THE EFFECT OF SOLUTE SIZE DISTRIBUTION

ON THE

ROASTING AND LEACHING OF A COMPLEX SULFIDE ORE

by

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Thesis submitted to the Graduate Faculty of the

Virginia Polytechnic Institute

in candidacy for the degree of

MASTER OF SCIENCE

in

Mining Engineering

August, 1963

Blacksburg, Virginia

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I. INTRODUCTION

Since 1951, a series of investigations have been conducted by the Department of Mining Engineering and the Virginia Engineering Experiment Station of the Virginia Polytechnic Institute for the purpose of finding an applicable beneficiation process for a complex sulfide ore found in Carroll County, Virginia. This deposit is called the Great Gossan Lead. It contains many valuable constituents including iron, copper, zinc, lead, and sulfur. Favorable results obtained from past investigations indicated economic potential for the mineral deposit. If a beneficiation process for the ore can be developed, the dormant Great Gossan Lead will probably be the largest undeveloped sulfide ore deposit in the Eastern United States.

Previous beneficiation studies have arrived at the following conclusions:

A. The significant sulfide minerals are pyrrhotite, marmatite, pyrite, and chalcopyrite.

B. Bulk flotation of the sulfide minerals is felt to be the most feasible concentration process.

C. Differential flotation of the individual sulfides is probably not feasible.

D. In order to effect the most complete utilization of the

minerals a combined treatment using flotation, roasting and leaching will probably be most effective.

Other studies on roasting and leaching of the ore with a fluidized-bed kiln and an autoclave have indicated:

A. The optimum roasting temperature for the removal of acid soluble zinc to meet the commercial specification of an iron ore is between 1550°F. and 1650°F.

B. The optimum roasting temperature for the removal of acid soluble copper is between 1350°F. and 1450°F.

C. The effect of leaching time is highly significant, but the leaching temperature has no appreciable effect.

Many other factors that may affect the roasting and leaching of the complex sulfide ore are unknown. The effect of the size of solid particles in the fluidized-bed kiln and the autoclave, the effect of pulp density in the autoclave, and the effect of the concentration of solvent are still to be determined.

This study has been carried out for the purpose of investigating the size effect of solid particles in the fluidized-bed kiln and the autoclave. The effect of pulp density in the autoclave has also been investigated.

Recently the fluidized-bed roasting technique has been utilized in the preparation of sulfide ores for leaching. Over the past several years, there have been intensive studies made of leaching

in autoclaves where the leaching process can be conducted under high pressures and high temperatures.

The major objective of most roasting operations is to oxidize the sulfide particles to oxides or sulfates. The oxidation must be carried out without fusing the charge. Other reasons for roasting are to volatilize certain impurities and to convert the roaster charge into porous sinter. Regardless of the type of roaster-reactor used, the sulfide particles must be exposed to a current of air and ignited. As the air strikes the heated particles they begin to react as follows:

$$4 \ FeS_2 + 11 \ O_2 \longrightarrow 2 \ Fe_2O_3 + 8 \ SO_2 \ ; \Delta H = - \ 808,320 \ Cal...(1)$$

$$2 \ Cu_2S + 3 \ O_2 \longrightarrow 2 \ Cu_2O + 2 \ SO_2 \ ; \Delta H = - \ 188,900 \ Cal...(2)$$

$$2 \ ZnS + 3 \ O_2 \longrightarrow 2 \ ZnO + 2 \ SO_2 \ ; \Delta H = - \ 222,400 \ Cal...(3)$$
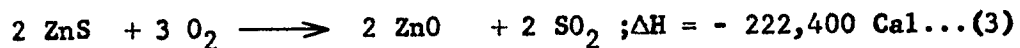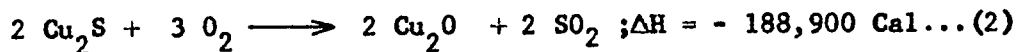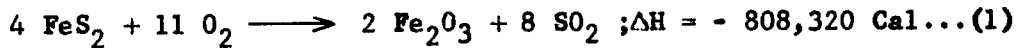
Another important chemical reaction that takes place in many roasting operations is "sulfatizing" or the formation of metallic sulfates rather than oxides. Hot SiO_2 and Fe_2O_3, which are almost always present in roasting operations, act as catalysts to promote the reaction:

$$2 \; SO_2 + O_2 \longrightarrow 2 \; SO_3 \; ; \Delta H = -46,000 \; Cal \dots \dots \dots \dots \dots (4)$$
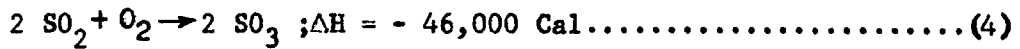
Some of the SO_2 formed by the burning of sulfur combines with O_2 to form SO_3. The SO_3 in turn reacts with metallic oxides to form sulfates:

