial and shipping interests to the central area of the deposit are as follows:

Pulaski, Virginia	-----	20 miles
Roanoke, Virginia	-----	70 miles
Richmond, Virginia	-----	200 miles
Norfolk, Virginia	-----	260 miles
Birmingham, Alabama	-----	410 miles

U. S. Highway 221 roughly parallels the outcrop from Galax to Hillsville. Virginia State Highway 100 crosses the ore deposit and connects with U. S. Highway 221, which goes to Pulaski. All-weather secondary roads branch from the main highways and cross the Gossan Lead in many places giving an access to most parts of the deposit.

The entire length of the deposit can well be served by railway transportation. Nearby Galax, Virginia, has a branch line of

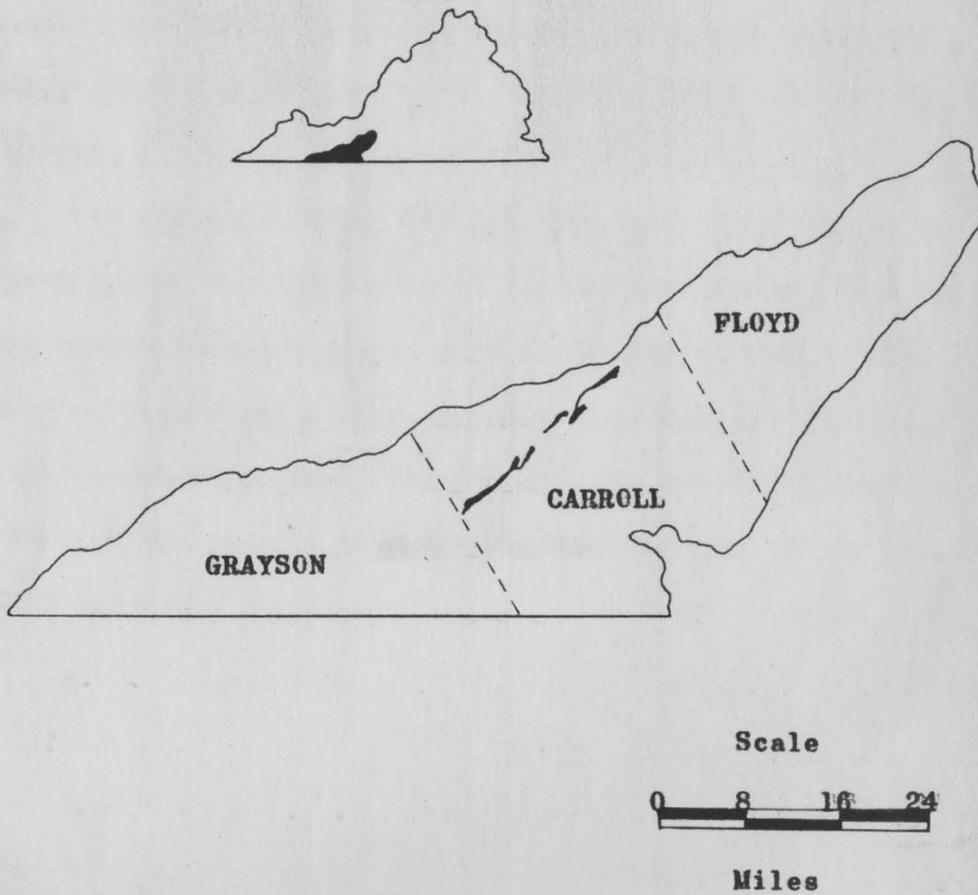


FIGURE 1. MAP OF CARROLL, GRAYSON AND FLOYD COUNTIES, VIRGINIA, AND THE GREAT GOSSAN LEAD ORE DEPOSIT.

the Norfolk and Western Railroad. In the past history of the Gossan Lead, branch lines extended to the Betty Baker and Lineberry segments of the deposit. These road beds could be repaired and made to serve any new mining development.

The deposit is located in an area where some of the cheapest electric power is provided both in the state as well as in the South. The Appalachian Power Company, with dams and generating plants on the nearby New River, has power lines traversing all sections of Carroll County and the Gossan Lead.

For any significant beneficiation process a large dependable water supply is a prerequisite. Little Lead Island Creek crosses the deposit at three places near the northeast end, Crooked Creek crosses it near the center, and Chestnut Creek cuts through it near the southwest end. In addition, the New River, the master stream of the area, flows near the southwest end of the Gossan Lead deposit.

Geology of Carroll County, Virginia

The general trend of the Gossan Lead ⁽¹⁾ is N.25°-60'E., but abrupt changes of strike are common. The dip of the Lead is moderate, typically about 45 degrees to the southeast, and it is characterized by a pronounced flattening on the northeast end. The Lead pinches and swells along the strike, ranging from a width of a few feet to a maximum width of 150 feet within short distances. The configuration of the Lead at depth is not well known although early drilling proved an ore body to a depth of some 700 feet in one locality. More recent drilling has indicated that the Lead may be continuous along its entire length despite the opinion of early workers that it is a series of disconnected lenses.

The main Lead and its offsets lie in a complex of crystalline schists and gneisses which has been termed by various workers as "Carolina Gneiss," "Lynchburg Schist," and "meta-sediments of lower Cambrian Age." The schists and gneisses are intruded by masses of relatively unmetamorphosed diorite, and by small bodies of granite and syenite. A fine-grained mica or sericite schist is the main host or country rock throughout the main Great Gossan Lead region, although lenses of gneissic material are found immediately adjacent to the Lead.

The most commonly observed schistose rock in contact with the Lead as both hanging and footwall rock consists essentially of muscovite or sericite, with minor amounts of chlorite and a garnet-

mica complex (the mica being either biotite or muscovite), and talcose masses. These talcose masses represent alteration of the muscovite-sericite schist adjacent to the lead.

The major structure responsible for emplacement of the ore-bearing fluids along the main lead can have one of several, or a combination of several, origins. It may be a major thrust fault or it may represent a major shear zone with predominating strike-slipage. In addition, accompanying the latter suggestion is the possibility that the offset deposits are subsidiary shears within the major fault structure. Detailed field work will be necessary to work out all of the complexities of the structural pattern. Following the emplacement of the primary sulfides at depth, erosion with subsequent weathering and leaching of the upper part of the vein zone formed a gossan with its usual oxides and carbonate ores of copper and iron. Secondary or supergene copper sulfides formed immediately below the water table. As secondary sulfide enrichment is intimately tied in with past water tables, base-leveling, penetration, and periods of uplift, the problem of determining older erosion surfaces may have some bearing not only on the geomorphic history of this region, but also on the actual age of the deposit.

Mineralogy of The Great Gossan Lead

The mineralogy of the muscovite-sericite schist wall rock is relatively simple. The common minerals are muscovite or sericite, with some biotite, chlorite, garnet, and quartz. Fragments of intensely altered country rock are also found within the ore body.

Identification of the primary sulfides of the Great Gossan Lead has been made from a study of polished sections of diamond drill cores and of selected hand specimens. From this study, the following conclusions were reached:

Pyrrhotite ($\text{Fe}_x\text{S}_{x+1}$) in the sulfides varies from 70 to 95 percent. The general chemical analysis of the pyrrhotite is: ⁽²⁾

	wt. %
Fe	60.2
S	39.3
Zn	0.2
(Insol-Acid-SiO ₂)	0.7
TOTAL	100.4

Marmatite [Zn (Fe, Mn) S], is of a chocolate brown color. It is assumed that the brown color of the mineral results from the presence of manganese. Marmatite accounts for 3 to 8 percent of the sulfides. Marmatite association with the gangue minerals is important and may result in the eventual loss of substantial amounts of the zinc during concentration.

Pyrite (FeS_2), representing 1 to 20 percent of the sulfides, was noted as replacing an equivalent quantity of pyrrhotite.

Chalcopyrite (CuFeS_2), averages 2 to 3 percent and is uniformly distributed in the sulfides.

Tetrahedric and/or Tenanite ($\text{Cu}_8\text{Sb}_2\text{S}_7$), are found with galena in contact with marmatite, but only rarely and in very minute amounts. This is similar to tetrahedrite with arsenic replacing the antimony.

Iron Oxide (magnetite - Fe_3O_4), hematite - Fe_2O_3 , and the hydrated iron oxides.

The following exists in very small amounts: Cubanite - (CuFe_2S_3); Galena - (PbS); Arsenopyrite - (FeAsS); and Lollingite - (FeAs_2) and/or leucopyrite - (Fe_3As_4).

The gangue consists largely of silicates with significant amounts of carbonate minerals which occur in stringers and veinlets up to 6 inches in thickness. The gangue minerals include quartz, muscovite, biotite, sodium micas, chlorite, iron and manganese garnets, hornblende, actinolite, talc, serpentine, epidote, carbonates, zircon, and small amounts of soda-rich plagioclase. Locally the gangue minerals may constitute as much as 50 percent of the ore. It is reported that the gangue was 40 percent of the ore at the Betty Baker mine. ^(1,2) The head sample analysis of the ore is shown in Table 1, and the analyses of the drill core are given in Tables 2 and 3.

TABLE 1

Analysis of Great Gossan Lead Head Sample

	Weight %
Fe -----	35.52
S -----	25.37
Zn -----	1.96
Cu -----	.63
Pb -----	.34
	63.72
Gangue by Difference -----	32.28

TABLE 2

Drill Hole Sample Analyses Betty Baker Mines*

Drill Hole Number	Ore Body Width, Feet	Analysis, percent				
		Fe	S	Insol.	Cu	Zn
BM-1	11.5	35.2	22.3	19.6	0.44	2.7
BM-2	28.0	29.4	17.7	27.2	0.35	2.0
BM-3	17.0	30.0	17.7	27.3	0.30	1.7
BM-4	49.6	31.4	19.6	27.6	0.28	1.8
BM-5	100.2	25.6	14.2	32.5	0.10	1.8
BM-6	11.7	28.0	16.0	32.4	0.43	1.4
BM-7	9.5	27.6	15.9	28.0	0.55	2.3

*Modified from Bureau of Mines Report of Investigation No. 4532.

TABLE 3

DRILL HOLE SAMPLE ANALYSES LINEBERRY MINE*

Drill Hole Number	Ore Body Width, Feet	Analysis, percent				
		Fe	S	Insol.	Cu	Zn
H-1	115.0	35.2	18.7	31.4	0.20	
H-2	72.0	40.0	22.7	24.1	0.50	0.55
H-3	6.9	29.8	19.7	28.9	0.32	1.64
H-4	15.5	38.1	21.7	22.4	0.41	0.10
H-5	40.3	35.2	18.7	27.0	0.93	0.26
H-6	22.0	29.9	15.9	33.5	0.36	0.36
H-7	19.8	32.4	16.9	29.6	0.35	0.28
H-8	36.7	26.5	11.6	39.2	0.25	0.06
H-9	4.6	25.4	12.0	37.1	0.20	0.08
H-10	57.8	34.9	19.1	29.8	0.40	0.49
H-11	48.5	24.2	11.4	41.6	0.25	0.35
H-12	5.7	25.6	13.8	38.8	0.41	0.07
H-13	85.3	23.2	10.7	22.1	0.12	0.08
H-14	1.8	29.2	14.6	33.7	0.37	0.19
H-15	33.4	29.4	13.6	16.9	0.14	0.28
H-16	27.5	24.2	11.9	41.6	0.29	0.18
H-17	17.4	29.6	15.5	34.4	0.85	0.14
H-18	18.5	25.7	14.2	38.7	0.30	0.16

*Modified from Bureau of Mines Report of Investigation No. 4532.

Principles of Fluidization

The fluidized state is achieved when a bed of particles is brought into a continuously agitated state by an upward moving fluid. (3) When a stream of gas or liquid is passed through a mass of solid particles, reproducible changes in the physical behavior are observed, and the solids pass through successive stages as the fluid velocity is increased.

Fluidization Stages: When the velocity of a gas or liquid flowing up through a mass of solid particles is insufficient to lift or support any of the solid, the mass is called a fixed bed or a moving bed, depending on whether the solid is stationary or moving with respect to the containing vessel. (4) With slight increases in the fluid velocity, the particles are fully supported and the expanding bed becomes fluidized. Just at the point of fluidization, or the critical mass velocity, the mass may form a quiescent fluidized bed. Finally, if the fluid velocity is still further increased, or if the solids feed rate is sufficiently low, the surface of the fluidized bed disappears and the whole mass becomes a dispersed suspension.

Behavior of a Bed of Solid Particles at the Critical Mass Velocity: At the critical mass velocity, the particles are fully supported by the fluid. Experimental data has indicated that before fluidization can begin, a definite amount of expansion is necessary,

which depends entirely on the original bed density for any one material. The limiting bed density at which fluidization begins has been termed "maximum fluid density," and the fractional voids associated with this condition has been called "minimum fluid voidage."⁽⁵⁾

Important Characteristics of a Fluidized Bed and Solids: The following discussion contains a description of various characteristics of a fluidized bed and solids, including voidage, particle density, and particle diameter.

Voidage: Observations have indicated that a bed of fine, solid particles must have a certain minimum voidage before the particles in the bed are sufficiently disengaged from each other to permit free motion within the bed.⁽⁶⁾ Leva et al noted from a study of fluidization characteristics of an irregularly-shaped, iron, the Fischer-Tropsch catalyst, that minimum fluid voidage depended upon the shape of the particles as well as upon the effective particle diameter.⁽⁷⁾ They further stated that the minimum fluid voidage was greater for sharp, rough particles than for round, smooth particles.⁽⁵⁾ Beds of small particles have larger minimum voidage than do large particles and the actual height of the bed of fixed particles before fluidization does not have any effect on the minimum fluid voidage.⁽⁸⁾

Particle Density: Lewis et al have shown that the critical mass velocity is directly proportional to the density of the solids.⁽¹⁰⁾ Matheson et al noted that increasing the density of the solids increased the maximum bed density.⁽¹¹⁾ Morse found that segregation was favored by increased particle density.⁽¹²⁾ Ketten-
ving et al observed that for a given particle size the mass and heat transfer coefficients increased with increasing particle density because of an increase in slip velocity with particle density.⁽¹³⁾

Particle Diameter: Leva et al reported that the minimum fluid voidage increased with a decrease in particle diameter, and that slugging was favored by large particles.⁽⁶⁾ Similarly, Miller and Logwinuk have shown that the critical mass velocity, for particles of a given density, increased with increasing particle size.⁽¹⁴⁾ Lewis et al observed that for a given length-to-diameter ratio of bed, the pressure drop across fluidized beds increased with an increase in particle size.⁽¹⁵⁾ Leva et al observed that channeling was favored by fine particles, whereas Morse found that the segregation of particles increased with increasing particle size.^(17,16) Also, Leva et al reported that the smooth range of fluidization was larger for small particles than for large ones.⁽⁷⁾

Particle Size Control

The particle size of solids is of critical importance in the fluidization process, because it affects fluidization, solids flow characteristics, bed densities, solids loss, and equipment erosion. The range of sizes used depends on the density of the solids and the nature of the process. Some typical size distributions for fluidization processes are shown in Table 4. (18)

In the operation of the fluidization process, after start-ups or upsets, there may be high solids losses from the system. Temporary failure of the dust recovery equipment may be experienced during start-up before the cyclone dip-legs are sealed in the fluidized bed. In some upsets, pressure surges cause high bed velocities. Under these conditions an elutriation of smaller particles takes place and leaves abnormally high contents of coarse particles in the system. This situation may be rectified in a number of ways. First, there is a natural tendency to restore the equilibrium particle size distribution through attrition of the coarse material. Second, the addition of fresh solids will tend to increase the amounts of fine- and intermediate-sized particles. However, with a high solids hold-up in the system and a relatively low fresh solids make-up rate, as in catalytic processes, considerable time would be required to restore the proper particle size distribution by these means. A third successful method uses high velocity steam jets submerged in the dense phase of the fluidized solids. This increases the rate of attrition of solids considerably, thereby increasing the fine-

TABLE 4

SIZE-WEIGHT DISTRIBUTION

Size US Sieve	Wt.% Rock
+ 20	1-4
20 - 48	24 - 26
48 - 60	20 - 30
60 - 100	20 - 45
100 - 200	0 - 10
- 200	- 0

and intermediate-sized particles and decreasing the number of coarse particles. It should be pointed out, however, that the use of such attrition agents cannot be justified in normal operations since they will increase the loss of solids from the system.

Another example of the importance of particle size control in operating the fluidization process was encountered in a process for the catalytic oxidation of naphthalene to phthalic anhydride utilizing a fluid catalyst. The reaction is exothermic, and heat must be removed from the reaction zone by continuously removing a stream of fluidized solids from the reaction upward through a shell and tube.

It is also possible to reduce the amount of coarse material in the fluidized solids system by selectively withdrawing the coarse particles. An elutriator or density classifier can be used to separate the fine and intermediate particles from the larger and more dense particles.⁽¹⁹⁾ The fine- and intermediate-sized particles are returned to the system and the coarse particles are discarded. Another method depends on an increased concentration of larger and denser particles existing at the bottom of fluidized beds when the peak of the size distribution curve has shifted considerably towards the coarse range. In this case a withdrawal of solids from the bottom of the fluidized bed will selectively remove material having a coarse-particles content greater than the average in the system.

Recovery and Losses of Solids

The loss of solids from fluidized systems can be related to the rate of attrition of the solids. Attrition produces fines which may not be retained by the recovery system. There is a lower limit in the size of particles which are produced because the attrition rate decreases with decreasing particle size, and under 5 microns further reductions in size are negligible. Consequently, if the lower limit of dust recovery remains substantially above 5 to 10 microns, an increase in recovery efficiency will not reduce solids losses appreciably, since the particles will eventually attrite to a size below the minimum retained by the system. When the lower limit of particle size is below approximately 10 microns, an increase in recovery efficiency will result in a considerable reduction of solids losses and accumulation of fines.

Losses may come from fines present in the fresh solids which can not be retained in the system. In addition, the manner in which fresh solids are added to the system may have an effect. It is believed that if fresh solids containing moisture or some volatile material are added to a high temperature system, the sudden vaporization of material in the pores will fracture the particles and produce fines.

Age and Residence Time of Solids

Solids in a fluidization system age during the operation and the effects of this aging are an important process consideration.

The difficulty in determining the effects of residence time and exposure to process conditions is that they are obscured by the continuous losses, withdrawals and additions of solids.

In catalytic processes it is desirable, therefore, to keep an accurate record of catalyst losses and replacement so that the average catalyst age may be calculated. The average catalyst age in a system where there is a loss, withdrawal, and make-up of catalyst, may be calculated from the relationship: ⁽¹⁸⁾

$$A = \frac{1-a}{a} \text{ ----- (A)}$$

where A = average age of solids in the system in days or other units of time.

a = fraction of inventory replaced per day or other unit of time on a fines-free basis.