$$FeO + SO_3 \longrightarrow FeSO_4 \; ; \Delta H = -63,100 \; Cal \dots \dots \dots \dots (5)$$

$$CuO + SO_3 \longrightarrow CuSO_4 \; ; \Delta H = -52,300 \; Cal \dots \dots \dots \dots (6)$$

$$ZnO + SO_3 \longrightarrow ZnSO_4 \; ; \Delta H = -54,500 \; Cal \dots \dots \dots \dots (7)$$
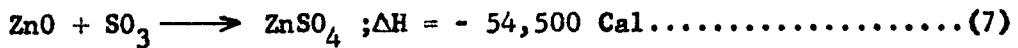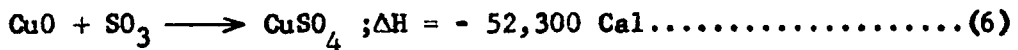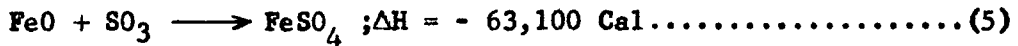
The formation of sulfates is promoted by low roasting temperatures and high SO_3 concentration. In general, high roasting temperatures will decompose sulfates into oxides and SO_3.

A fluidized-bed kiln-type reactor provides ideal conditions for gas-solid reaction because each solid particle is in constant motion and is continually in contact with the moving gas stream.

The calcines obtained as the products of fluidized-bed roasting are introduced to the autoclave and leached with dilute sulfuric acid. In the autoclave the copper oxide and zinc oxide are dissolved according to the following:

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \dots\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O \dots\dots\dots\dots\dots\dots\dots\dots\dots (9)$$

The iron oxide, Fe_2O_3, is practically insoluble in the leach solution and therefore separated as residue. Since zinc ferrite, $ZnFe_2O_4$, is also insoluble in the dilute sulfuric acid solvent, the roasting temperature should be low to prevent the formation of zinc ferrite. Zinc in this form cannot be recovered by leaching, and its presence prevents the residual iron from meeting commercial specifications for blast furnace feed. Because the zinc mineral in the Great Gossan Lead Ore is marmatite $Zn(Fe,Mn)S$, it is very difficult to prevent the formation of a certain amount of zinc ferrite.

Chemical kinetics is also involved with this investigation. Chemical equilibra and thermodynamics involve only the initial and final states of the chemical reaction. In this investigation, however, interest lies in the intermediate steps which lead to the final products. The rates of these intermediate steps and the factors which determine the rate of reaction, such as concentration, temperature, pressure, leaching agent and catalysts, are of particular interest.

When the reagents are in two different phases, the reaction can take place only at the surfaces where the two phases are in contact. The reaction velocity is then a function of the area of contact between the phases and the diffusion rates of reagents and products through the phase boundaries.

It is evident that the surface effect becomes greater as the degree of subdivision of matter is increased. The characteristics of fine dissemination of the sulfide minerals in the Great Gossan Lead Ore have been clarified by previous microscopic studies. Many of the discrete grains of pyrrhotite, chalcopyrite and marmatite have been found to be in the size range of 5 microns. It is therefore possible that the extent of exposed surface area of the sulfide minerals in both the roasting and leaching processes is a significant factor affecting the reactions.

In the process of leaching there are two main reasons for the high initial rate of dissolution. The concentration of the solvent is usually at a maximum, and the greatest possible surface of soluble mineral is exposed. As dissolution proceeds, the rate decreases. The small minerals dissolve completely, decreasing the active surface of contact, and the strength of the solvent is depleted. The minerals that remain may be almost completely encased

in gangue minerals that present very little surface to the solvent. These phenomena involve the factors of leach concentration, size of solid particles and pulp density in the autoclave.

II. LITERATURE STUDIES

Occurrence of the Great Gossan Lead Sulfide Ore Deposit

Location

The Great Gossan Lead is located in the Blue Ridge Plateau of Virginia, about 10 to 15 miles northwest of the crest of the Blue Ridge Mountains. The Lead has been traced more or less continuously for about 16.5 miles with a maximum width of about 150 feet and an average width of some 20 feet. The main Lead has its southern terminus near Galax in western Carroll County and trends northeastward through Carroll County to a point near Sylvatus, a few miles west of the Floyd County line. Offsets of the main Lead are found in the Sutherland and Toncray Leads of Floyd County, and a major offset is in the extreme eastern part of Grayson County [1,2].

Geology

In general, the Great Gossan Lead is oriented with the strike N.25-60°E. and dip 45°S.E. The main Lead and offset lie in a complex of crystalline schists and gneisses [1]. The schists and gneisses are intruded by masses of relatively unmetamorphosed diorite, and by small bodies of granite and syenite. A fine-grained mica and sericite schist is the main country rock throughout the main Lead region. The component mineral grains of the schist are small, although they are usually in aggregates of a size coarser than that of the sulfide grains that are sometimes found as discrete

grains in the schistose folds. The major structure responsible for the emplacement of the ore-bearing fluids along the main Lead may have several, or a combination of several origins. Detailed field work will be necessary to work out the structural pattern. After the formation of the structural framework, the mineralizing fluids ascended along the major fractures and began the replacement and alteration of the country rock immediately adjacent to the rock openings, forming a hypothermal deposit of primary sulfides. 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 enrichment of copper sulfides occurred immediately below the water table. Although C. S. Ross [3] indicated a late Paleozoic age for the formation of the Great Gossan Lead, the age of the deposit is still unknown.

Mineralogical Characteristics of the Ore

A. Component Minerals. The primary sulfides of economic significance are as follows (in order of decreasing abundance):

1. Pyrrhotite - Fe_8S_9
2. Marmatite - $Zn(Fe,Mn)S$
3. Pyrite - FeS_2
4. Chalcopyrite - $CuFeS_2$

In addition to these, galena (PbS), arsenopyrite (FeAsS), löllingite (FeAs$_2$), and/or leucopyrite (Fe$_3$As$_4$), tetrahedrite (essentially a copper antimony sulfide) and/or tennanite (similar to tetrahedrite with arsenic replacing the antimony), cubanite (CuFe$_2$S$_3$), and iron oxides (magnetite - Fe$_3$O$_4$, hematite - Fe$_2$O$_3$, limonite - Fe$_2$O$_3$.nH$_2$O) have been identified. The latter minerals are generally present to the extent of less than one percent. The high-grade secondary minerals which were mined early in the history of the Lead and of which only minor quantities may still be seen are chalcocite and covellite. Earlier the presence of oxidized copper ores, including carbonates, had been reported in the gossan. The significant gangue minerals are quartz, carbonates, chlorite, micas and garnets.

B. Chemical Properties. The relative abundance of pyrrhotite in the sulfides varies from 70 to 95%. An analysis of a nearly pure specimen of pyrrhotite gives its composition as Fe 60.8% and S 39.2%. The zinc-bearing sulfide mineral has been determined to be marmatite rather than sphalerite. An analysis of a minus 325-mesh flotation concentrate of the marmatite shows the average composition: Zn, 55.33%; Fe, 8.29%; Cu, 1.24%; Mn, 0.20%; and S, 35.05%. Marmatite accounts for 3 to 8% of the sulfides. Pyrite, representing 1 to 20% of the sulfide minerals, is noted in the more heavily mineralized sections where it replaces an equivalent quantity of pyrrhotite. The chalcopyrite distribution in the sulfide is fairly uniform and averages 2 to 3%. An analysis of the Great Gossan Lead head sample

show its composition as follows [4]:

Element	Weight %
Fe	35.52
S	25.37
Zn	1.96
Cu	0.63
Pb	0.34
Total	63.82

Gangue (by difference)36.18

C.   Physical Properties.   Previous qualitative microscopic studies on the ore have revealed the peculiar physical features of the sulfide minerals present [1]. The sulfide-gangue intergrowths feature smooth boundaries of the minerals. The grain sizes for the sulfide and gangue aggregates average about 65-mesh and 28-mesh respectively. Notable exceptions are the garnets and silicates which have hair-line veinlets of sulfides - principally chalcopyrite. Many of the gangue grains show 5-10 micron inclusions of sulfides - principally marmatite. The boundary contacts between the various sulfides vary from smooth to interlaced. Pyrrhotite and pyrite occur in discrete grains as coarse as 35-mesh, although the marmatite contains pyrrhotite inclusions of 5 microns or less. Discrete marmatite grains are usually smaller than 150-mesh. Microscopic examination of the typical marmatite-pyrrhotite relationship has indicated that about 50 per cent of the zinc sulfide grains will be found in the size range of 5 to 15 microns. The chalcopyrite is usually finer

than the marmatite. Discrete chalcopyrite particles average less than 10 microns. Galena occurs largely as very small locked particles of 5-10 microns in the marmatite. The iron oxides and arsenopyrite generally appear as 5-15 micron discrete grains in the gangue. The tetrahedrite-tennanite occurs with a grain size of 10 microns or less, and always as inclusions in galena.

Ore Reserves

It has been estimated that the Great Gossan Lead might contain over 200 million tons of ore reserves [4]. Because of this tremendous size, it has the potential to be a major source of iron ore. The main source of iron would be from the pyrrhotite, which is the principal component mineral of the ore deposit. Also, considerable quantities of copper, zinc, lead, and sulfur could be obtained from the minor component minerals - pyrite, chalcopyrite, marmatite, and galena.