This applies to systems which have been operating for a considerable length of time and represents the equilibrium average age approached if the replacement rate has been maintained constantly throughout the entire period. It should be noted that the replacement rate is on a fines-free basis, since it can be assumed that fines entering with the make-up will be rapidly lost from the system.

If the replacement rate is not constant and if operating conditions are changed from time to time, the age should be calculated from the following relationship: ⁽¹⁸⁾

$$A = (A_0 + n) r^n - \left[\frac{(r)}{(1-r)} (1-r^{n-1}) - (n-1)r^n \right] \quad (B)$$

where A_0 = average age of solids in the system at the start of run or new operating conditions;

A_0 = A calculated at end of previous run or conditions.

n = number of operating days or unit of time of run,

$r = 1 - a$ = fraction of inventory retained per day or per unit of time.

This relationship is derived from the general equation for average age of solids in a fluidization system expressed as: (18)

$$A = (A_0 + n)r^n + \sum_0^{n-1} ar + 2ar^2 - 3ar^3 \dots \dots \dots + (n-1)ar^{(n-1)} \dots \dots \dots (C)$$

The calculation of catalyst age from the above equations is not entirely rigorous because it assumes that the losses during any period are distributed equally for all particle sizes and ages. This is not true since all solids particles do not attrite equally. The strength and attrition-resistance of particles vary so that the weaker particles fracture at a higher rate and are lost more quickly. There is evidence that the older particles are more dense and attrition-resistant, and, therefore, are lost from the system at a lower than average rate. With older catalyst in the system, there is a greater difference in the attrition-resistance between aged material and the fresh solids resulting in a higher loss of fresh solids.

Heat Transfer

Heat Transfer Between Fluidized System and Surface of Heat

Exchange: The rate of heat transfer between the fluidized system and the surface of heat exchange is closely related to the general behavior and geometry of the fluidized system, the rate of particle mixing within the bed, heat transfer between particles and the adjacent fluids. The rate of heat transfer between the fluidized system and the surface of heat exchange is given by the customary expression: (20)

$$q = hA (t_f - t_w)$$

where h is the heat transfer coefficient between the fluidized system and the surface of heat exchange. This heat transfer coefficient will be governed by the following factors: (10,21)

1. Properties of the materials

Fluidizing fluid -- thermal conductivity, density
viscosity

Fluidizing particles -- thermal conductivity,
shape, size, size distribution, density,
specific heat.

2. Design of fluidization chamber -- location and geometry of heat transfer surface.

3. Operating conditions -- flow rate of fluids, feed or recycling rate of solids, bed height, and concentration of solids in bed, etc.

A complete correlation of the heat transfer coefficient with all of these variables has not yet developed. (20)

Heat Transfer Between Fluidized Bed and External Wall:

Assuming a reversible system, the heat transfer between a fluidized bed and its container wall is described mathematically as:

$$h = 0.0118 \left[\frac{PmG}{D_p^3} \right]^{0.263} \text{----- (D)}$$

For a non-spherical particle, the particle diameter, D_p , is given by:

$$D_p = 6/\delta. \text{----- (F)}$$

where δ is the area of surface per unit volume of a particle.

In view of the postulated mechanism of heat transfer in a fluidized system, Eq. (D) represents some sort of preliminary and empirical correlation which does not include all important variables required for a generalized correlation. The equation is derived from a study of glass beads with diameter of the beads, solid concentration, and velocity of air as the variables. (21)

Heat Transfer Between Fluidized Bed and Internal Surface

Immersed Therein: Mickley and Thrilling indicated a general trend for the heat transfer between fluidized bed and internal surface. (21)

The sets of data are correlated graphically by three dimensionless groups. These dimensionless groups are Nusselt number (hD_p/K), Reynolds number ($D_p U_{mf} \rho / \mu$), and ratio of superficial velocity of the fluid to the minimum superficial velocity necessary for fluidization U/U_{mf} . The Reynolds number ($D_p U_{mf} \rho / \mu$) represents the continuous phase along the immersed heating surface. The ratio of superficial velocities, (U/U_{mf}), could be considered as an index to represent the effect of the particle movement. With the exception of small particles at the lower velocities where channeling is unavoidable, all the points lie close to a straight line represented by: (19)

$$\frac{hD_p}{K} = 3.75 \left(\frac{D_p U_{mf} \rho}{\mu} \log \frac{U}{U_{mf}} \right)^{0.47} \text{-----} (F)$$

Mass Transfer

For the design of a reactor, catalytic reactions have been postulated to take place consecutively in the following steps: (20)

1. Mass transfer of reactants to the exterior surface of catalyst particle from the main body of the fluid.

2. Mass diffusion of reactants into the pore structure of the catalyst particle.
3. Activated adsorption of reactants at the interface of catalyst.
4. Chemical reaction between activated reactants adsorbed at the interface.
5. Activated desorption of products at the catalytic inter-surface.
6. Mass diffusion of products out of the pore structure of the catalyst particle.
7. Mass transfer of products from the gross exterior surface of catalyst to the main body of fluid.

The rate of mass transfer of a given system under a fixed condition of operation is characterized by the mass transfer coefficient. For the mass transfer across the fluid film between solid surface and fluidizing fluid, the transfer coefficients of mass are defined by the following equation:

Gas as fluidizing fluid

$$K_g = \frac{dN}{dA} \frac{1}{P - P_i} \text{----- (G)}$$

In the case of gas, the driving force of the mass transfer is given by the difference of partial pressures of adsorbate between the main body of fluid and solid surface, $P - P_i$.

A convenient method for relating the mass transfer coefficient and physical properties of the fluid is through a dimensionless

group. For a dilute solution, mass transfer factor, J_d , is defined by:

$$J_d = \frac{P_{BM} K_g}{G/M_g} \left(\frac{\mu}{\rho D} \right)^{2/3} \text{----- (H)}$$

where M_g is the molecular weight of the fluidizing gas, P_{BM} is the average pressure of the inert gas not involved in diffusion.

$(\mu / \rho D)$ represents Schmidt's number, another dimensionless group which consists of viscosity, μ , density ρ , and diffusivity, D . The subscript g refers to gas phase. (20)

Mathematical Correlations

Great differences exist in the methods employed by various investigators in making experimental measurements for particle size, density measurements, fraction voids, and the like. (21) Each time a new investigation on fluidization is planned, it is necessary to specify the procedure to be followed in detail. Campbell explained that many of the mathematical relationships developed in fluidization are satisfactory for commercial use, yet they are unsafe in universal applications. The mathematical correlations to be discussed are the determination of particle diameter, particle density, and fraction voids.

Determination of Particle Diameter: The Gregg and Gress methods for determining the average diameter of spherical particles are probably the best and easiest methods if the particles are uniform in shape. (23)

Gregg has presented a method for determining particle size based on the average projected length and breadth of at least 20 representative particles. (23) Gregg's expression may be stated as follows:

$$D_p = \sqrt{\frac{4 \times C \times B \times L}{\pi}} \text{----- (I)}$$

D_p = average particle size, inches.

B = average breadth or width or the particle perpendicular to the longest axis of the particles, inches.

L = average length of the particles along the longest axis of the particles, inches.

C = an experimentally determined constant equal to 0.77 for rounded particles and 0.75 for rough particles, dimensionless.

Gregg has pointed out that the average breadth, B , is related to the size of the aperture in a sieve through which the particles will pass.

Particle Density: The density or specific gravity of solids is generally obtained by means of water displacement using pycnometers or various specific gravity methods which are available for this purpose. (18) The equation used is as follows:

$$\rho_p = \frac{W_1 \times S_1 \times d_1}{W_2 - W_3 \left(\frac{S_1}{S_2} \right)} \text{----- (J)}$$

where:

ρ_p = absolute density of solid particles, lb/cu.ft.

W_1 = dry weight of solids, gm.

S_2 & S_1 = specific gravity of water at temperature T_1 and T_2

d_1 = density of water at temperature T_1 , lb/cu.ft.

W_2 = weight of water to fill gravity bottle at T_1 , gm

W_3 = weight of water to fill gravity bottle at temperature T_2 minus weight of water displaced by solid particles at temperature T_2 , gm

Voidage: The fraction voidage volume within a bed of solids may be obtained from the following equation: (14)

$$\gamma = (L - L_0)/L \text{ ----- (K)}$$

where:

γ = fraction voids, dimensionless

L = height of bed containing voids in feet

L_0 = height of voidless bed, in feet

$$L_0 = W/\rho_p A$$

where: W = weight of solids charged into vessel, lb.

ρ_p = absolute density of solids, lb./cu.ft.

A = cross-sectional area of vessel, sq.ft.

Physical Consideration of Separation

There are three methods available for separation of the Great Gossan Lead Ore. They are froth flotation, sink-float, and magnetic separation.

Froth Flotation: Flotation may be defined as a method of materials separation developed for the concentration of metallic minerals.⁽²⁵⁾ Its principle depends on the affinity of air bubbles for properly prepared mineral surfaces. In froth flotation, a froth is formed by introducing air into a pulp of the finely divided ore and water which contains a frothing agent. Those minerals that have an affinity for air bubbles rise to the surface in the froth and are thus removed from those that are completely wetted. The frothing agents that are most commonly used for bubble stabilization are tall oil, pine oil and cresylic acid.⁽²⁶⁾ The substances which cause air bubbles to adhere to the material which is to be floated are termed collectors. The choice of collectors in a flotation process depends upon the materials to be separated.

Much work concerning the froth flotation of pyrrhotite has been done at the Virginia Polytechnic Institute. Corriveau has stated that bulk sulfide concentrates are available recovering 98 percent of the sulfide and assaying 49.5 percent iron, 36.1 percent sulfur, 3.3 percent zinc, 0.87 percent copper and 0.67

percent lead.⁽²⁾ However, the differential flotation of the individual sulfides would require extremely fine grinding. The significance of this is that in order to obtain high grade concentrates, recovery will have to be sacrificed or vice versa.

Sink-Float: Technically, the simplest and most effective method of separating a mixture of particles of different specific gravities is to suspend them in a liquid of intermediate density, whereupon the heavier particles sink and the lighter float.

As a commercial operation, however, the sink-float method has definite limitations imposed by the lower size limit of particles which can be handled. Material finer than three-sixteenths of an inch introduces complicated changes in medium viscosity, which affect the sharpness of separation and further introduces problem in the removal of medium from the products. For this reason, sink-float is most effective for materials for which the size of liberation is above three-sixteenths of an inch.

Magnetic Separation: The art of separating one substance from another by means of a magnetic field is called magnetic separation. The art and machines developed for making such separations are highly specialized.⁽²¹⁾ Minerals and metallic substances which are permeable to some extent and which are attracted by a magnetic field are called paramagnetic, and the relatively few that are repulsed are classified as diamagnetic.

Paramagnetic substances are usually classified into three groups, namely, strongly magnetic or ferro-magnetic (magnetite, ilmenite), weakly magnetic (hematite, pyrolusite), and nonmagnetic (quartz or calcite). (27)

In order to obtain statistical information for the limited concentration obtained by the initial differential flotation tests, magnetic fractionations were carried out on the -324 +400 mesh size fraction of the reground bulk sulfide concentrate using a Frantz Isodynamic separator. (2) In the execution of the fractionations, overlapping due to locked particles can be expected. Furthermore, it is known that the magnetic susceptibility of pyrrhotite varies with its composition and also not to be ignored is the fact that the difficulties in separation are magnified by the preponderance of such a magnetic mineral as pyrrhotite. (2)

Chemical Consideration of Separation

Roasting

Roasting can be defined as heating sulfide ores in the presence of air below the fusion point of the constituent minerals but at such temperatures which will convert metallic sulfides to oxides.

Material to be leached is roasted (heated in contact with air to oxidize sulfides to oxides or sulfates) for one or more of the following reasons.

1. To convert the metal into a soluble form.
2. To volatilize certain soluble impurities that could contaminate the solution.
3. To render the metallic compounds porous so that they are readily attacked by the solvent.

The roasting temperature must be accurately regulated, if it is too low, iron will be solubilized and if too high, some of the copper will be rendered insoluble. (28)

The quantity of sulfate found in the reaction products does not always correspond to the actually created quantity, since the formation and decomposition reactions of sulfates are combined. Depending on the conditions under which the process is conducted, these reactions may have different velocities, which can result in the accumulation or in the disappearance of sulfate in the products of oxidation. The raising of the oxygen concentration promotes the formation of sulfate according to the reaction previously cited. (4)

The chemical stability of the sulfate is of great importance. Thus lead sulfate may be more easily detected at calcination temperature than zinc sulfate. For accumulating the latter in the products of oxidation special fixation mixtures are required to slow down its decomposition, (for example, Na_2SO_4), or the partial pressure of O_2 can be increased, so as to shift the equilibrium of the reaction (4) and (10), from right to left. As a consequence

of the reaction between the metal sulfide and its sulfate, sulfur gas and metal are formed.

The separation of SO_2 according to equation (5), on page 45, may pass through a series of intermediate stages. As a result of one of these intermediate phases an unstable compound-- sulfur monoxide -- is formed, which has been observed by N. P. Diev, and A. N. Okunev as being an intermediate product of the oxidation of some sulfides.

Thornhill, P. G. and Pidgeon, L. M. found that the pyrrhotite, on the other hand, roasted at measurable rates over a relatively wide temperature range. (29) When 65 to 80 mesh particles of this mineral were roasted linearly at 550°C ., the oxidation rate of the 30 to 40 mesh particles was retarded after the formation of about 160 times of oxide. The oxidation rates, in the linear parts of the rate curves, are given in Table 5.

They concluded that the pyrrhotite used in their experimental work probably falls into the latter class, since in this case the defect structure is obtained at the outset. Accurate lattice parameter measurements were not made on the partially roasted sulfide to determine whether the sulfide kernels had suffered further depletion in iron. Determination of the roasting rates by measurement of the thickness of oxide shells was successfully done only in the case of sphalerite and pyrrhotite. The columnar nature of the sulfide-oxide interfaces obtained in the pyrrhotite roast rendered

TABLE 5

Oxidation of Pyrrhotite

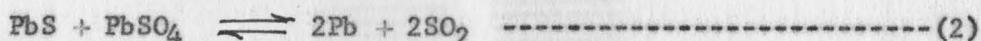
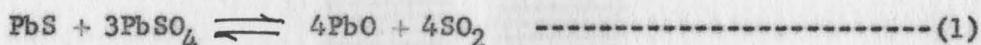
Mesh	Thermal Average Particle Diameter	Temp. $^{\circ}$	Oxidation Rate μ per minute
30-40	500 μ	502	0.14
		532	1.40
		550	2.00
65-80	190 μ	550	2.55

accurate measurement difficult and even impossible. On the other hand, kinetic studies on the roasting of those sulfides which undergo selective oxidation are understandably complicated by the fact that the oxidation takes place according to the mechanisms which differ from one stage of a roast to the next, and the irregular nature of the multi-layered oxides on products precluded all but the roughest estimation of oxidation rates. (30)

In summing up; all of the reactions of the sulfides with sulfates and of the sulfides with oxides of the various metals, one can see that the first groups (i.e., the interaction of MeS with MeSO_4), proceeds at a faster rate and at a lower temperature.

Kinetics of Roasting: In the early stage of investigations the kinetics of this process were studied. The influence of the oxygen concentration and of the temperature on the rate of oxidation of sulfides was in most cases characterized by the degree of desulfurization, i.e., the amount of sulfurous gas liberated during oxidation. The stages of this process taken separately were not investigated. The next step was the study of the chemistry and of the mechanics of the oxidation process of sulfides.

The principle of the kinetics of roasting is illustrated by the work of G. G. Urazov and L. R. Edel'son⁽³¹⁾ who studied the reactions of lead sulfide with lead sulfate, and found that considering the following two possible equations:



the reaction proceeds more successfully according to equation (2), because in this case a considerably higher partial pressure of sulfurous gas is developed, whereas in equation (1) the reaction equilibrium is shifted from right to left and the reaction sharply comes to an end.

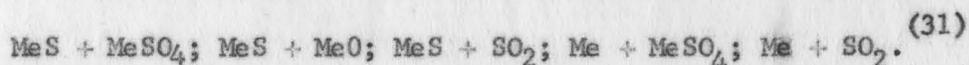
Later on, V. D. Ponomarev and I. R. Polyvyanyi, who studied the kinetics of the reactions of lead sulfide with sulfate according to the same stoichiometric equation, showed that in the range of 600-900°C. the reaction proceeds vigorously enough, but at temperatures in excess of 700°C. the reaction according to equation (1) proceeds very rapidly.⁽³¹⁾ In addition it was established that the interaction of sulfide with sulfate is imperative for oxidizing and agglomerating calcination in layers.

V. D. Ponomarev and I. R. Polyvyanyi, also studied the kinetics of the oxidation of lead sulfides by atmospheric oxygen and established that this process is characterized by a kinetic phase and a diffusion phase with the borderline at 700°C. The mechanics of oxidation of lead sulfide changes when passing from lower to higher temperatures.

Mechanics of oxidation of sulfides: The different opinions on the reaction of sulfide with oxygen may be summarized as follows:

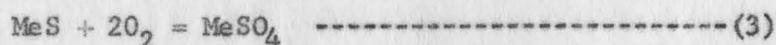
1. According to the so-called oxide theory, metal sulfides reacting with oxygen are directly oxidized to oxides. The sulfates are a formation originating from the reaction of metallic oxides with sulfur oxides.
2. Another so-called sulfate theory claims that the oxidation of sulfides goes through an intermediate stage of sulfates formation, the decomposition of which results in metal oxides and sulfur.
3. There is also a third view, according to which the mechanics of sulfide oxidation is dependent on temperatures: at a low temperature the primary product of oxidation is sulfate, while at a high temperature oxidation proceeds directly to oxides with intermediate sulfate formation.

Danilova studied the reactions in the Me-S-O system:

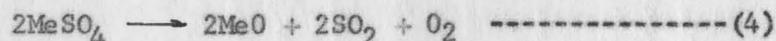


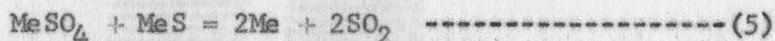
This investigation was made to establish the chemistry of the interactions between the sulfides of heavy metals and oxygen, which may be represented by the following basic reactions:

Oxidation of sulfide to sulfate:

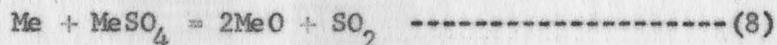
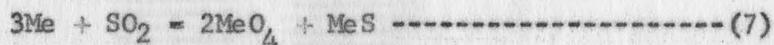
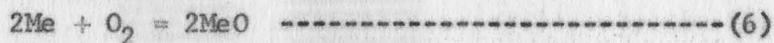


Decomposition of Sulfate:





Oxidation of metal:



Roasting Reaction of Ferrous Sulfide: K. Niwa, T. Wada, and Y. Shiraishi studied the rate and mechanism of oxidation of ferrous sulfide by means of the spring balance and X-ray diffraction analysis over the temperature range from 500° to 700°C. The results of their investigations are as follows:⁽³²⁾

1. The complete oxidation to oxides begins at 600°C.
2. At the initial stage of oxidation, a slight increase of weight was found. It was observed by X-ray techniques that the deficiency of the iron ion in FeS occurs in this stage. This is interpreted as follows: iron ion reacts with oxygen by migrating from the interior of the FeS crystal to the surface, without evolution of SO₂, until the deficiency of iron attains a limiting value.
3. Above 600°C. the rate of oxidation does not change with temperature, so the rate-determining factor is diffusion of gas. Since the observed rate of oxidation depends upon the quantity of the sample, the diffusion in the bed of sample may determine the rate.