Results of Previous Beneficiation Investigations

Flotation Investigations

A series of flotation studies, including bulk sulfide flotation, pilot plant tests, and differential flotation, have been conducted at the Virginia Polytechnic Institute. Statistical analyses of the experimental results have shown:

A.   The Lead ore is amenable to a relatively simple bulk sulfide flotation procedure. Theoretically, bulk sulfide concentrates ,

recovering 98% of the sulfides and assaying 53.5% iron and 38.5%

sulfur, can be obtained. For a recovery comparable to the theoretical

value, a bulk sulfide concentrate from the Betty Baker area, represen-

tative of the most complex material found in the deposit, will assay

49.5% iron, 36.0% sulfur, 3.3% zinc, 0.78% copper, and 0.67% lead[1].

B.   Differential flotation of the individual sulfide requires

extremely fine grinding, which may be uneconomical. The sulfides

must be ground finer than minus 325-mesh in order to liberate the

marmatite, chalcopyrite, and galena from the iron sulfide. Differen-

tial flotation from a reground bulk sulfide concentrate does not offer

much promise. Differential flotation after depressing marmatite by

using sodium sulfide (Na_2SO_3) offers the best promise of making high-

grade iron, copper-lead, and zinc concentrates [1].

C.   For overall high recoveries a treatment combining roast-

ing and leaching of a bulk sulfide concentrate is believed to be

most promising.

Roasting Investigations

Studies with applications of roasting and leaching techniques

have been carried out at the Virginia Polytechnic Institute. Explora-

tory roasting tests were first performed in a 1-inch diameter fluidized-

bed column. The preliminary test results justified continuation of

the work with application of a 4-inch diameter fluidized-bed kiln.

Studies on the roasting temperature effect in fluidized-bed kilns

were conducted by C. H. Shiuh [5]. The roasting conditions used by

Shiuh in his experiments were: feed rate, 8 grams per minute; air supply, 1 cu. ft. per minute; range of roasting temperature, 1050°F. to 1650°F. A mixture of bulk sulfide flotation concentrates and table concentrates was used for roasting. An optimum range of roasting temperature for the removal of zinc content from roasted calcine by a subsequent leaching process was determined to be 1550-1650°F. An optimum range of roasting temperature for the removal of copper content from roasted calcine by a subsequent leaching process was determined as 1350-1450°F.

Leaching Investigations

Earlier tests of leaching roasted calcine under static conditions in uniquely designed pressure vessels were conducted by W. E. Foreman, staff member of the Department of Mining Engineering, Virginia Polytechnic Institute [4]. A statistical analysis of the test results indicated that the significance of the errors exceeded that of the variables and no clear cut conclusion was possible. Consequently, leaching experiments, utilizing a one-gallon stirred autoclave, have been carried out. In connection with the fluidized-bed roasting experiments, Shiuh has studied the effect of leaching time and temperature in the process of leaching the fluidized-bed calcine with dilute sulfuric acid solvent in the autoclave [5]. The leaching conditions used in the experiments were: solvent, 13 ml. concentrated sulfuric acid diluted with 2000 ml. distilled water; pulp density, 200 grams of roasted calcine per 2000 ml. distilled water plus 13 ml. sulfuric acid; leaching temperature, 250°F. and 450°F; leaching time,

1-hour single leaching and 1-hour double leaching (totalling 2 hours for each double leaching). The experimental results indicated that the effects of leaching time and roasting temperature were significant, but the leaching temperature had no appreciable effect.

Principles of Roasting Sulfide Ore with a Fluidized-Bed Kiln

General Description

Sulfide ore or concentrate is not usually in a form to undergo direct reduction and thus conversion to another state is necessary. This is commonly affected by roasting, which may be defined as heating below the fusion point with an access of air. Although many other avenues of approach were explored, oxidizing and/or sulfatizing roasting followed by leaching with dilute sulfuric acid solution or water appears to hold promise as a successful procedure for treating cupriferous and nickeliferous pyrrhotites. The method of fluidization or fluosolids roasting, in which finely divided solid materials are kept in suspension by a rising current of air, was developed by the Dorr Company in 1945. This process is now in use for roasting zinc concentrates, arsenopyrite-gold concentrates and for production of sulfur dioxide from iron pyrite. Copper sulfides, especially those containing large amounts of iron sulfides, pyrite and pyrrhotite, can be given a sulfatizing roast which makes the copper soluble in water or weak acid [6,7]. Close temperature-control enables a 90 per cent water-soluble product to be obtained with only 1.5% iron going into solution. This opens up interesting

possibilities in that copper sulfide concentrates could be roasted, leached, and treated electrolytically, by-passing the smelter altogether.

Mechanism of Chemical Reactions in Fluidized-Bed Roasting of Sulfide Ore.

The fluidized-bed kiln-type reactor provides an ideal condition for gas-solid reaction because each solid particle is in constant motion and is continually in contact with the moving gas stream on all sides. As previously shown by the equations (1) through (7), the iron sulfide, copper sulfide, and zinc sulfide are converted into iron oxide, copper oxide, and zinc oxide respectively by the oxidation reactions, and some of the oxides are converted into iron sulfate, copper sulfate, and zinc sulfate by the sulfatizing reactions during the process of fluidization roasting. As the reagents are in two different phases - gaseous and solid, the reaction can take place only at the surfaces where the two phases are in contact. The reaction velocity is then a function of the area of contact between the phases and the diffusion rates of reagents and products through the phase boundaries. Since these oxidation and sulfatizing reactions give off a large amount of reaction heat, the roasting process is self-sustaining once the reactions begin, provided a proper temperature control is maintained. In many cases higher temperatures would cause fusion, volatilization, or some other phase change that must be avoided in

a particular operation. Reactions such as equations (2) and (3),
when conducted in roasting furnaces, must be maintained at a low
temperature level so that none of the solid material fuses. Regu-
lation of temperature often provides a measure of control over
other reactions involving gangue minerals or impurities. The
temperature may also affect the nature of the primary reaction.
When sulfides are roasted in air, they usually form metal oxides
and SO_2 as shown by the equations (1), (2) and (3). At low tempera-
tures, however, the oxygen may combine directly with the sulfide
to form a sulfate. Some authorities feel that in all cases the
sulfates form first and that the high temperature then decomposes
the sulfates into SO_2 and metal oxides; in any event the roasting
temperature is very important in determining the nature of the com-
pound formed. It is possible to attain selective roasting of
mixtures of different sulfides by proper temperature control [8].

Theories of Sulfatizing Roasting of Sulfide Ore

Some authorities have claimed different theories related to
the formation of sulfates in the process of sulfatizing roasting of
sulfide ores. Ashcroft [9,10], working with Rhodesian ores, found
that the reaction in sulfatizing roasting proceeds primarily and
definitely to the formation of copper sulfates and not oxides, and
that the formation of oxides and liberation of SO_2 are secondary
reactions caused by the decomposition of previously formed sulfates.
He summarized his results as:

A. Iron oxide probably acts as an efficient catalyzer in the formation of copper, zinc, and nickel sulfates.

B. At temperatures above 550°C. or thereabout, formation of cupric ferrite ($CuO \cdot Fe_2O_3$) begins when copper oxide and iron oxide are brought into juxtaposition, and at 700°C. the reaction is prohibitively rapid. Cupric ferrite is insoluble in any dilute acid-leaching normally used in copper leaching.

C. The ordinary rabbled furnace is inimical to the production of all water-soluble copper sulfate by reason of the omnipresent reaction:

$$CuSO_4 + CuS + O_2 \longrightarrow 2CuO + 2SO_2 \dotfill (10)$$

D. A reaction similar to the above resulting in the decomposition of sulfates is apt to occur in the presence of carbon or of any reducing gas, such as flue gas:

$$CuSO_4 + CO \longrightarrow CuO + SO_2 + CO_2 \dotfill (11)$$
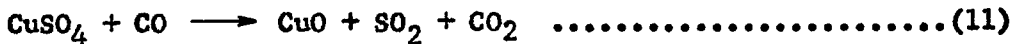
E. Iron sulfate is not, as is usually stated, decomposed at a temperature so far below the decomposition temperature of copper sulfate that a mere roasting at a carefully regulated temperature may be employed to produce, quantitatively, soluble copper and insoluble iron.

Peretti [11] refuted the claim of Ashcroft that copper oxide production resulted only from secondary decomposition of sulfates that were formed as primary products. He showed that a layer of Cu_2O appeared directly adjacent to the Cu_2S during roasting of

briquettes of cupric sulfide, CuS. The reactions proposed were:

$$2CuS \longrightarrow Cu_2S + \frac{1}{2} S_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(12)$$

$$\frac{1}{2} S_2 + O_2 \longrightarrow SO_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(13)$$

$$Cu_2S + \frac{3}{2} O_2 \longrightarrow Cu_2O + SO_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(14)$$

$$Cu_2O + \frac{1}{2} O_2 \longrightarrow 2CuO \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(15)$$

At temperatures above 663°C., CuO was the only final solid phase reported. Below 663°C., increasing amounts of sulfate were found mixed with the CuO. When the outer layer was wholly CuO, it was black, porous, and easy to cut with a knife. The specimen containing sulfate became harder and less porous as the sulfate content increased until at 478°C. and 430°C., the pieces became so hard and dense as the holding time increased that the reaction practically ceased in a CuO layer between 3 and 4 millimeters in thickness.