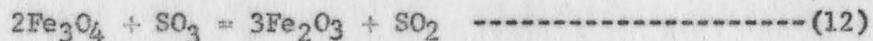
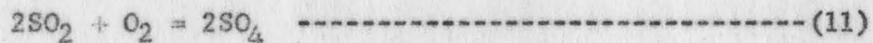
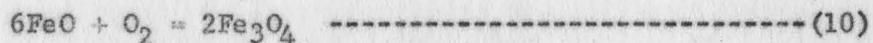
Advantages of Roasting: The advantages in roasting when operating under autoclave conditions are:

1. Greatly increased rates of the reaction.
2. Favorable displacement of thermodynamic equilibrium.
3. The possibility of using certain gaseous or highly volatile reagents such as C_2 , H_2 .

Together with the application of high temperature, high pressure techniques are also used.

1. The direct leaching of Cu and Zn sulfides with acid (H_2SO_4) is generated by autoxidation of the sulfides.
2. The precipitate of metallic Cu and Zn from aqueous solutions of their salts by hydrogen reduction.

Roasting of Iron Sulfide: V. I. Smirnov indicated the following scheme for oxidation of iron sulfide:

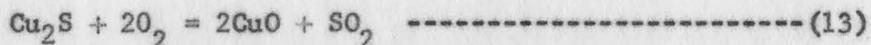


G. I. Chufarov and B. D. Averbukh found that oxidizing of iron sulfide by oxygen at low temperatures results in a first reaction of oxidation representing an association of the oxygen with the sulfide to form sulfate. ⁽³¹⁾ The sulfate is strongly dissociated at temperatures above 450°C. Products of reaction

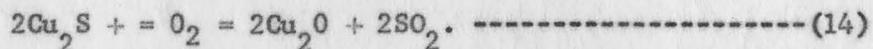
are Fe_2O_3 and Fe_3O_4 ; and the ratio of $\text{Fe}_2\text{O}_3:\text{Fe}_3\text{O}_4$ increases with the burning of sulfur. The gradual rise of the extent of iron oxidation in the course of calcination leads to the assumption that an intermediate metallic phase was formed, which was gradually oxidized to ferrous, ferrosulferric and ferric oxide.

V. I. Smironev also confirmed the sulfate theory which explains the mechanics of oxidation as follows: at first sulfates are formed due to adsorption of oxygen at the surface of crystals and then by the atomic dissociation of oxygen molecules and the penetration of oxygen into the crystal lattice of the sulfide. (31)
At 620-650°C. the sulfate formed on the surface interacts with the sulfide and as a result of this an oxide film is formed and sulfur gas is liberated.

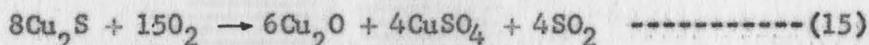
Roasting of Cupric Sulfate: N. P. Diev and Yu. V. Karyakin expressed similar views in their earlier works on oxidation of sulfides with oxygen-enriched air. They assumed that an oxidizing cuprous sulfide, the basic reactions depending on oxygen content are: (31)



or

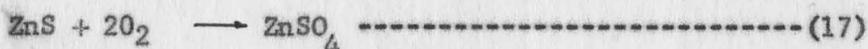
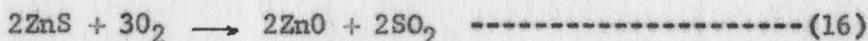


Since, however, secondary reactions could take place between cuprous sulfide and the products of oxidation so formed, the total reaction of oxidation could be expressed by the following equation:



Therefore, metallic copper does not react with sulfurous gas within the temperature range between 20-1290°C. in the absence of oxidizing or reducing agents. This is why in the calcination process of sulfides, metallic copper and lead are present in the reaction products, while zinc is never detected.

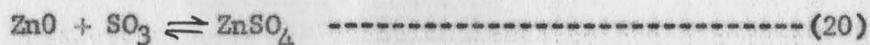
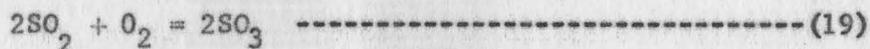
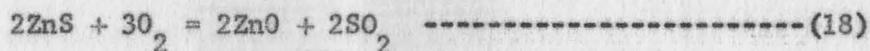
Roasting of Zinc Sulfide: Zinc concentrate containing sphalerite is roasted in multiple hearth furnaces, and the following reactions take place: ⁽¹⁶⁾



The roasting temperature is low in order to form some ZnSO_4 (water -- soluble zinc) and also to prevent the formation of zinc ferrite (ZnFe_2O_4). The ferrites are practically insoluble in the solvents used ($\text{H}_2\text{O} + \text{H}_2\text{SO}_4$), so that any zinc in this form is not recovered. In the treatment of zinc minerals the fluidized-bed roasting technique has been applied as a preparation for leaching.

With marmatite, $(\text{Zn}, \text{Fe})\text{S}$, it is very difficult to prevent the formation of a certain amount of zinc ferrite.

Regarding the mechanics of oxidation of zinc sulfide, most investigators support the oxide theory, that ZnS is oxidized as follows:



The possibility of the formation of ZnSO_4 through the oxidation of ZnS together with the indirect sulfate formation from zinc and sulfur oxide was assumed as early as 1911 by V. Ya. Mostovich. ⁽³¹⁾ He later confirmed the possibility of direct formation of sulfate from the sulfide by oxidation of lead sulfide.

Leaching

Leaching consists of placing oxidized minerals in solution with the addition of an appropriate solvent under specific conditions. Oxidation results in a loss of electrons in oxidizing agents such as oxygen, chlorine, and nitric oxide. These substances require electrons to achieve their most stable state, and therefore will actively remove electrons from minerals, forming charged metallic ions in solutions.

In recent years, interest in hydrometallurgical processes has been greatly intensified. Many of the newer developments in this field involve leaching operations which are conducted at elevated temperatures and elevated pressures. Some of the obvious advantages which may be derived through the use of such techniques are: ⁽³³⁾

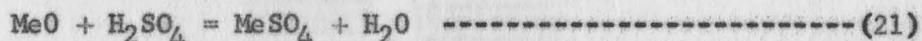
1. The rate of reaction is increased by operating at temperatures above the boiling point of the leach solution.
2. Chemical reactions will proceed rapidly at high pressure and temperatures.
3. Chemical reactions can be effectively carried out only in closed vessels under pressure.
4. It is possible to use certain gaseous or highly volatile reagents such as O_2 , H_2 , and NH_3 .
5. Favorable displacement of thermodynamic equilibrium. (32)

Under the high temperature and pressure of this process the ore will be leached with sulfuric acid, for which the skillful handling of acid becomes a distinct feature.

In a sulfuric acid solution, the reacting species may be H^+ , HSO_4^- , SO_4^{2-} , or the undissociated H_2SO_4 . Only one of the species is likely to be involved in the slow steps of the reaction. It is assumed that there is very little dissociation of the bisulfate ion, and that the dissociation of sulfuric acid to bisulfate ion and hydrogen ion is nearly complete. Only the H^+ ion is directly associated with the surface reaction and the effects of the HSO_4^- , SO_4^{2-} , and undissociated H_2SO_4 are secondary.

The effective factors considered are leaching time, temperature, pressure and concentration of H_2SO_4 .

Dilute sulfuric acid is used in the forming of solutions from oxidized metals. The chemical reaction is: ⁽³⁴⁾



Thermodynamic Consideration: By the use of thermodynamics it is possible to define the equilibrium in a chemical system and to predict how the equilibrium will shift with changing conditions such as temperature, pressure, concentration, etc. In general an increase in the concentrations or partial pressures of the reactants will shift the equilibrium of a reaction in the forward direction, while an increase in the concentrations of the products will have the reverse effect. Where any of the reactants or products are gases or highly volatile substances, the role of pressure in influencing the thermodynamics becomes readily apparent. The principles and procedures involved in such thermodynamic calculations are well known, and several comprehensive tabulations of thermochemical data are available.

The thermodynamic aspects of a number of systems of hydro-metallurgical interest were discussed in detail by Pourbaix and conveniently represented by him in the form of potential-pH diagrams. ⁽³⁵⁾ A typical diagram for the system, Cu-H₂O, defining the regions of stability of different forms of copper as functions of the potential and pH, is shown in Fig. 2. ⁽³⁴⁾

On the same diagram the thermodynamics of the reduction of oxygen (at 1 atm) are represented by:

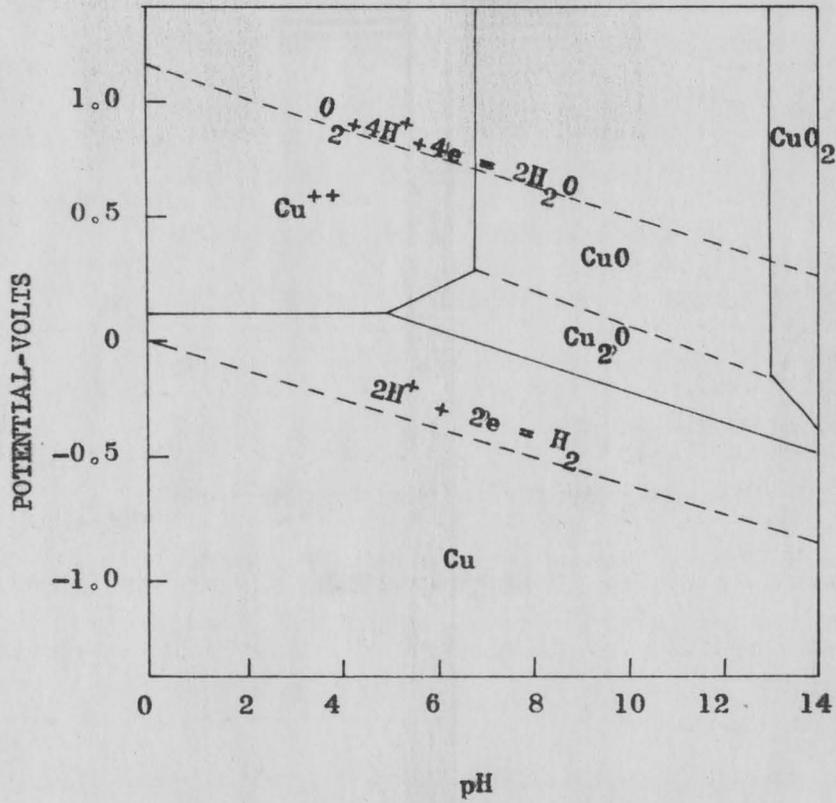
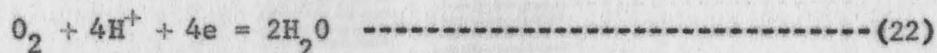
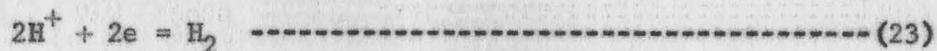


FIGURE 2. POTENTIAL-pH DIAGRAM FOR THE
Cu-H₂O SYSTEM

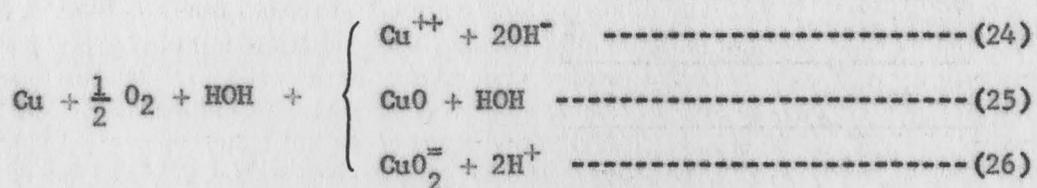


and the oxidation of hydrogen (at 1 atm) is:



From the diagram the following thermodynamic information is readily apparent. (35)

1. Throughout the pH range considered (0 to 14) metallic copper is thermodynamically stable in contact with an aqueous solution, in the absence of oxygen or other oxidizing agents.
2. Oxidation of the copper can be effected by gaseous oxygen at ordinary pressures, since the potential for the reduction of oxygen lies well above that for the oxidation of copper throughout the diagram. Several oxidation products are possible, corresponding to different reaction paths, which may be represented as:



In the pH region between 6 and 13, the insoluble oxides, Cu_2O and CuO are thermodynamically favored, while at lower and higher pH values, the copper can dissolve as Cu^{++} and $\text{CuO}_2^=$, respectively.

3. All the oxidized forms are thermodynamically reducible to metallic copper by gaseous hydrogen at ordinary pressures, since the potential for the oxidation of hydrogen lies well below that for copper throughout the diagram. (34)

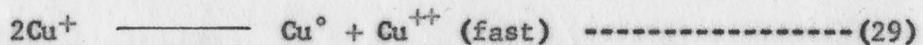
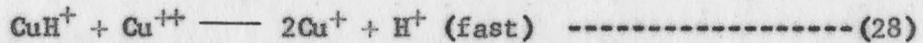
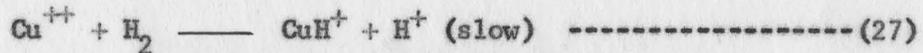
Kinetic Considerations: Hydrometallurgical processes in general, and the leaching reaction in particular, can be conducted under conditions in which the thermodynamics are very favorable and the limitations are therefore largely of a kinetic nature. In particular, where the thermodynamics of several alternative reactions do not differ greatly, kinetic factors may determine what products are formed. Because of these considerations, it appears increasingly important to understand the kinetic aspects of hydrometallurgical processes.

Most hydrometallurgical processes involve heterogeneous reactions occurring at a solid-liquid interface. Most of the heterogeneous reactions of interest in the present connection may be regarded as involving the following sequence of steps: (36)

1. absorption of gaseous reactants, if any, by the solution;
2. transport of dissolved reactants from the main body of the solution to the solid-solution interface;
3. adsorption of reactants on the solid surface;
4. reaction on the surface;

5. desorption of the soluble products from the surface;
and
6. transport of the desorbed products into the main body
of the solution.

For example, Forward and Halpern found that the cupric salts can react homogeneously with hydrogen in aqueous solutions under certain conditions, and hence no catalyst is required to initiate the reduction.⁽³⁸⁾ The homogeneous reaction proceeds rapidly above 100°C. and the rate is directly proportional to the concentrations of Cu^{++} and of H_2 . In the light of recent kinetic studies, it seems probable that in the overall reduction of Cu^{++} , the following sequence of steps occurs:



In conclusion, it is observed that the hydrometallurgical processes are more closely related to ore dressing than any other extractive method.

In hydrometallurgy, as the name implies, the solvent is either water or an aqueous solution, containing nonaqueous solvents to abstract dissolved metals from the aqueous leaching solution.

Hydrometallurgical methods have made considerable progress in recent years owing both to the improvement in practice and to the fact that hydrometallurgy is particularly suited to the treatment

of many low-grade ores. In addition hydrometallurgy is a very important method of treating sulfide zinc concentrates. (39)

Pressure Leaching and Precipitation: For the past several years there has been an intensive study made of leaching in autoclaves where the leaching process can be conducted under high pressures and with higher temperatures than are possible in open vat leaching.

There are two advantages to pressure leaching at atmospheric pressure:

1. It permits much greater concentration of gaseous reagents such as O_2 and H_2 .
2. It permits higher operating temperatures which usually mean much faster dissolutions.

Practically, leaching and precipitation can not be carried on at excessively high temperatures because the materials will not stay in solution, also excessively high temperatures would require extremely high pressures.

Leaching Rate and Contact Time: There are two main reasons for the high initial rate of dissolution; the concentration of the solvent is usually at a minimum, and the greatest possible surface of soluble mineral is exposed. As dissolution proceeds, however, the rate slows down for a number of reasons -- the small minerals dissolve completely and thus greatly decrease the active surface of contact; the strength of the solvent may be depleted; and the minerals that

remain may be almost completely encased in gangue minerals so that they present very little surface to the solvent. Most of the dissolution takes place in the early stages of leaching. In practice we can never get 100 percent extraction and we must decide on the extraction time that will give the maximum economic return. (39)

Systems Consisting of Solid and Liquid Phases: It is well recognized that the rate of solution of solute in a solvent is greatly accelerated by pulverizing the material so as to expose a larger area to the solvent. Quite apart from this effect, the actual equilibrium solubility of very small crystals is greater than that of large crystals. The greater solubility of the very small crystal is analogous to the higher vapor pressure of small droplets of liquid. This increase in solubility with decreasing size is not a significant factor unless the crystals are extremely small. However, if a mixture of large crystals and very small ones is allowed to stand, the small ones disappear and the larger ones grow larger. (36)

Rate of Solution of Solid: The rate at which solids dissolve in an unsaturated solution depends upon the concentration gradient in the immediate vicinity of the solid and upon the surface area of the solid. The latter fact is sometimes called Wenzel's Law.

The first substantial treatment of the problem of the reaction velocity at a solid-liquid interface, by Noyes and Whitney, led to the following reaction: (40,41)

$$\frac{dc}{dt} = m (C_s - C) \text{ ----- (L)}$$

in which C is the concentration in the bulk of the solution at time t ; C_s is the saturation concentration; and m is a constant of proportionality; only if the experimental conditions remain the same -- specifically if the surface area of the solid stays the same and if the thickness of the viscously flowing film adjacent to the solid does not change.

It is convenient to express the change in concentration with time dc/dt , in terms of the velocity constant k and of the ratio v/s of the volume of solution to the proposed interface.

$$\frac{dc}{dt} = \frac{K}{v/s} (C_s - C) \text{ ----- (M)}$$

This equation on the rearrangement of the variable and integration gives:

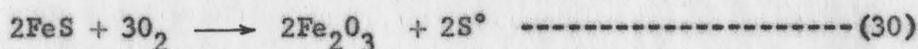
$$K = \frac{V}{S\theta} \ln \frac{C_s - C_1}{C_s - C_2} \text{ ----- (N)}$$

in which C_1 and C_2 are the initial and terminal concentrations; C_s is the saturation concentration and θ is the elapsed time. In equation (N), S is expressed in square centimeters, V in cu, cm, θ in minutes, K in cm per minute, and the various C 's in any consonant units, such as grams per liter.