Investigation by McCabe and Morgan [12] supports the claim of Peretti. They reported the following sequence of products, beginning at the sulfide surface, when roasting discs of synthetic chalcocite at 600°C.: Cu_2O, a mixture of Cu_2O and $CuSO_4$, $CuSO_4$, $CuO \cdot CuSO_4$, and CuO at the outer surface.

Thornhill and Pidgeon [13] studied the roasting of sulfide and reported the formation of firm, protective oxide shells when roasting pentlandite particles at temperatures below 650°C. They suggested that much of the oxide growth took place by ionic migration through the continuous oxide layer. The oxidation rate was found to increase with fineness of grind when roasting pyrrhotite. Whereas 65 to 80-mesh particles roasted linearly at 550°C., the

oxidation rate of 30 to 40-mesh particles was retarded after the
formation of about 160 microns thickness of oxide. The roasted
pyrrhotite particles were deeply penetrated by oxide column.

Wadsworth's study [14] of sulfatizing Cu_2S indicated that
oxidation reactions generally take place by diffusion. However,
entrapped gases in certain temperature ranges almost stop oxidation
before the process is completed.

Lewis [15] determined that the optimum temperature for oxida-
tion of chalcocite to give water-soluble copper is about 450°C.
with both air and oxygen and that oxygen is a more effective oxidi-
zing agent than air for conversion to water-soluble substances. At
about 450°C. the following reactions were confirmed:

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \quad \dots\dots\dots\dots\dots(16)$$

$$2CuO + Cu_2S \longrightarrow 4Cu + SO_2 \quad \dots\dots\dots\dots\dots(17)$$

Fursman [16] also determined that basic copper sulfate begins
to form at a little above 300°C. and in the presence of cupric
oxide the temperature of formation is probably much lower because
of the reaction:

$$CuO + CuSO_4 \longrightarrow CuO \cdot CuSO_4 \quad \dots\dots\dots\dots\dots(18)$$

Observations of Baroch [17], working with copper ore at Bagdad,
Arizona, indicated that reactions take place in three distinct stages,
which may overlap to some extent, but which take place only in the
order given. Each stage requires a definite temperature range and
the best oxidation conditions possible in order to be completed with-
in practical time limits. He was successful in almost completely

transforming the copper into a water-soluble state as by:

A.   First stage, 370° to 380°C., decomposed all but a trace
of true sulfides while the sulfur was driven off or oxidized to
form sulfates. Temperatures above 455°C. should be avoided before
this stage is completed, otherwise a true magnetite will be formed
that is difficult to reoxidize to the less soluble ferric form. The
probable reaction is:

$$FeS + 10Fe_2O_3 \longrightarrow 7Fe_3O_4 + SO_2 \dots\dots\dots\dots\dots\dots\dots\dots(19)$$
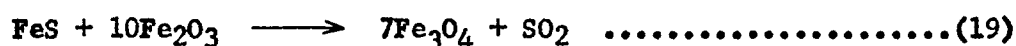
B.   Second stage, 455° to 540°C., is the oxidizing or demag-
netizing period during which the desired higher oxides of copper
and iron are formed.

C.   Third stage, 590°C., selectively destroyed the water-soluble
sulfates of iron.

The Effect of Zinc Ferrite

Zinc sulfide will not dissolve in the leaching solution nor
will it reduce in the zinc retort. When roasting zinc concentrates
that contain iron there is always a certain amount of zinc ferrite,
$ZnO \cdot Fe_2O_3$, formed. The zinc ferrite is as undesirable as the sul-
fide because it will not dissolve in the leach solution nor reduce
in the retort. The roasting temperature for zinc concentrate is low
in order to form some zinc sulfate (small amounts of sulfate are
desirable in feed for zinc leaching) and also to prevent the forma-
tion of zinc ferrite. However, when the zinc mineral is marmatite,
(Zn,Fe)S, it is very difficult to prevent the formation of a certain

amount of zinc ferrite. One of the reasons for the trend toward fluidized-bed roasting is that it may minimize the formation of ferrite.

Nii, Kimura, and Hisamatsu [18] have studied the formation of zinc ferrite from a stoichiometric mixture of ferric oxide and zinc oxide. Their investigations indicated that the ferric oxide, which was ignited at higher temperatures, showed lower reactivity with zinc oxide, and the rate of formation of ferrite decreased with the increase in ignition temperature. The effect of ignition temperature was more apparent when the ferrite is formed at low temperature. The activation energies of formation of ferrite increase from 39 to 62 kcal./mol. gradually, according to the increase in ignition temperature.