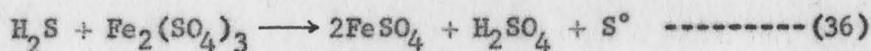
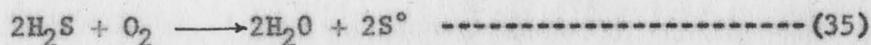
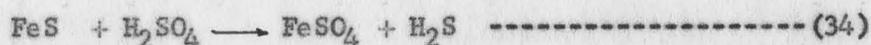
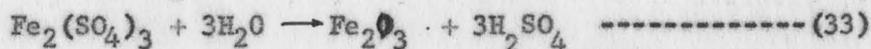
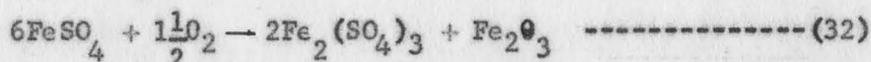
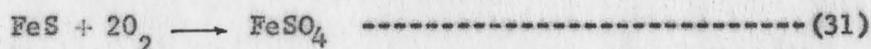
It is interesting to observe that equations (M) and (N) take no account of the effect of agitation on the dissolution velocity constant K . For the case of rotary stirring at 400 rpm and on an

exposed horizontal surface of the crystal estimated at being below the impeller, the "International Critical Tables" gives K values that range between 0.18 for potassium iodide and 0.021 for hydrated calcium sulphate (gypsum).⁽⁴²⁾

Leaching of the Ferric Oxide: The oxidation of iron sulfides has also been studied in neutral and acid solutions. At temperatures of 100° to 125°C., with moderately high oxygen pressures and with a solution pH below 1.5, pyrrhotite reacts to form elemental sulfur.⁽³⁶⁾

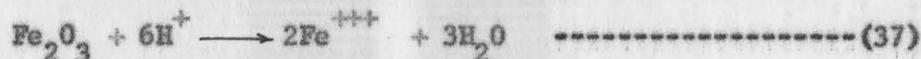


While the kinetics of the reaction have not been investigated in detail, the following mechanism has tentatively been proposed to explain the results:



This mechanism is intended to account for the fact that no elemental sulfur is observed to form unless a solution pH of below about 1.5 is established. At temperatures below 130°C. only about 10 to 15 pct of the sulfur is oxidized to sulfate form.

Fryor and Evans investigated the decomposition of ferric oxide by aqueous solutions of various acids. Hydrated oxide dissolved readily in most acids as follows:



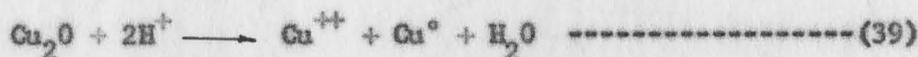
but the reaction proceeds very slowly even under the most favorable thermodynamic conditions. Acids whose anions form complexes with Fe^{++} decompose the oxide more rapidly than those of non-complexing anions.

Leaching of the Cupric Oxides: The thermodynamics of this system have been discussed and are summarized in the form of potential -pH diagram in Fig. 2.

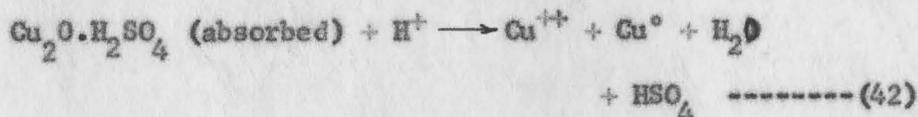
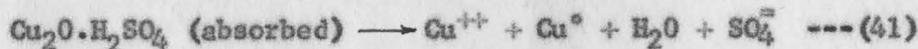
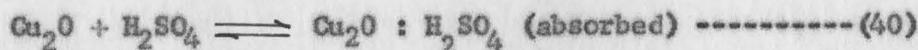
The reaction involving acid solutions in the presence of oxygen is:



Wadsworth and Wedia have examined the decomposition of cuprite by sulfuric acid solutions. The reaction is represented by:

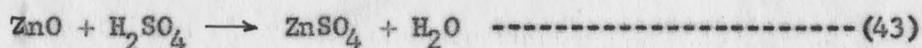


The following mechanism has been proposed to explain the kinetics:



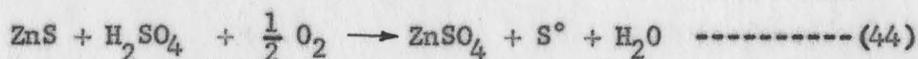
This may occur either through reaction (41) or (42), with the rates being additive. Also results of a series of tests, carried out at variable rates of stirring, showed that the stirring effect was eliminated above 300 rpm. (34)

Leaching of the Zinc Oxide: Current hydrometallurgical practice for treating zinc sulfide concentrates in order to produce a high-grade zinc product involves roasting the concentrate to zinc oxide or sulfate. Dilute sulfuric acid is used in the dissolution of oxidized zinc according to the reaction:



Many investigators have studied the recovery of zinc by the direct leaching of zinc sulfide at elevated temperatures and pressures. (10)

Bjorling mentioned the reaction:

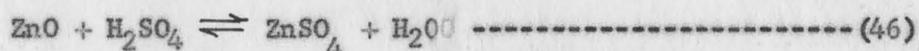
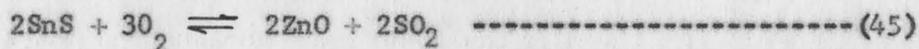


and found that the ZnS can readily be oxidized quantitatively to Zn^{++} and S° in a solution containing H_2SO_4 in sufficient amounts to combine stoichiometrically with the zinc in ZnS without nitric acid being present. (43)

H. Veltman and F. A. Forward found that leaching a zinc concentrate with an oxygen over-pressure of 20 psi for four hours extracts 97 percent of the zinc when about one pound of sulfuric acid per pound of zinc sulfide was added to the autoclave. (44)

The pulp density was 14 percent, As the zinc concentrate used in this experiment contained marmatite (Zn,Fe)S, it is apparent that the substitution of some iron in the ZnS lattice does not adversely affect the progress of the reaction. The galena (PbS) reaction with H_2SO_4 is more rapid than the corresponding reaction with ZnS and reaches equilibrium by the time 5 percent of ZnS has reacted. Therefore, in most of the experiments described, a stoichiometric amount of H_2SO_4 was also added for the lead present. (44)

M. H. Stanczyk and G. Rampacek have shown that leaching a concentrate assaying 55 percent Zn, 32 percent S, 6 percent Fe, and containing minor quantities of copper with the equivalent at 0.25 pound of H_2SO_4 per pound of contained zinc sulfide was obligatory for high zinc extraction. The typical reaction between zinc sulfide and sulfuric acid is shown as follows:



When using an adequate H_2SO_4 and maintaining a temperature of at least 200°C., about 96 percent of zinc was extracted in one-hour providing the pulp was maintained at 10 percent solids. A minimum partial pressure of 75 psi of oxygen sufficed for good zinc sulfide dissolution. Pulp agitation was not critical, but the best extraction was obtained at impeller speeds of 1000 rpm. (45)

EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was to study the possibility of enriching the iron content of a complex sulfide ore from the Betty Baker Mine, Great Gossan Lead, Carroll County, Virginia, by employing a combination of fluidized roasting with high temperature and high pressure leaching processes. The satisfactory conditions for each of these processes were investigated with regard to the concentration of sulfuric acid and the temperature of the operational processes.

Plan of Experiment

The plan of experimentation included a study of the physical and chemical treatments required for the recovery of iron by removing impurities such as copper and zinc.

Physical Treatment - A flow sheet showing the present physical treatment of the complex sulfide ore is given in Fig. 3. Closed circuit crushing by roll mill was employed to reduce the particle size of the sample to pass through a 14 mesh screen. The particles were then classified according to size. The fine particles undergo flotation and the coarse ones were tabled. This physical treatment removes the impurities from the ore by mechanical means.

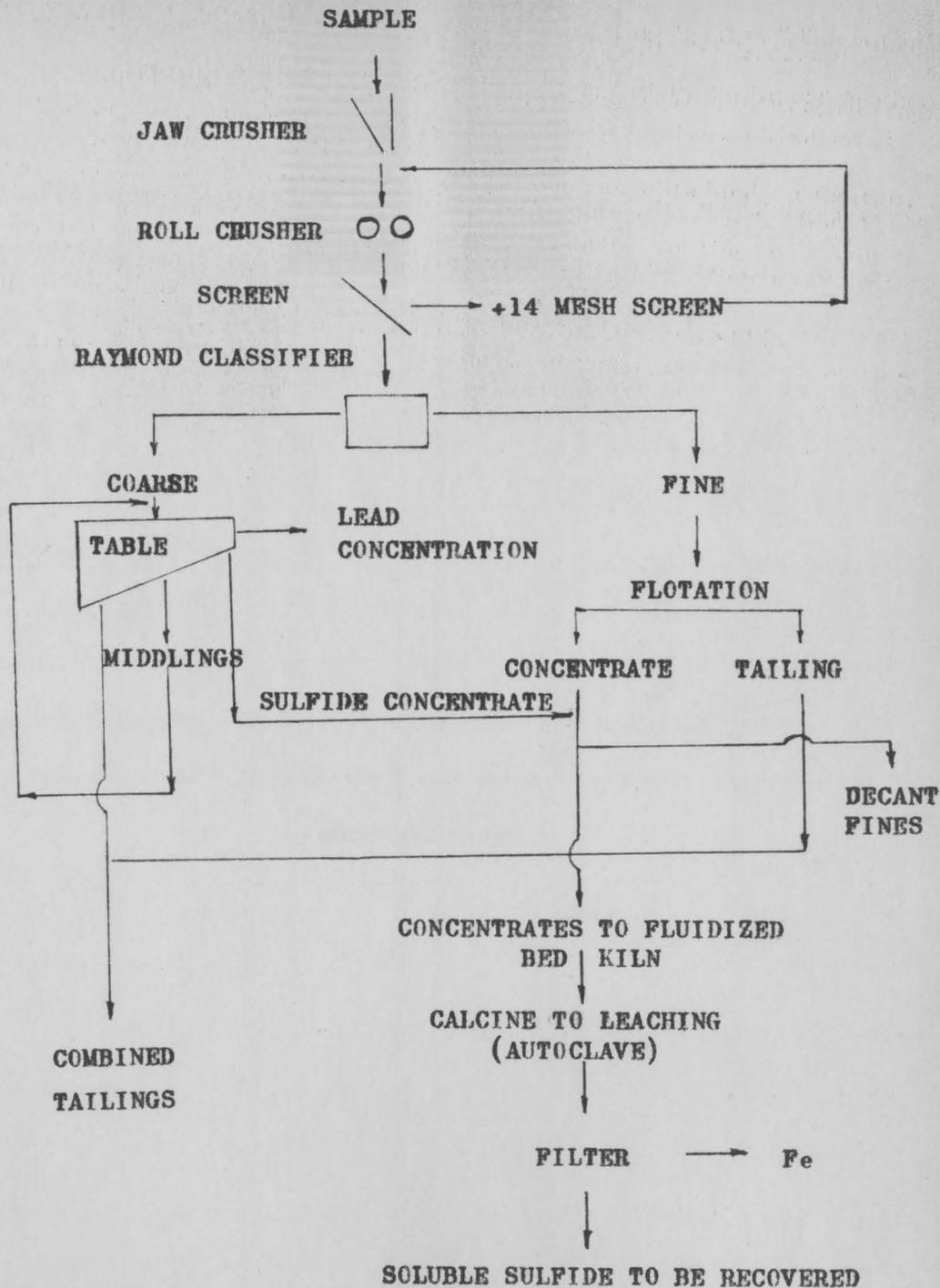
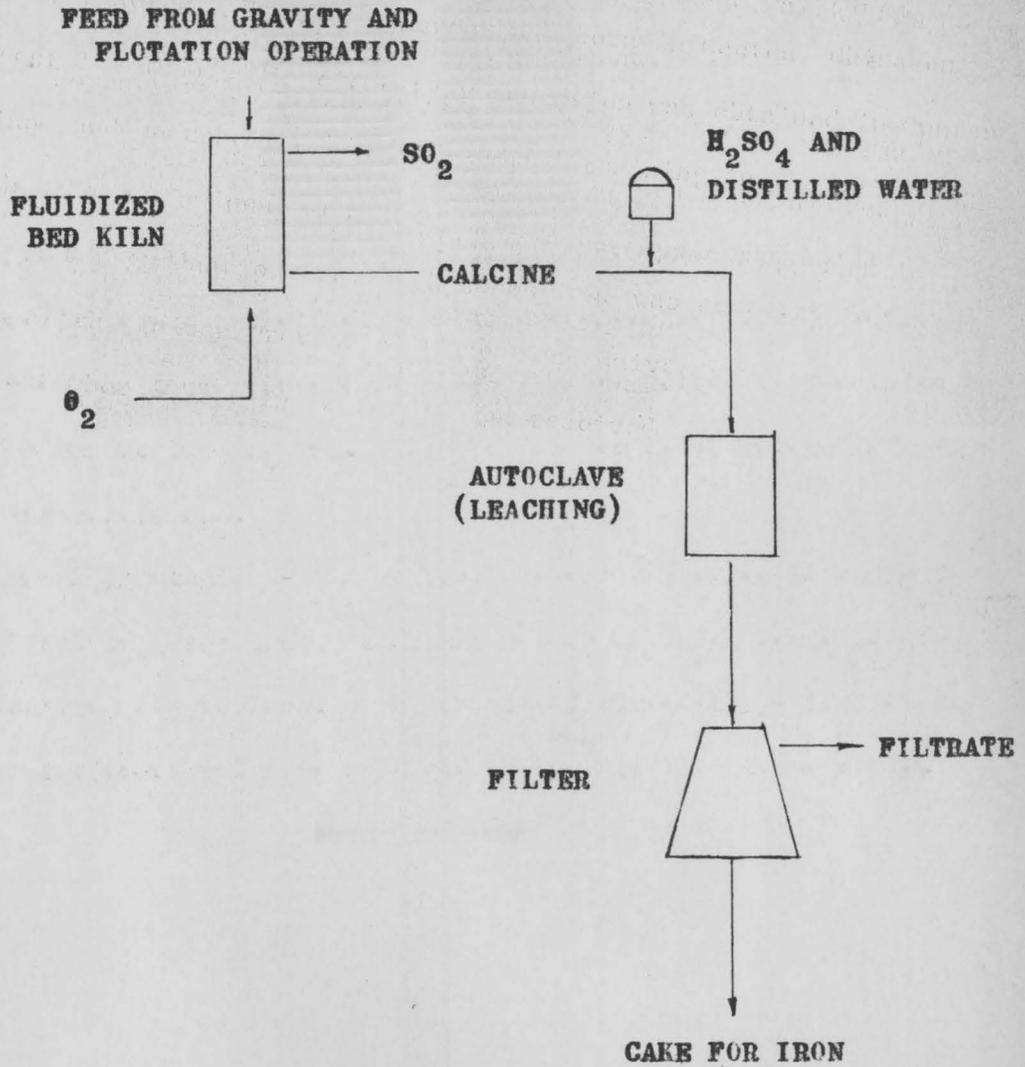


FIGURE 3. BENEFICIATION OF THE GREAT GOSSAN
LEAD ORE

Chemical Treatment - The chemical unit operations performed on the ore were roasting and leaching. A flow sheet is shown in Fig. 4. A series of leaching action in linear sequence removes the impurities by chemical means and eventually a filter cake of iron remains.

Roasting Studies - Studies were made to determine whether the sulfide ore (pyrrhotite, marmatite and chalcopyrite) in the flotation and table concentrates could be converted to the oxide form as Fe_2O_3 , ZnO and CuO . The studies sought to determine optimum roasting conditions.

Leaching Studies - The roasted ore was subjected to sulfuric acid leach to determine whether the copper and zinc could be extracted from the residue. Studies also included the effect of the concentration of sulfuric acid and of the leaching temperature.



**FIGURE 4. FLOWSHEET OF PROPOSED ROASTING AND
LEACHING OF THE GREAT GOSSAN LEAD ORE**

EXPERIMENTAL MATERIALS

The materials used in performing the experimental portion of the investigation are presented in the following tables.

TABLE 6

Materials Used in the Leaching Process

1. Concentrated Pyrrhotite
2. Roasted Calcine
3. Sulfuric Acid
4. Distilled Water

TABLE 7

Materials Used in the Chemical Analysis

Fe	Zn	Cu	S
Hydrochloric acid	Hydrochloric acid	Hydrochloric acid	Hydrochloric acid
Stannous chloride	Nitric acid	Nitric acid	Nitric acid
Mercuric chloride	Potassium hydrochloride	Sulfuric acid	Potassium chlorate
Potassium dichromate	Ammonium hydrochloride	Ammonium hydrochloride	Barium chloride
Ammonium ferrous sulfate	Ammonium chloride	Hydrogen sulfide	Distilled water
Distilled water	Bromine water	Bromine water	
	Metallic lead	Acetic acid	
	Potassium ferrocyanide	Metallic zinc	
	Uranyl nitrate	Potassium iodide	
	Distilled water	Sodium thiosulfate	
		Starch solution	
		Sodium hydroxide	
		Distilled Water	

EXPERIMENTAL APPARATUS

The apparatus used in performing the experimental portion of the study included the following.

Fluidized Bed

The kiln was constructed of number 316 stainless steel and consisted of two flanged sections bolted together, see Fig. 5, 6, and 7, and sheet asbestos was used for gaskets between the flanges. To supply heat to the kiln, two General Electric stainless steel 1000 watt heating coils, with a maximum operating temperature of 1750°F., were wrapped around the section which contained the bed. The heating coils voltage was controlled by hand using a 2 KVA variable transformer. A 304 stainless steel plate containing a number of 1/32" holes drilled on 1/4" centers was mounted between the air chamber and the reaction chamber. The air supply first passed through a needle valve and then into an air flow-meter where the pressure was measured, and the air then went to the inlet on the air chamber. The feed to the kiln was first put into a Vibra Screw Feeder which discharged into a stand pipe. From the stand pipe, feed passed into a screw feeder and was conveyed into the kiln.