Latest report revealed that trials had been successfully conducted at the hydrometallurgical plant of Cerro de Pasco Corp. in La Oroya, Peru, to roast marmatite concentrates at a temperature as high as 1150°C. in a fluidized bed. At this high temperature, the insoluble zinc ferrite, formed from the ZnO and Fe_2O_3 in the roaster feed at temperatures above 650°C., was decomposed into acid soluble ZnO and insoluble Fe_3O_4. The extraction of zinc by leaching the calcines roasted at 1150°C. indicated 2-3% more than that by leaching the calcines roasted at 950°C. [19].

Kinetics and Thermodynamics in a Fluidized Bed

The motion of solid bodies in a fluidized bed has been studied by Yu. P. Gupalo [20] with a radiometric method. The experimental results indicate that in the presence of an ascending stream near the column axis, the medium in a fluidized bed can be regarded as a Newtonian fluid in which the viscosity does not change with the time rate of deformation to a first approximation.

It is known that the size of the particles and their specific gravity influence heat exchange between a gas and particles in a fluidized bed. The heat-transfer coefficient of the particles toward the gas, other conditions being equal, increases with an increase in the size of the particles and their specific gravity. Gel'perin and Ainshtein [21] explained this phenomenon, theoretically and experimentally, and proposed the following relationships on the influence of the size and specific gravity of solid particles on their heat transfer coefficient toward a gas in a fluidized bed:

A. The coefficient of heat transfer from particles of a given size and specific gravity to a gas is a function of the velocity of the gas and is expressed by the equation:

$$a = A w^n \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (20)$$

where, a - the heat-transfer coefficient of the particles toward the gas.

A - constant.

w - mean velocity of the gas.

n - constant.

B.   If the "effective" coefficient of heat transfer (a) is determined, the total quantity of heat transmitted from the gas to the particles can be expressed by the equation:

$$q = a \cdot \Delta t \cdot f \cdot N \quad \ldots \ldots \ldots (21)$$

where,

>   q - the total quantity of heat transmitted from the gas to the particles.
>
> Δt - the difference in temperatures between the gas and the surface of the particles.
>
>   f - the surface of one particle.
>
>   N - the total quantity of particles.

C.   The dependence of the heat-transfer coefficient on the size of the particles and their specific gravity is expressed by the power function:

$$a \sim d^p r^q \quad \ldots \ldots \ldots (22)$$

where,

>   d - the size of the particles.
>
>   r - the specific gravity of the particles.

and,

> $p/q = 3.$

Formulas for Determination of the Optimum Conditions in Fluidized-Bed Roasting of Complex Sulfide Ores

In general, the major purpose of the fluidized-bed roasting of complex sulfide ore is to extract copper, zinc and other valuable

components from the calcine. High extraction of metallic components can be attained by the precise control of roasting conditions. Nakajima, Nishihara and Kondo [22], in a work on the application of fluidized-bed roasting for hydrometallurgy, proposed a series of formulas to determine the optimum conditions in the sulfatizing roasting of pyrrhotite, chalcopyrite, and other sulfide minerals and metallurgical wastes, suitable for the extraction of copper and zinc. The proposed formulas are shown below.

A. Determination of air supply:

$$A = \frac{0.7(S)}{(SO_2)} \left[B(1-a) + \left\{ k(b + a/2) - B \right\} (SO_2) \right] \quad ..(23)$$

where,

A - quantity of air supply per 1 kg. dry ore, in Nm^3.

(S) - sulfur content in 1 kg. dry ore, in kg.

(SO_2) - volumetric ratio of SO_2 content in the roasting gas.

a - conversion rate of SO_3 formed from SO_2.

B - extraction of sulfur.

k - air consumption rate

$$k = \frac{\text{air consumption at sulfur extraction} = B}{\text{air consumption at complete extraction of sulfur by oxidation}}$$

b - oxygen factor, that is the number of moles of oxygen required to form 1 mole of SO_2.

B. Determination of feed rate:

$$F = \frac{A_T}{A} \, U_f \, \frac{36 \times 273}{273 + t} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(24)$$

$$= \frac{A_T d L}{\theta} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(25)$$

$$= \frac{V(SO_2)}{0.7B(1-a)(S)} \left[1 - \frac{k(b + a/2) - B}{B(1-a)} \, (SO_2) \right] \dots\dots\dots(26)$$

where,

A_T - cross-section area of the fluidized-bed kiln, in m^2.

U_f - fluidizing velocity of the ore particles, in cm/sec.

t - roasting temperature, °C.

θ - average retention time of the ore in the kiln, hr.

d - apparent specific gravity of the ore, in kg/m^3.

L - thickness of the filling layer in static state, m.

V - air supply per unit time, in Nm^3/hr.