The screw feeder on the kiln was externally cooled with water coils and had a variable speed drive to correct for sulfur deposits

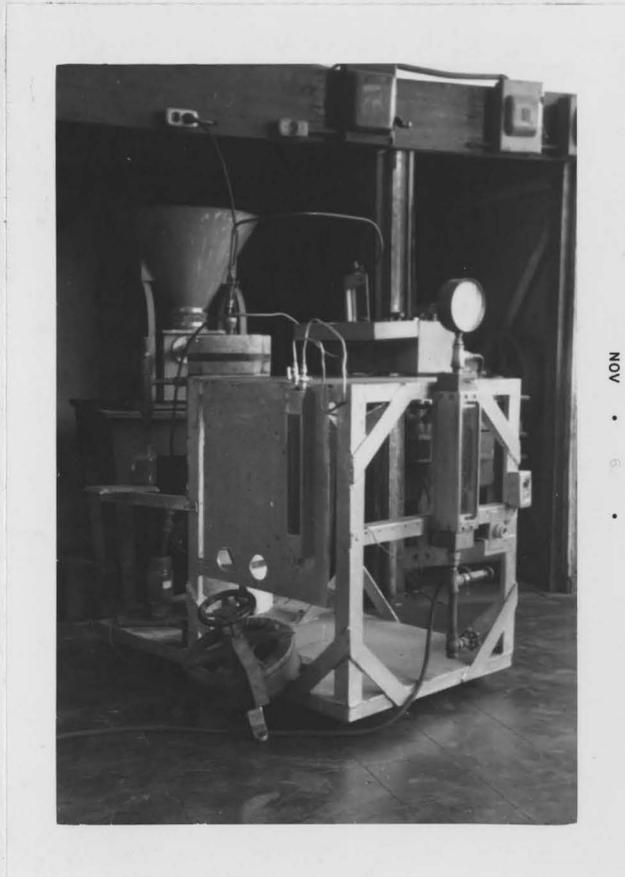


FIGURE 5. PHOTOGRAPH OF THE FLUIDIZED BED SHOWING HEATING AND SAMPLE COLLECTING SYSTEMS



FIGURE 6. PHOTOGRAPH OF THE FLUIDIZED BED SHOWING FEEDING AND DATA RECORDING SYSTEMS

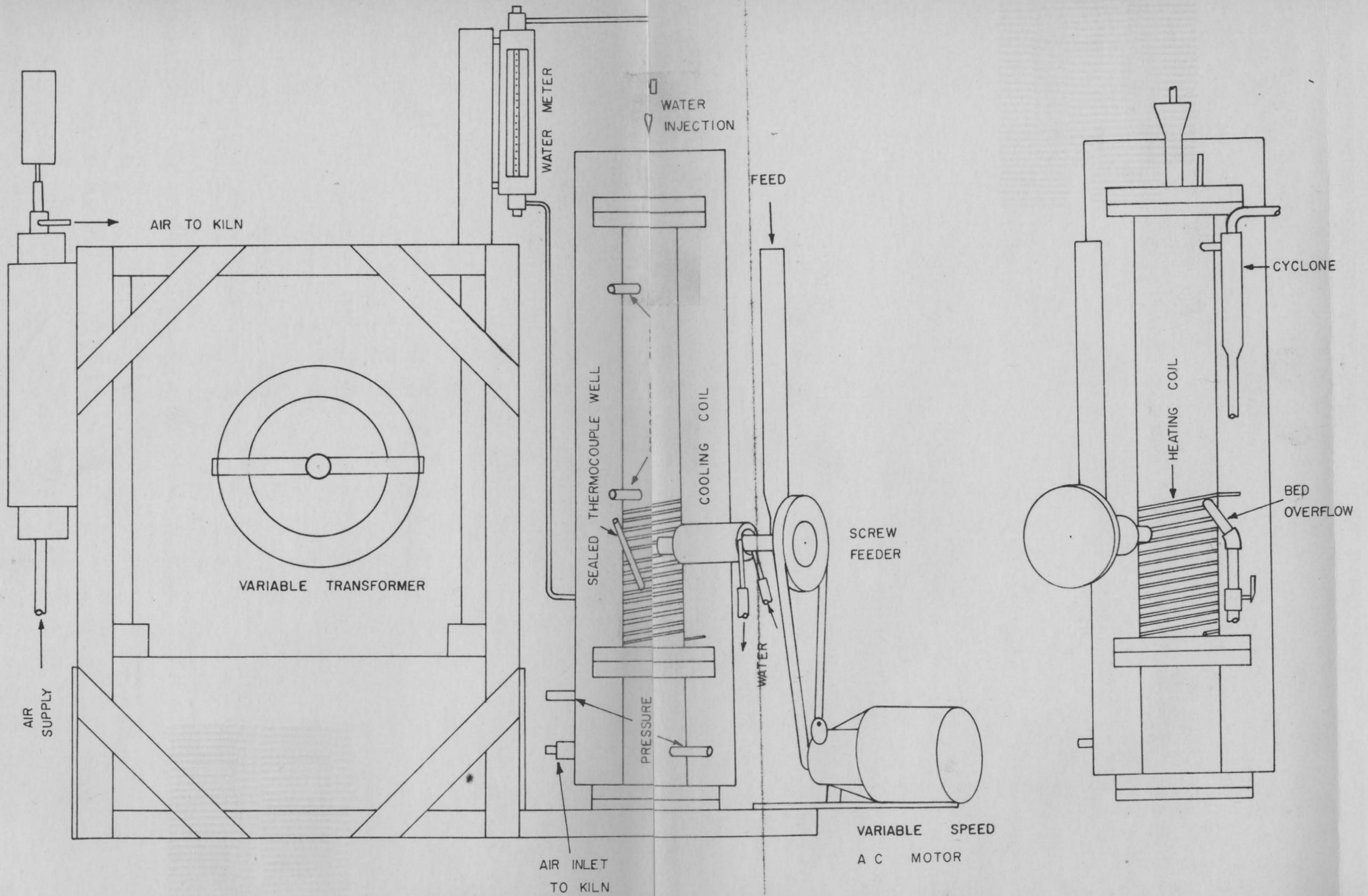


FIGURE 7. THE STRUCTURE OF THE FLUIDIZED BED KILN

clogging the screw. Water was injected directly into the bed for temperature control purposes by the use of a meter and needle valve. The kiln was insulated with a magnetic pipe insulation capable of a maximum temperature of 1850°F. The bed temperature was measured with a Leeds and Northrup Potentiometer and a chromel-alumel thermocouple in a sealed thermocouple well.

Autoclave

The standard one gallon stirred autoclave is made with all wetted parts constructed from 316 stainless steel. It is equipped with an electric motor for stirring during leaching (see Fig. 8).

The heater is provided with three male plugs for connecting to the power source to permit quick connection and disconnection. Power to the heater is controlled with a variable transformer, acting in response to signals from a thermocouple mounted in the thermowell. The temperature also can be adjusted by circulating water through the cooling coil in the autoclave.

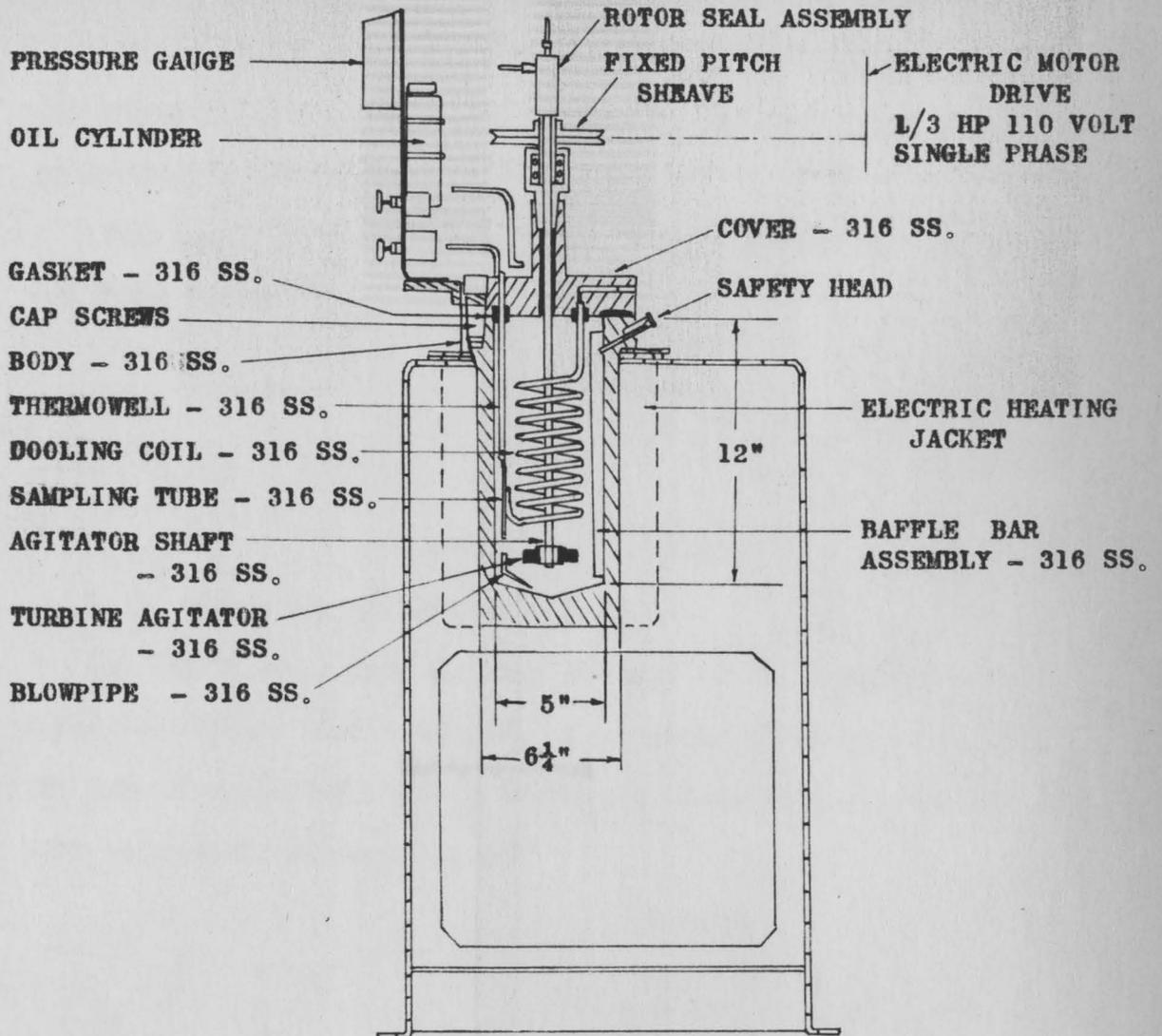
A blow pipe connected through the cover, extends to the bottom of the pressure vessel, and is fastened with a panel mounted valve for emptying the vessel.

The trade name for the stirring mechanism in the one gallon autoclave is "Dispersimax." This device is a turbine type agitator provided with a hollow shaft used in conjunction with the removable



FIGURE 8. PHOTOGRAPH OF THE AUTOCLAVE

baffles in the vessel. When in operation, a low pressure area is created at the turbine impeller. The gases are drawn down through the hollow shaft and dispersed through the liquid, and the bubbles are broken up by baffle. This type of agitation provides uniform suspension and insures constant circulation of the reaction gases through the liquid.



MAX. GAUGE PRESSURE 0 TO 5000 PSI.

WIRE FOR 110 VOLT, SINGLE PHASE SERVICE.

ELECTRIC MOTOR DRIVE, 1/3 HP MOTOR -110 VOLT,
 -60CYCLE SINGLE PHASE -CL. 1 GPD, 1725 R.P.M.

FIGURE 9. THE STRUCTURE OF THE STANDARD
 ONE GALLON STIRRED AUTOCLAVE

DESCRIPTION OF ORE SAMPLE

The sample used for these series of tests was obtained from the former Betty Baker Mining area, six and one-half miles north of Hillsville, Virginia.

The amount of iron, sulfur, zinc, copper and lead in the ore are shown below: (28)

	Percent
Fe	35.52
S	25.37
Cu	0.63
Zn	1.96
Pb	<u>0.34</u>
TOTAL	63.82

Gangue (by difference) = 36.18

It can be noted from the previous work on the flotation and table concentrate that a -65 mesh Tyler grind followed by a tabling and bulk flotation will give a 70.60 percent recovery of sulfides with an analysis as shown below: (28)

	Percent
Fe	48.27
S	36.38
Cu	0.88
Zn	2.62
Pb	<u>0.48</u>
TOTAL	88.63

Gangue (by difference) = 11.37

It is evident that the bulk flotation sulfides, if the metal values could be separated economically, would be an attractive material for exploitation.

According to the past research efforts the following estimates can be used for impurities in iron ores without penalties.*

Copper to iron ratio	1 to 1000
Zinc to iron ratio	1 to 10000
Sulfur to iron ratio	1 to 1000
Lead to iron ratio	1 to 1000
(depending on markets)	or 1 to 10000

Assuming that a 58 percent iron product would be achieved, this would allow the following amounts for impurities:

	Percent
Copper	0.06
Zinc	0.006
Sulfur	0.06
Lead	0.06 or 0.006

*Foreman, W., research, contacted Dr. G. C. McBride and obtained these data.

EXPERIMENTAL PROCEDURES

Roasting of Sulfide Concentrates

The plan in this investigation was to convert the sulfides of zinc and copper into soluble oxides or sulfates by roasting in a fluidized bed kiln (see Fig. 5 and 6).

The fluidized bed technique has become important in processes involving the contact between solids and gases because of the high rate of heat and mass transfer possible. In a fluidized bed a stream of gas is blown up through a mass of solid particles at a high rate. The main advantage of a fluidized system lies in its capability for maintaining a uniform temperature throughout the bed.

The kiln was operated by charging the bed with about five pounds of sulfide ore. The choice of a good sample collecting temperature of 1400°F. was determined from the results of the previous researcher, C. H. Shih.⁽²⁸⁾ The temperature within the kiln was raised to 900°F., the air turned on, and the reaction started. For temperature control and cooling purposes, water was used as previously described when discussing the apparatus. The bed temperature was read with a Leeds and Northrup Potentiometer and a chromel-alumel thermocouple in a sealed thermocouple well. The kiln was allowed to run for two hours at constant temperature by adjusting the variable speed drive in the Vibra Screw Feeder

and by adjusting the voltage with the variable transformer. The coarse material from the bed overflow outlet was collected in a sealed jar. The fines were removed by a cyclone and also collected in a sealed jar. The cyclone overflow and kiln gases were discharged into the atmosphere. The two samples of coarse and fine material were combined for leaching tests.

Leaching of the Roasted Calcine

The procedures for operating the autoclave to leach the roasted calcine is presented in Appendix H. The selection of the approximate amount of milliliters of H_2SO_4 was investigated by C. H. Shiuh. (28)

Curve Fitting

Purpose: After obtaining the experimental data and plotting a curve, the data was fitted with a continuous function.

Theory: The basic idea of fitting a curve to a polynomial of any degree is quite simple. (46) For example:

x	y
x_0	y_0
x_1	y_1
x_2	y_2

If the values in the above table are known, it is possible to fit a second order equation to these values so that the data is represented as follows:

$$y = Ax^2 + Bx + C$$

where A, B, and C are constants.

The known values of x, y are substituted into the proposed equation, and results in the following set of linear equations:

$$y_0 = A(x_0)^2 + B(x_0) + C$$

$$y_1 = A(x_1)^2 + B(x_1) + C$$

$$y_2 = A(x_2)^2 + B(x_2) + C$$

Here there are three equations with three unknowns which can be solved for the value of A, B, and C.

x	y	Δy	$\Delta^2 y$
x_0	y_0	$y_1 - y_0$	
x_1	y_1	$y_2 - y_1$	$(y_2 - y_1) - (y_1 - y_0)$
x_2	y_2		

where: Δy is called the first difference,
 $\Delta^2 y$ is called the second difference,
 and so on.

The following equation may be used for curve fitting:

$$y = y_0 + \mu^{(1)} \Delta y_0 + \frac{\mu^{(2)}}{2!} \Delta^2 y_0 + \frac{\mu^{(3)}}{3!} \Delta^3 y_0 + \dots$$

$$\dots \dots \frac{\mu^{(m)}}{m!} \Delta^m y_0$$

where:

$$y_0 = f(x_0)$$

$$\mu = \frac{x - x_0}{h}$$

$$h = x_1 - x_0 = x_2 - x_1 = \dots\dots\dots$$

$$\mu^{(m)} = \mu(\mu - 1)(\mu - 2) \dots\dots (\mu - m + 1)$$

For example:

When 250°F. of 8 cubic centimeters H_2SO_4 were applied in single leaching, the following calculation can be made:

x	y	Δy	$\Delta^2 y$	$\Delta^3 y$
Concentration	% Zn			
$x_0 = 8$	$y_0 = 0.480$			
$x_1 = 12$	$y_1 = 0.210$	-0.270	0.195	
$x_2 = 16$	$y_2 = 0.135$	-0.075	0.050	-0.145
$x_3 = 20$	$y_3 = 0.110$	-0.025		

A third order polynomial will be sufficient to fit this curve

Now, $x_0 = 8$, $y_0 = 0.48$, $h = 4$.

Therefore:

$$\mu = \frac{x - 8}{4} = \frac{x}{4} - 2$$

$$y = 0.48 + \left(\frac{x}{4} - 2\right)(-0.27) + \frac{1}{2} (0.195) \left(\frac{x}{4} - 2\right)$$

$$\left(\frac{x}{4} - 3\right) + 1/6 \cdot (-0.145) \left(\frac{x}{4} - 2\right) \left(\frac{x}{4} - 3\right)$$

$$\left(\frac{x}{4} - 4\right)$$

$$= 2.185 - 1.3818 \left(\frac{x}{4}\right) + 0.315 \left(\frac{x}{4}\right)^2 - 0.0241$$

$$\left(\frac{x}{4}\right)^3$$

The other curves are plotted with the same method. The functions are obtained by fitting the points and plotting the curves from these fitted equations.

DATA AND RESULTS

A thorough literature review and previous work made it possible to select the most critical parameters involved in the roasting and leaching operations. These parameters are (1) leaching temperature, and (2) the concentration of sulfuric acid in the leaching process.

The first number on all of the tests after the "GL" designation is the leaching test. The second number is the feed rate for the roasting test. The third number will be used later in this section, "1" meaning single leaching and "2" meaning double leaching. For example, GL-32-8-1 means leaching test number 32 at a feed rate of 8 grams per minute in the roasting test followed by a single leach.

Test 1 - This test was conducted to investigate the particle size of the Great Gossan Lead Ore in the roasting processes in the Fluidized Bed Kiln. The data and results are presented in Table 8 and Fig. 10.

Test 2 - The purpose of this test was to investigate the maximum recovery of iron during the process of the leaching in the autoclave. The data and results are presented in Table 9 and Fig. 11.

Test 3 - In this test, a double leaching was applied to determine the maximum recovery of iron in the leaching process. The data and results are presented in Table 10 and Fig. 12.

Test 4 - In this investigation, a series of tests were performed to determine an optimum leaching temperature and concentration of sulfuric acid in the extraction of acid soluble zinc oxide in the autoclave. The data and results are presented in Table 11 and Fig. 13.

Test 5 - In this investigation, a double leach was performed to determine the optimum leaching temperature and concentration of sulfuric acid for extraction of acid soluble zinc oxide. The data and results are presented in Table 12 and Fig. 14.

Test 6 - This test was designed to obtain a suitable leaching temperature and enough concentration of sulfuric acid in the extraction of acid soluble copper oxide in a single leaching. The data and results are presented in Table 13 and Fig. 15.

Test 7 - In this test, a double leaching was used to determine the optimum leaching temperature and the concentration of sulfuric acid for the extraction of acid soluble copper oxide. The data and results are presented in Table 14 and Fig. 16.

TABLE 8

Tyler Standard Screen Size of the Gossan Lead Ore for the Roasting
in the Fluidized Bed.

Screen Scale Ratio 1.414		Tyler Mesh	Sample Weight	Lead Ore Percentage	Cummula- tive Weights Percentage
Opening					
Inches	Millimeters				
.065	1.651	10	0.000	0.0	0.0
.046	1.168	14	0.005	0.1	0.1
.0328	.833	20	0.080	2.0	2.1
.0232	.589	28	0.740	18.8	20.9
.0164	.417	35	0.970	24.7	45.6
.0116	.295	48	0.650	16.5	62.1
.0082	.208	65	0.260	6.6	68.7
.0058	.147	100	0.250	6.4	75.1
.0041	.104	150	0.230	5.8	80.9
.0029	.074	200	0.290	7.4	88.3
.0029	.074	-200	0.460	11.7	100.0
(passed)	(passed)				
			3.935	100.0	

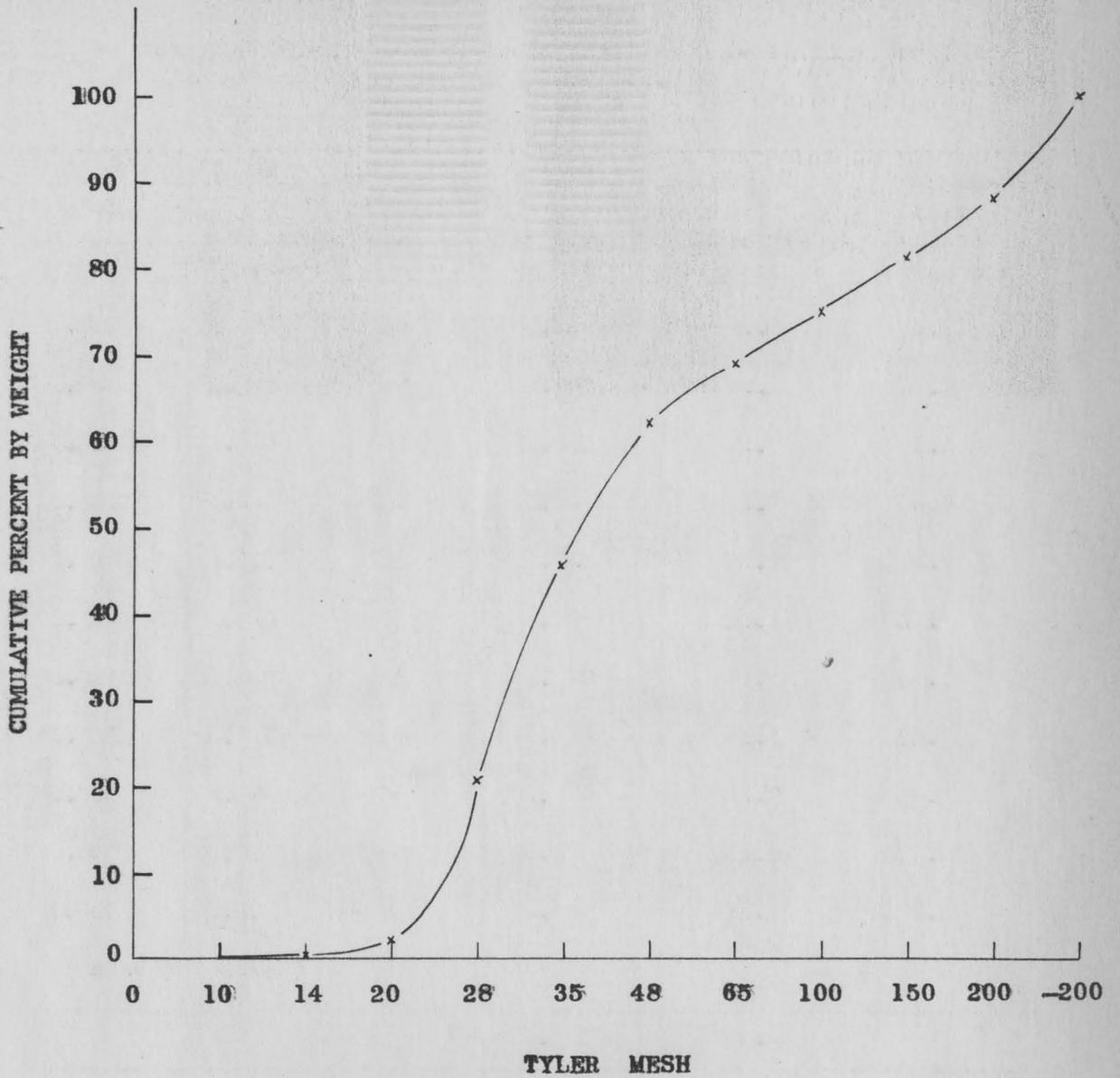


FIGURE 10. OPTIMUM ORE SIZE DISTRIBUTION CURVE
FOR ROASTING

TABLE 9

Chemical Analysis of Leached Products For Single Leaching of Iron With 8 to 20 cc of H_2SO_4
At 250°-550°F.

	Temp. °F.	H_2SO_4 cc.	Moist. %	Ignition %	Insoluble %	Sulfur %	Iron %	Iron % Recovery
Gossan Lead								
Ore			1.32	2.54	10.09	5.84	58.03	
GL-32-8-1	250	8	0.26	1.38	11.13	3.55	57.93	92.51
GL-33-8-1	250	12	0.41	1.43	11.19	2.83	57.79	91.55
GL-34-8-1	250	16	0.21	1.19	11.15	3.15	56.45	90.07
GL-35-8-1	250	20	0.22	1.53	11.14	3.83	55.30	88.12
GL-36-8-1	350	8	0.16	1.88	11.20	3.23	57.50	90.85
GL-37-8-1	350	12	0.11	2.65	11.19	3.13	56.40	88.58
GL-38-8-1	350	16	0.23	1.96	11.17	3.65	54.30	85.90
GL-39-8-1	350	20	0.06	1.86	11.16	3.53	50.95	80.87
GL-40-8-1	450	8	0.18	1.97	11.16	2.83	56.00	88.67
GL-41-8-1	450	12	0.13	2.05	11.20	3.18	54.90	86.62
GL-42-8-1	450	16	0.17	2.22	11.18	2.20	51.25	81.04
GL-43-8-1	450	20	0.11	1.64	11.15	2.40	47.35	75.28
GL-44-8-1	550	8	0.19	2.19	11.12	3.35	55.15	87.41
GL-45-8-1	550	12	0.17	1.80	11.15	2.55	53.40	84.71
GL-46-8-1	550	16	0.16	1.66	11.18	2.40	49.50	78.69
GL-47-8-1	550	20	0.14	1.57	11.22	2.09	41.15	65.05

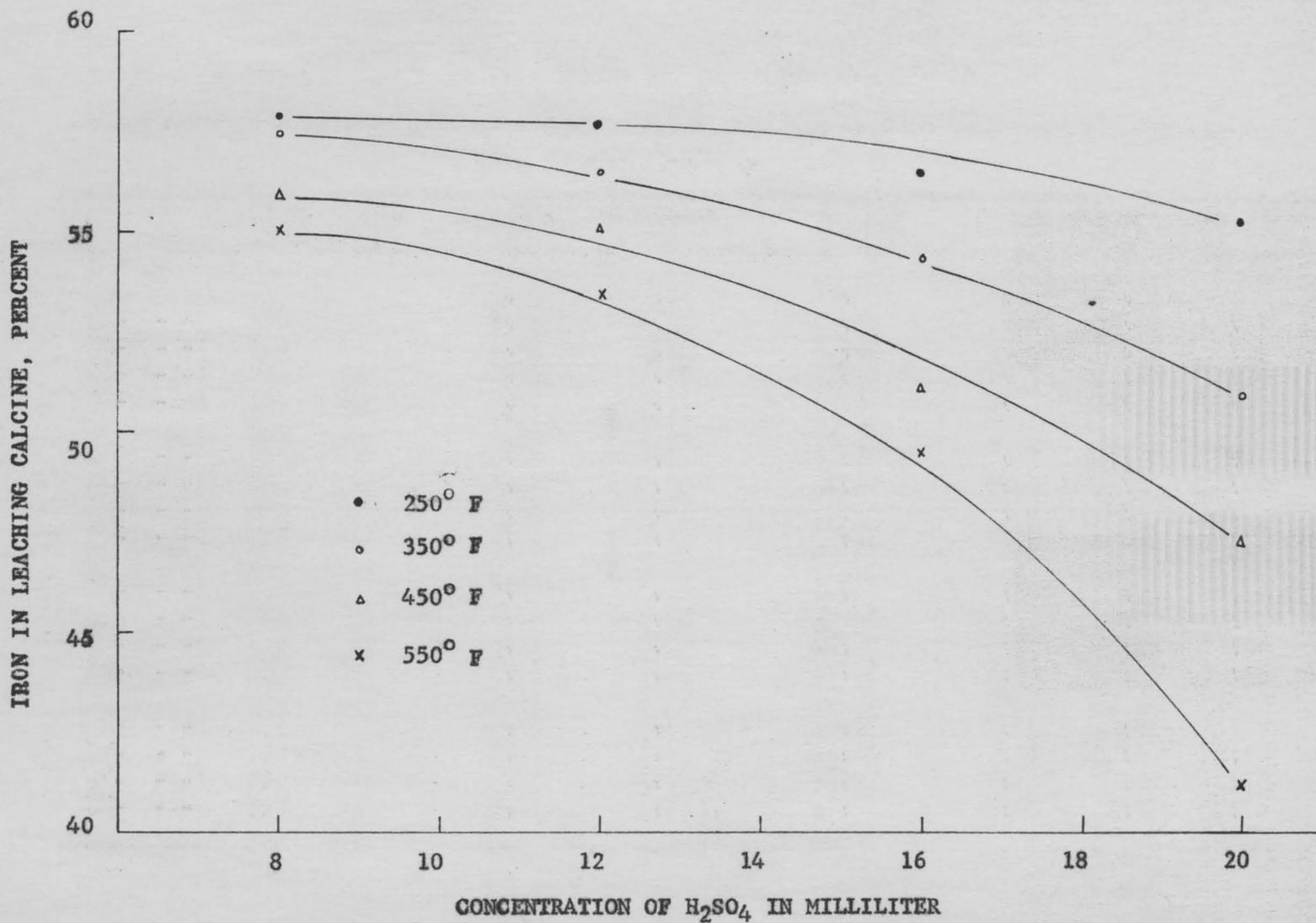


FIGURE 11. OPTIMUM SINGLE LEACHING OF IRON AT 250°-550°F FOR THE ROASTING TEMPERATURE AT 1400° F.

TABLE 10

Chemical Analysis of Leached Products for Double Leaching of Iron With 8 to 20 cc.
of H_2SO_4 at 250°-550°F.

	Temp. °F.	H_2SO_4 cc.	Moisture %	Ignition %	Insoluble %	Sulfur %	Iron %	Iron % Recovery
Gossan Lead Ore			1.32	2.54	10.09	5.84	58.03	
GL-48-8-2	250	8	0.26	1.38	11.20	3.55	57.85	91.78
GL-49-8-2	250	12	0.41	1.43	11.21	2.83	57.50	91.22
GL-50-8-2	250	16	0.21	1.19	11.20	3.15	55.85	88.72
GL-51-8-2	250	20	0.22	1.53	11.19	3.83	54.55	86.44
GL-52-8-2	350	8	0.16	1.88	11.21	3.23	56.95	89.90
GL-53-8-2	350	12	0.11	2.65	11.20	3.13	55.75	87.38
GL-54-8-2	350	16	0.23	1.96	11.18	3.65	53.45	84.58
GL-55-8-2	350	20	0.06	1.86	11.21	3.53	49.56	78.31
GL-56-8-2	450	8	0.18	1.97	11.18	2.83	53.60	84.70
GL-57-8-2	450	12	0.13	2.05	11.22	3.18	53.15	83.70
GL-58-8-2	450	16	0.17	2.22	11.21	3.20	48.90	77.12
GL-59-8-2	450	20	0.11	1.64	11.19	2.40	44.15	70.93
GL-60-8-2	550	8	0.19	2.19	11.19	3.35	51.55	81.18
GL-61-8-2	550	12	0.17	1.80	11.18	2.55	49.15	77.76
GL-62-8-2	550	16	0.16	1.66	11.23	2.40	44.70	70.78
GL-63-8-2	550	20	0.14	1.57	11.24	2.09	37.75	60.57

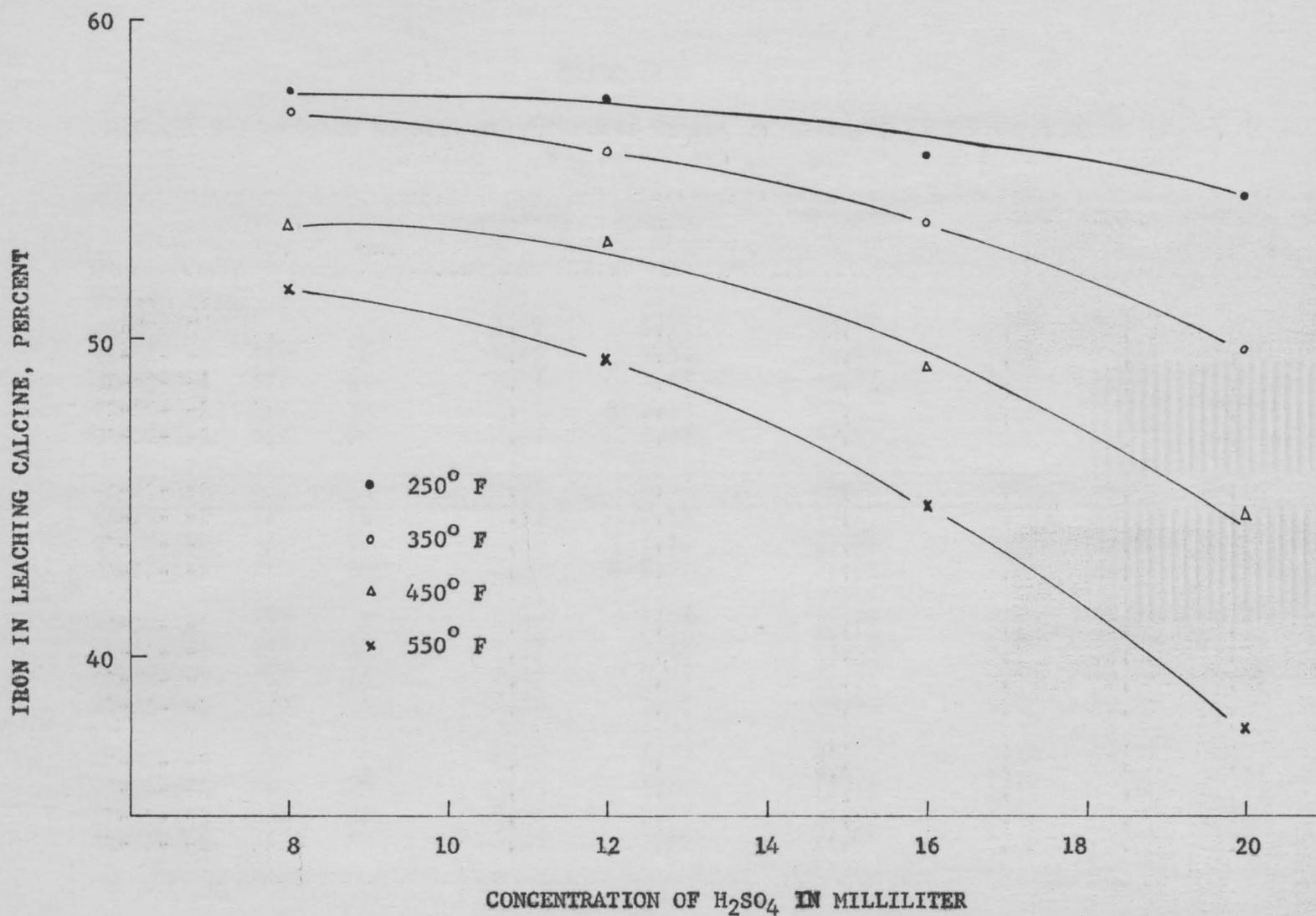


FIGURE 12. OPTIMUM DOUBLE LEACHING OF IRON 250°-550°F FOR THE ROASTING TEMPERATURE AT 1400° F.

TABLE 11

Chemical Analysis of Leached Products For Single Leaching of Zinc With 8 to 20 cc.
of H_2SO_4 at 250°-550°F.

	Temp. °F.	H_2SO_4 %	Moisture %	Ignition %	Insoluble %	Sulfur %	Zinc %	Zinc % Recovery
Gossan Lead Ore			1.32	2.54	10.09	5.84	1.795	
GL-32-8-1	250	8	0.26	1.38	11.15	3.55	0.480	74.22
GL-33-8-1	250	12	0.41	1.43	11.19	2.83	0.210	89.25
GL-34-8-1	250	16	0.21	1.19	11.15	3.15	0.136	92.98
GL-35-8-1	250	20	0.22	1.53	11.14	3.83	0.105	94.59
GL-36-8-1	350	8	0.16	1.88	11.20	3.23	0.373	80.95
GL-37-8-1	350	12	0.11	2.65	11.19	3.13	0.165	81.63
GL-38-8-1	350	16	0.23	1.96	11.17	3.65	0.093	95.24
GL-39-8-1	350	20	0.06	1.86	11.16	3.53	0.080	95.89
GL-40-8-1	450	8	0.18	1.97	11.16	2.83	0.293	85.00
GL-41-8-1	450	12	0.13	2.05	11.20	3.18	0.091	95.36
GL-42-8-1	450	16	0.17	2.22	11.18	3.20	0.053	97.29
GL-43-8-1	450	20	0.11	1.64	11.15	2.40	0.038	98.05
GL-44-8-1	550	8	0.19	2.19	11.12	3.35	0.245	90.33
GL-45-8-1	550	12	0.17	1.80	11.15	2.55	0.075	96.15
GL-46-8-1	550	16	0.16	1.66	11.18	2.40	0.032	98.36
GL-47-8-1	550	20	0.14	1.57	11.22	2.09	0.025	98.72

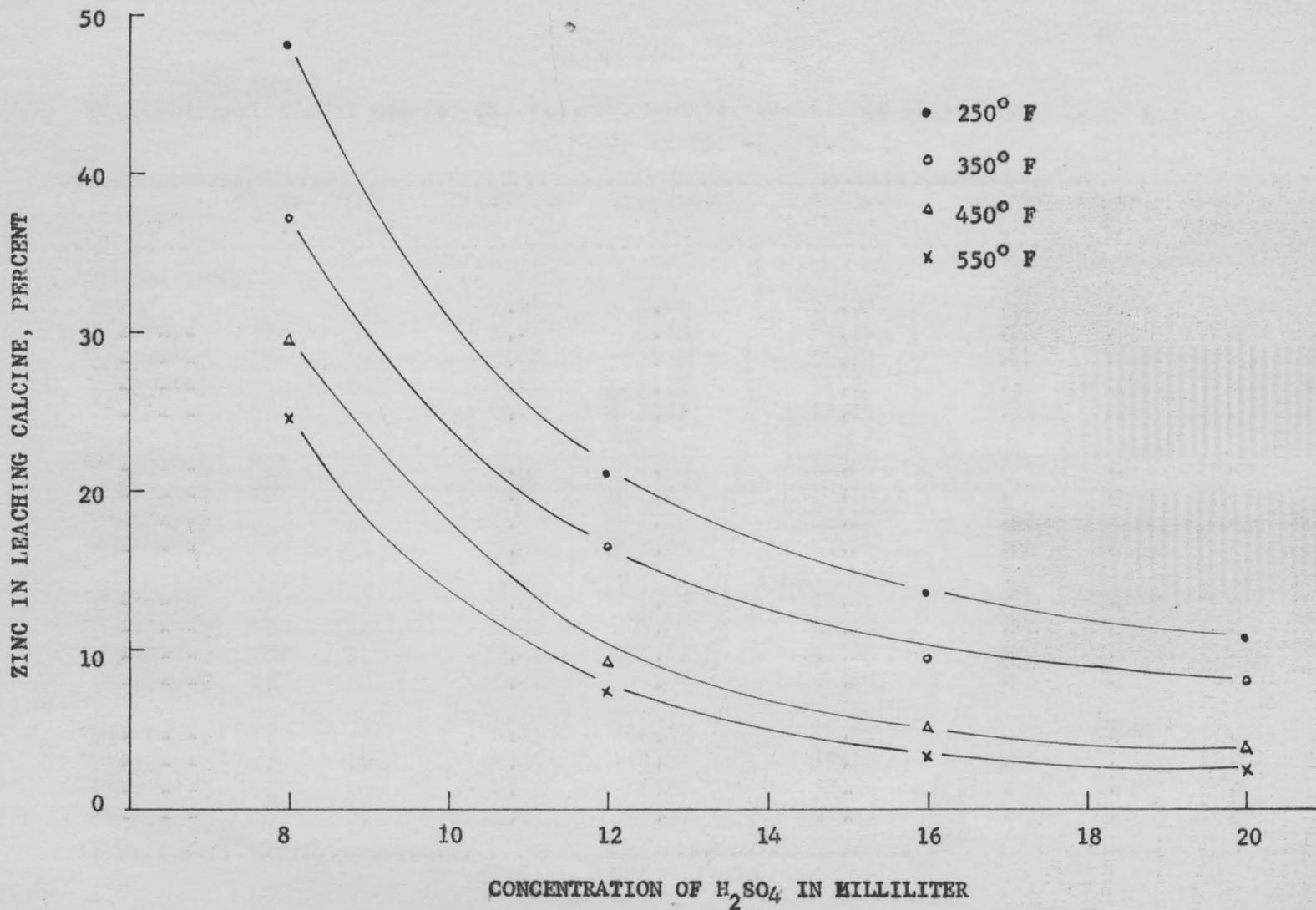


FIGURE 13. OPTIMUM SINGLE LEACHING OF ZINC AT 250°-550° F FOR THE ROASTING TEMPERATURE AT 1400° F.

TABLE 12

Chemical Analysis of Leached Products for Double Leaching of Zinc with 8 to 20 cc.
of H_2SO_4 at 250°-550°F.

	Temp. °F.	H_2SO_4 cc.	Moisture %	Ignition %	Insoluble %	Sulfur %	Zinc %	Zinc % Recovery
Gossan Lead Ore			1.32	2.54	10.09	5.84	1.795	
GL-48-8-2	250	8	0.26	1.38	11.20	3.55	0.395	79.74
GL-49-8-2	250	12	0.41	1.43	11.21	2.83	0.187	90.43
GL-50-8-2	250	16	0.21	1.19	11.20	3.15	0.105	94.61
GL-51-8-2	250	20	0.22	1.53	11.19	3.83	0.087	95.54
GL-52-8-2	350	8	0.16	1.88	11.21	3.23	0.335	82.90
GL-53-8-2	350	12	0.11	2.65	11.20	3.13	0.144	92.70
GL-54-8-2	350	16	0.23	1.96	11.18	3.65	0.071	96.37
GL-55-8-2	350	20	0.06	1.86	11.21	3.53	0.064	96.28
GL-56-8-2	450	8	0.18	1.97	11.18	2.83	0.261	86.67
GL-57-8-2	450	12	0.13	2.05	11.22	3.18	0.071	96.39
GL-58-8-2	450	16	0.17	2.22	11.21	3.20	0.039	98.01
GL-59-8-2	450	20	0.11	1.64	11.19	2.40	0.032	98.36
GL-60-8-2	550	8	0.19	2.19	11.19	3.35	0.225	88.54
GL-61-8-2	550	12	0.17	1.80	11.18	2.55	0.048	97.54
GL-62-8-2	550	16	0.16	1.66	11.23	2.40	0.021	98.92
GL-63-8-2	550	20	0.14	1.57	11.24	2.09	0.019	99.03

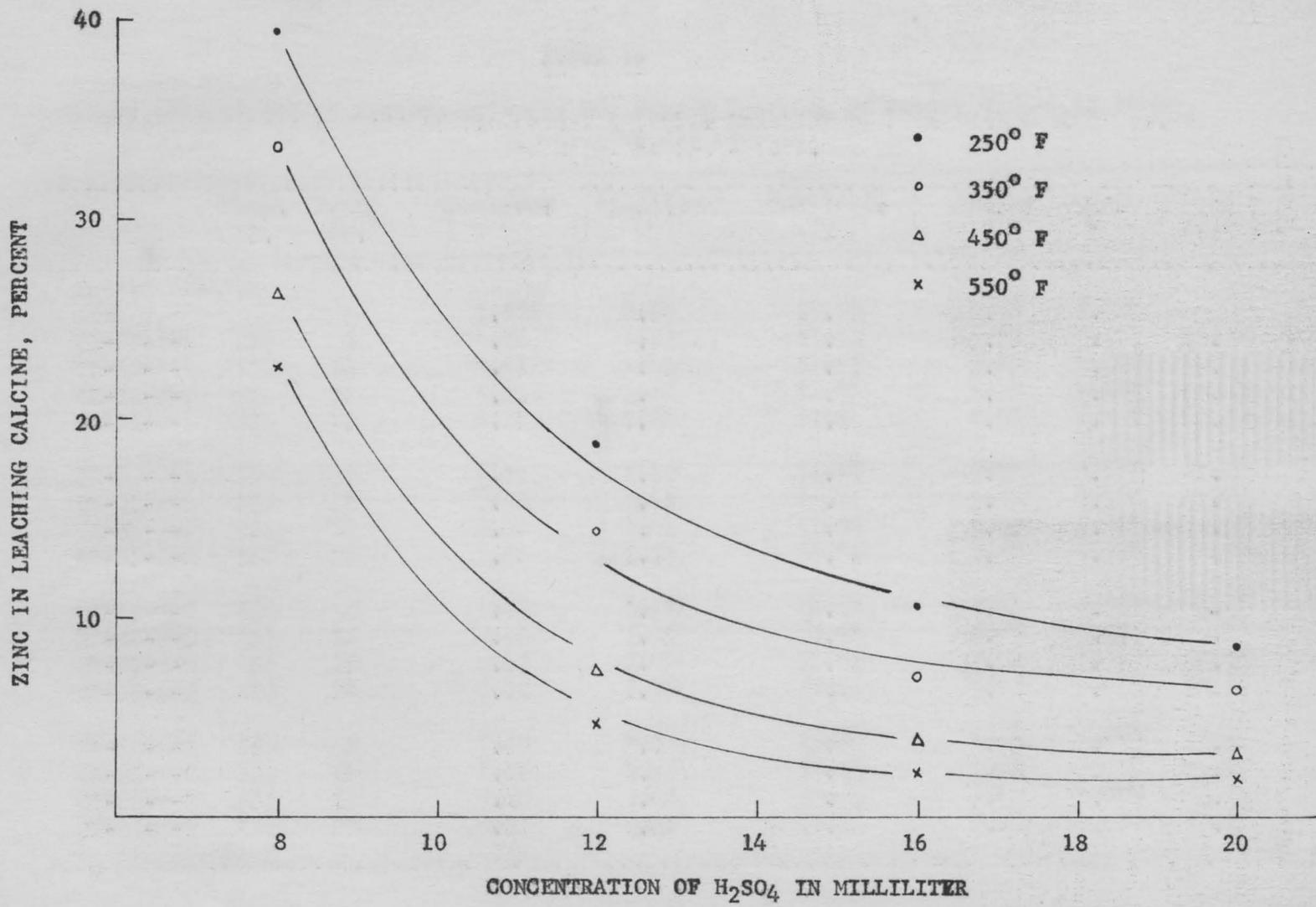


FIGURE 14. OPTIMUM DOUBLE LEACHING OF ZINC AT 250°-550° F FOR THE ROASTING TEMPERATURE AT 1400° F.

TABLE 13

Chemical Analysis of Leached Products For Single Leaching of Copper with 8 to 20 cc
of H_2SO_4 at 250°-550°F.

	Temp. °F.	H_2SO_4 cc.	Moisture %	Ignition %	Insoluble %	Sulfur %	Copper %	Copper % Recovery
Gossan Lead Ore			1.32	2.54	10.09	5.84	0.388	
GL-32-8-1	250	8	0.26	1.38	11.13	3.55	0.309	26.20
GL-33-8-1	250	12	0.41	1.43	11.19	2.83	0.238	43.61
GL-34-8-1	250	16	0.21	1.19	11.15	3.15	0.159	62.06
GL-35-8-1	250	20	0.22	1.53	11.14	3.83	0.127	69.73
GL-36-8-1	350	8	0.16	1.88	11.20	3.23	0.280	33.84
GL-37-8-1	350	12	0.11	2.65	11.19	3.13	0.181	57.53
GL-38-8-1	350	16	0.23	1.96	11.17	3.65	0.120	71.61
GL-39-8-1	350	20	0.06	1.86	11.16	3.53	0.103	75.55
GL-40-8-1	450	8	0.18	1.97	11.16	2.83	0.228	46.00
GL-41-8-1	450	12	0.13	2.05	11.20	3.18	0.108	74.52
GL-42-8-1	450	16	0.17	2.22	11.18	2.20	0.089	78.95
GL-43-8-1	450	20	0.11	1.64	11.15	2.40	0.061	85.49
GL-44-8-1	550	8	0.19	2.19	11.12	3.35	0.210	50.22
GL-45-8-1	550	12	0.17	1.80	11.14	2.55	0.084	80.08
GL-46-8-1	550	16	0.16	1.66	11.18	2.40	0.056	86.69
GL-47-8-1	550	20	0.14	1.57	11.22	2.09	0.043	89.83

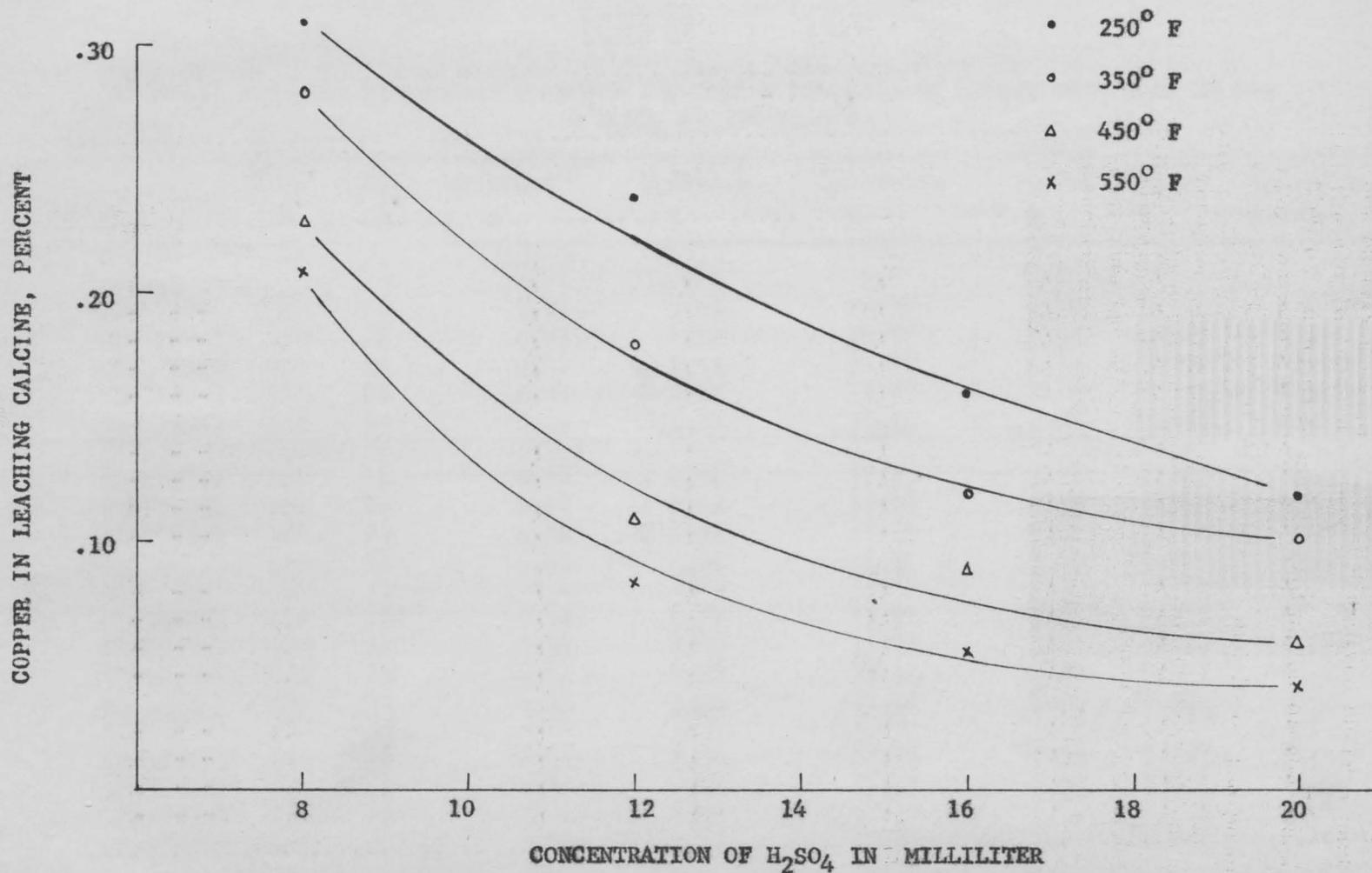


FIGURE 15. OPTIMUM SINGLE LEACHING OF COPPER AT 250°-550° F FOR THE ROASTING TEMPERATURE AT 1400° F.

TABLE 14

Chemical Analysis of Leached Products for Double Leaching of Copper with 8 to 20 cc.
of H_2SO_4 at 250°-550°F.

	Temp. °F.	H_2SO_4 cc.	Moisture %	Ignition %	Insoluble %	Sulfur %	Copper %	Copper % Recovery
Gossan Lead Ore			1.32	2.54	10.09	5.84	0.3885	
GL-48-8-2	250	8	0.26	1.38	11.20	3.55	0.282	33.09
GL-49-8-2	250	12	0.41	1.43	11.21	2.83	0.218	48.41
GL-50-8-2	250	16	0.21	1.19	11.20	3.15	0.134	68.16
GL-51-8-2	250	20	0.22	1.53	11.19	3.83	0.110	73.93
GL-52-8-2	350	8	0.16	1.88	11.21	3.23	0.259	38.85
GL-53-8-2	350	12	0.11	2.65	11.20	3.13	0.156	63.43
GL-54-8-2	350	20	0.23	1.96	11.18	3.65	0.111	73.76
GL-55-8-2	350	20	0.06	1.86	11.21	3.53	0.087	79.44
GL-56-8-2	450	8	0.18	1.97	11.18	2.83	0.215	49.19
GL-57-8-2	450	12	0.13	2.05	11.22	3.18	0.103	75.74
GL-58-8-2	450	16	0.17	2.22	11.21	2.20	0.071	83.25
GL-59-8-2	450	20	0.11	1.64	11.19	2.40	0.049	88.39
GL-60-8-2	550	8	0.19	2.19	11.19	3.35	0.183	56.89
GL-61-8-2	550	12	0.17	1.80	11.18	2.55	0.061	85.56
GL-62-8-2	550	16	0.16	1.66	11.23	2.40	0.044	89.58
GL-63-8-2	550	20	0.14	1.57	11.24	2.09	0.035	94.74

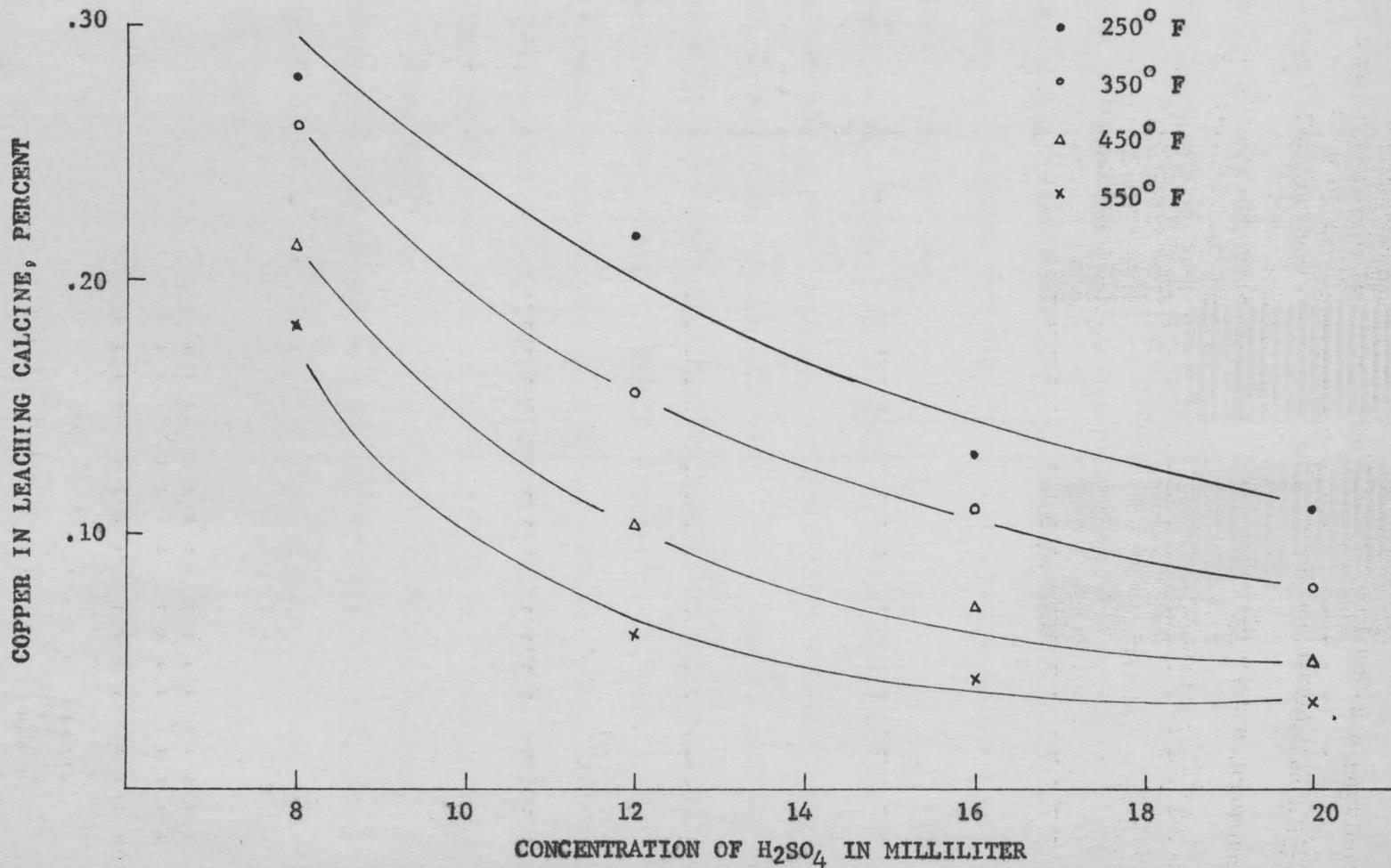


FIGURE 16. OPTIMUM DOUBLE LEACHING OF COPPER AT 250°-550° F FOR THE ROASTING TEMPERATURE AT 1400° F.

DISCUSSION OF RESULTS

In this investigation sulfuric acid was used to leach the roasted sulfide ore. This acid reacted with the CuO , ZnO , and Fe_2O_3 to form sulfates of which ZnSO_4 and CuSO_4 are soluble in the solution.

Test 1 - From the previous investigations the researcher found the optimum size of the Great Gossan Lead Ore. The screen analysis indicated that the size of the ore was as shown on Table 8 and Fig. 10.

Test 2 - From Table 9 and Fig. 11 it may be observed that the percentage of iron decreases as the amount of sulfuric acid and the leaching temperature increases. This means the greater the quantity of sulfuric acid and the higher the leaching temperature, the less the percentage of iron retained in the residue. (47,48)
For example, the extraction of iron decreases from 92.51 percent to 65.05 percent when the concentration of sulfuric acid increases from 8 cubic centimeters at 250°F . to 20 cubic centimeters at 550°F .

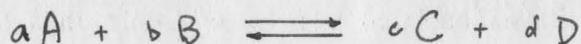
From Test 1 and Test 2 we know that the percentage of iron decreases as the amount of H_2SO_4 and the leaching temperature increases. What is the reason that the percentage of iron drops down that fast?

1. The small amount (1/10) of filtrate is being used in the quantitative chemical analysis.

2. The indicator is applied to determine the percentage of iron by watching the change of color. It is impossible to determine the correct color by eyes for slight changes.

It is suggested that the "Spectrophotometer" be used in the future.

The theory of the solubility of iron in H_2SO_4 with high temperature is as follows:



where:

A = Iron

B = H_2SO_4

C, D = the results

$$K_a = \frac{a_c^c a_d^d}{a_A^a a_B^b} = \frac{K_1}{K_2}$$

where:

K_a = Equilibrium constant

K_1, K_2 = Reaction rate

a = Activity

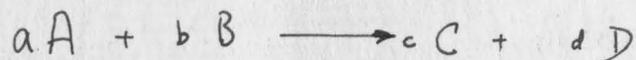
CASE I: The concentration of H_2SO_4 :

$K_a = \text{Zero}$

The reaction is steady. There is not too much difference between the variety of the amount of H_2SO_4 .

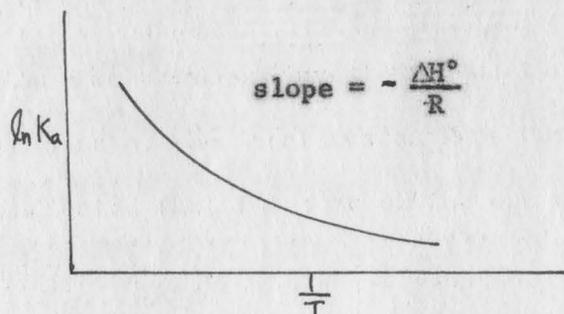
$$\text{if } K_a > 1$$

$$\text{ie. , } K_1 > K_2$$



Therefore, the higher the K_a , the more iron is dissolved.

CASE II: The variation of Temperature:



Where ΔG = Free energy

T = Temperature

$$dG = VdP - SdT$$

$$\left(\frac{dG}{dT}\right)_P = -S$$

$$\frac{d\Delta G}{dT} = -\Delta S = \frac{-\Delta H + \Delta G}{T}$$

$$\frac{d}{dT} \left(\frac{\Delta G}{T} \right) = \frac{1}{T} \frac{d\Delta G}{dT} + \left[\frac{-\Delta G}{T^2} \right]$$

$$\frac{d}{dT} \left(\frac{\Delta G}{T} \right) = \frac{-\Delta H}{T^2}$$

Since,
$$\frac{d}{dT} \left(\frac{\Delta G}{T} \right)^\circ = \frac{-\Delta H^\circ}{T^2}$$

$$\Delta G^\circ = -RT \ln K_a$$

$$\text{So, } \frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2}$$

$$\frac{d \ln K_a}{d \frac{1}{T}} = \frac{-\Delta H^\circ}{R}$$

where: ΔH° = Heat of reaction (49)*
 R = Gas constant.

Conclusion: The heat of reaction increases the higher the temperature or the higher the K_a , the more iron is dissolved.

Test 3 - The results of these double leaching tests are shown in Table 10 and Fig. 12. It can be seen that iron decreases from 91.78 percent to 60.57 percent as the amount of acid increases from 8 cubic centimeters to 20 cubic centimeters, and the leaching temperature increases from 250°F. to 550°F.

This investigation indicates that the greater the amount of sulfuric acid and the higher the leaching temperature, the less the recovery of iron.

Test 4 - From these results we know that the greater the sulfuric acid concentration and the higher the leaching temperature, the greater the zinc extraction. The results of these tests are presented in Table 11 and Fig. 12.

* ΔH° = Heat of reaction is 47,561 g-cal. according to the thermochemical measurements, and 47,437 from the electromotive force and its temperature coefficient.

Test 5 - From Table 12 and Fig. 14 it may be observed that the zinc extraction with the double leaching method is higher than with the single leaching method.

For instance, the zinc extraction increases from 74.22 percent to 99.03 percent.

Test 6 - From the data and results in Table 13 and Fig. 15, it can be seen that the copper extraction increases from 26.25 percent to 89.83 percent as acid concentration and temperature increases.

Test 7 - From Table 14 and Fig. 16 it may be observed that the copper extraction increased from 33.09 percent to 91.74 percent. This information shows that an increase of acid and leaching temperature produces an increase in extracted acid soluble copper. This is due to a more complete oxidation of copper sulfide at the higher leaching temperature and more sulfuric acid.

This investigation also indicates that the double leaching is more successful than the single leaching.

SUMMARY AND CONCLUSION

In this investigation the variable factors involved are the temperature, the concentration of the leaching agent, and the percentage of the impurities recovered in the process. Also there is a correlation between the time spent in leaching and the significant percentage of the impurities removed. The data from the experiment will now be studied and a conclusion drawn concerning the ultimate advantage to be derived from combining these factors.

The experimental results indicate that higher leaching temperatures gives a higher percentage yield of the impurities to be recovered. For example, zinc has a recovery of 79.74% when leached at 250°F., 8 cubic centimeters, H_2SO_4 while its rate will increase to 88.54 percent at 550°F., 8 cubic centimeters, H_2SO_4 . On the other hand with a higher concentration of the leaching agent, it is found that the recovery of the impurity metal is also higher. With the same sample of calcine at 550°F., 8 cubic centimeters, H_2SO_4 , 79.74 percent of zinc is recovered, but with an increase in concentration to 20 cubic centimeters, H_2SO_4 , 99.03 percent zinc is obtained. It is therefore apparent that the highest leaching temperature with the most concentrated leaching agent gives the highest percentage of impurity metal recovery. Yet the amount of iron in the calcine dissolves in direct proportion to the increased amount of these two factors. The loss of iron induces errors in the reporting of the useful percentage of the calcine.

Hence it is desirable to interpret the data so that the recovery of the impurities in the calcine is optimum with a reasonable but not an undue amount of iron dissolved under a particular combination of temperature and concentration of the leaching agent.

First studied are Tables 9 and 10 of the percentage of iron retained at various leaching agent concentrations so that a reasonable range of iron is retained.

From these values, it may be concluded that a temperature of 450°F. and an acid concentration of 16 cubic centimeters, H_2SO_4 , represents the best leaching condition for impurities with a minimum loss of iron.

As for the leaching process itself, double leaching provides more time for reaction and as expected, the recovery rate is higher. This can be shown by the recovery rates under the same temperature and concentration but with different durations of leaching. It is found that in this investigation double leaching may provide a higher recovery percentage, but the additional time it requires can offset the slight advantage in accuracy. Therefore, the best experimental results may be obtained by a slow single leaching. There are two reasons why this experiment was stopped at a temperature of 550°F. First, the amount of iron loss increases prohibitively at this higher temperature. Secondly, it is impossible because of mechanical limitations to physically operate the reactor at higher temperatures than 550°F.

RECOMMENDATION FOR FUTURE WORK

Oxidation leaching of Zinc and Copper Sulfides in Acidic Pulps at Elevated Temperatures and Pressures

This technique is suggested to be used for leaching tests in the future because the rate of reaction is proportional to the temperature and pressure.

Aqueous Chlorine Used ;in Low Temperature and pressure

The use of an acid chlorine solution under a condition of low temperature and pressure is suggested for the leaching process because recently scientists have found that the reaction rate under such conditions is quite fast.

Ammonia Leaching

It is suggested that studies be made to determine the feasibility of using ammonia in the leaching process for the recovery of zinc and copper from the leach solution since acid leaching yielded impure leach solutions and caused severe corrosion to the stainless-steel autoclave. However, leaching of ammonical pulps should be more attractive than acid leaching since the leached solution should be relatively free of iron impurities and the corrosion of equipment is negligible.

Leaching Time

All the leaching tests in this investigation were performed for one hour. It is therefore recommended that a much longer

leaching time be investigated for all tests in the future so that more zinc and copper will be dissolved by the sulfuric acid.

Impeller Speeds in 1000 Revolutions Per Minute or More in the Autoclave.

It is suggested that impeller speeds of 1000 revolutions per minute or more be used in the autoclave during leaching, since the reaction rate is proportional to the speed of the impeller.

APPENDICES

APPENDIX A

Calculation for air needed in roasting operation.

8 grams (feed rate) x 33.4% (sulfur content)

= 2.67 grams of sulfur per minute,

or 2.67 grams of O_2 per minute ($S + O_2 = SO_2$)

$$\frac{2.67}{21} = \frac{X}{79}$$

$X = N_2 = 10.50$ grams of air per minute

20% excess air

$$20\% \times (10.50 + 2.67) = 2.54$$

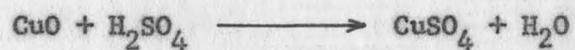
Total air needed would be:

$10.50 + 2.67 + 2.54 = 15.26$ grams of air per minute.

or $\frac{15.26}{456} = 0.0335$ pound per minute

or 0.55 cubic feet of air per minute at 20% excess air.

APPENDIX B

Calculation of sulfuric acid needed for leaching operation

Total sulfuric acid needed would be:

200 gram (calcine in autoclave in grams) x 2.0% (zinc content
in the calcine) = 10.00 cubic centimeters.

APPENDIX C

Procedure of chemical analysis of iron

1. Weigh 1.000 gram of iron-bearing material into a 250 milliliter beaker.
2. Add 25 milliliters of strong HCl.
3. Heat for one hour with watch glass cover on until residual is free.
4. Dilute with distilled water to 2 or 3 times.
5. Filter.
6. Heat filtrate to 196°F.
7. Add SnCl_2 solution until the filtrate is colorless, then add two drops more.
8. Dilute it to 200 cubic centimeters with distilled water.
9. Cool to room temperature.
10. Add saturated HgCl_2 .
11. Titrate with $\text{K}_2\text{Cr}_2\text{O}_7$ (Potassium Dichromate), using $\text{K}_4\text{Fe}_2(\text{CN})_6$ as indicator.

APPENDIX D

Procedure of chemical analysis of zinc

1. Weigh 1.000 gram of dried sample into a 250 milliliter beaker.
2. Add 15 milliliter of concentrated HNO_3 .
3. Heat until brown fumes are almost gone.
4. Add one gram of HClO_3 .
5. Heat and evaporate to dryness.
6. Cool to room temperature.
7. Add 10 to 15 grams of reagent-grade NH_4Cl .
8. Add 20 milliliter of strong NH_4OH .
9. Dilute to 75 milliliter with distilled water.
10. Add 20 milliliter of $\text{Br}_2(\text{H}_2\text{O})$ (bromine water).
11. Boil 10 minutes.
12. Allow precipitate to settle.
13. Filter.
14. Wet the filter paper with hot water.
15. Let it be acid with HCl .
16. Dilute to 200 milliliter with distilled water.
17. Add metallic lead.
18. Boil until all copper is precipitated.
19. Add 50 milliliter of H_2O and 5 milliliter of strong HCl .
20. Heat filtrates until 70°F .
21. Titrate with $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ using uranyl nitrate as an outside indicator.

APPENDIX E

Procedure of chemical analysis of copper

1. Weigh 1.000 gram of dried sample into a 250 milliliter beaker.
2. Add 7 milliliters of strong HCl and then heat.
3. Add 10 milliliters of strong HNO₃ and then heat.
4. Add 7 milliliters of strong H₂SO₄ and then heat.
5. Evaporate until sulfuric acid fumes are strong.
6. Cool to room temperature.
7. Add 30 milliliters of distilled water.
8. Heat until all soluble salts are in solution.
9. Cool.
10. Add 4 grams of metallic zinc.
11. Heat until the zinc dissolves.
12. Add 25 milliliters of H₂S water.
13. Filter.
14. Wash the precipitates many times with distilled water.
15. Add 7 milliliters of strong HNO₃.
16. Boil until the nitrous fumes are gone.
17. Filter.
18. Wash the filter paper with 5 milliliters bromine water.
19. Cool to room temperature.
20. Let it be just alkaline by using NH₄OH.
21. Then let it be acid again with a few drops of acetic acid.
22. Add 2 or 3 cubic centimeters 80% acetic acid.

23. Cool to room temperature.
24. Add 3 grams KI.
25. Add 5 milliliters of starch solution.
26. Titrate with thiosulfate.

APPENDIX F

Procedure of chemical analysis of moisture and ignition

1. Weigh 1.000 gram of sample in a crucible.
2. Put the crucible and contents in a dry oven and dry at 105°C.
for one hour.
3. Cool and weigh.
4. Heat strongly at 1400°F. for one and a half hours.
5. Cool in a desiccator.
6. Weigh.

APPENDIX G

Procedure of chemical analysis of sulfur

1. Weigh 1.000 gram of sample in a 250 milliliter beaker.
2. Add 20 cubic centimeters of concentrated HNO_3 .
3. Heat.
4. Add 1 gram KClO_3 .
5. Add excess HCl and evaporate to dryness.
6. Add 10 to 20 cubic centimeters of HCl and evaporate to dryness.
7. Add 15 to 40 cubic centimeters strong HCl and evaporate the solution until a skim forms.
8. Add 5 to 10 cubic centimeters of HCl and dissolve the iron.
9. Dilute the solution in the same amount of hot water.
10. Filter.
11. Warm the filtrate to 60°C .
12. Add 10 cubic centimeters, 10% BaCl_2 .
13. Let it stand for 4 hours and settle.
14. Filter.
15. Ignite at 1400°F . for one hour.

APPENDIX H

The procedure for operation of the autoclave to leach the roasted calcine.

1. Remove the rotor seal assembly.
2. Remove V-belt.
3. Remove the hex-socket cap screw from the cover.
4. Remove the cover assembly by grasping the stuffing box and lifting straight up.
5. Remove and clean the cover gasket.
6. Remove and clean the baffle assembly and replace it.
7. Add 2000 cubic centimeters of distilled water and 10 or 12, 16 or 20 cubic centimeters of sulfuric acid in the autoclave.
8. Connect heater to power source.
9. Add 200 grams of roasted ore.
10. Replace cover gasket.
11. Replace cover assembly in same position it was in originally.
12. Screw the right hex-socket cap into the body and tighten it.
13. Replace V-belt.
14. Replace rotor seal assembly and connect shaft cooling water inlet.
15. Connect cooling water to connection.
16. Insert thermocouple wires into thermocouple well in cover.
Connect the other end of the thermocouple wires to a Leeds and Northrup Potentiometer.

17. Connect motor to power source.
18. Close all panel mounted valves.
19. The temperature of solution to be maintained to within $\pm 0.5^\circ$ by both a variable transformer and the water cooling system.
20. Vessel is now ready for operation.
21. The leaching time used is one hour.
22. After the leaching operation is accomplished, the cool water is introduced in the cooling system.
23. Be sure all pressure is relieved then follow the steps from one to six.
24. Discharge the leaching solution and leaching product by a vacuum pump and filter.
25. The residue was washed with enough solution to remove the solubilized zinc and copper.
26. After washing the residue was dried, weighed and analyzed.

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ABSTRACT

This investigation deals with the application of high pressure and high temperature leaching techniques to separate out zinc and copper from the iron constituents of a calcined sulfide ore. An important variable in this study proved to be the concentration of the leaching reagent -- sulfuric acid.

The leaching temperature was varied within a range of 250°F. to 550°F., and 8 cubic centimeters to 20 cubic centimeters of sulfuric acid in 2000 cubic centimeters of distilled water was employed as the leaching agent concentration.

The major equipment utilized for roasting was the fluidized bed and an autoclave for leaching. After the physical and chemical treatments of roasting and leaching of the calcine, the resulting constituents were studied by means of quantitative chemical analysis.

Numerical theories were used to correlate the points obtained into continuous functions of the leaching temperature, concentration of sulfuric acid and the recovery percentage. From these curves, it is concluded that the recovery of the impurities in the calcine is proportional to the leaching temperature and the concentration of the leaching agent. However, under certain circumstances, the leaching action causes loss of iron in the calcine, and the minimizing of the loss in leaching is also studied.