C. Determination of the concentrations of gases in the kiln:

The maximum amount of copper, zinc and the valuable components from

the calcine will be extracted when the concentrations of gases in

the kiln meet the following:

$$CD^2K^2(SO_2)^3 = 2 \left[q - \frac{3}{2} \, C \, (SO_2) \right]^2 \quad \dots\dots\dots\dots\dots\dots(27)$$

where,

$$C = \frac{k}{B} \, b(1 - q) + q$$

$$D = \frac{k}{B} \, (b + \frac{1}{2})(1 - q) + q$$

q - concentration of oxygen in the intake gas, for air q = 0.21.

K - the equilibrium constant for the reaction, $SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3$.

Principles of Leaching Copper and Zinc From Roasted Ore

General Description

Hydrometallurgical methods have made considerable progress in recent years because of the improvements in practice and because it is particularly suited to the treatment of many low-grade ores. Gold ore, oxidized uranium and vanadium ores, and oxidized copper ores are all treated by hydrometallurgy. In addition hydrometallurgy is a very important method of treating sulfide zinc concentrates. Recent studies on the application of hydrometallurgy to the preparation of pyrrhotite as an iron ore have also indicated great promise. Leaching or lixiviation, which dissolve the metal, and precipitation, whereby the dissolved metal is removed from the leaching solution, are the two essential steps in a hydrometallurgical process. Calcine, an oxidized material formed by roasting sulfide concentrates, is one of the materials suitable for leaching. Many different solvents have been used for leaching purposes. Some have been very successful while others have not. In general the solvent to be used for leaching must possess the following characteristics: (i) it must dissolve the ore minerals rapidly enough to make commercial extraction possible, and it should not attack the gangue minerals, (ii) it must be cheap and readily obtainable in large quantities, and (iii) if possible, it should be such that it can be regenerated in the subsequent precipitation process. Water can be used for leaching such minerals as $CuSO_4$ and $ZnSO_4$. Dilute

sulfuric acid is used in the dissolution of oxidized copper and zinc according to the reactions shown previously by the equations (8) and (9). An aqueous solution of sulfuric acid is commonly used as the leaching agent in the treatment of calcine produced by roasting sulfide ore.

Pressure Leaching

For the past several years there has been an intensive effort made to leach in autoclaves under high pressures and with higher temperatures. High pressures are advantageous when gaseous reagents such as oxygen and hydrogen are used because the amount of gas kept in solution depends upon the pressure of the overlying gas. Recent work has shown that it is possible to dissolve sulfides directly in water, acid, or ammoniacal solutions if they are heated sufficiently and maintained under high enough pressure so that sufficient oxygen is forced into solution. The previous leaching methods for sulfides required roasting to convert them to soluble compounds [23].

In a study concerning oxygen pressure leaching of complex sulfide concentrate utilizing an autoclave, Umetsu, Tozawa and Sasaki [24] reported their experimental results as follows:

A.   An aqueous pulp of the complex sulfide concentrates (-200-mesh) with a composition of 10.6% Cu, 20.5% Fe and 34.7% S was treated with oxygen at elevated temperature and pressures in a liter stainless steel stirred autoclave.

B.   Ninety-nine per cent of the zinc and 95% of the copper in the concentrates were extracted under the following conditions:

1.   pulp density: 10.7% solid.

2.   leaching time: 1 hour.

3.   temperature: 185°C.

4.   total pressure: 40 atm.

C.   Ninety-nine per cent of the zinc and 90% of the copper were leached at 170°C., under 20 atm. in 4 hours.

D.   At a temperature of 185°C. and a total pressure of 40 atm., pulp density and leaching time were varied as:

1.   pulp density: 10.7-24.4% solid (30-80 grams in 250 c.c. water).

2.   leaching time: 1-5 hours.

The results indicated that more than 95% of the zinc in the concentrates were leached under these conditions, and 90% of the copper was extracted when the pulp density was 24.2% solid with a reaction time of 4 hours.

E.   The amount of iron leached increased with the increase in pulp density. However, the concentration of iron in the pregnant solution tended to be a constant value for every pulp density when the leaching time became longer.

Pressure leaching has two advantages over leaching at atmospheric pressure. It permits much greater concentration of gaseous reagents such as O_2 and H_2, and it permits higher operating temperatures which usually means faster dissolution.

In some cases both of these factors are important, while in other cases only one of them may be significant. It is of interest to note some pertinent facts about the solubility of substances in superheated water. The critical point for water is 374°C. and 218 atmospheres (about 3200 psi). At this pressure and temperature liquid water and steam becomes a single phase. At temperatures between the freezing point of water and its normal boiling point the solubility of the permanent gases decreases as the temperature rises, so that it is possible to practically expel all the dissolved air from water by boiling it. On the other hand, many salts and bases show increasing solubility when the temperature rises. At the higher temperatures that can be maintained in an autoclave, these effects are reversed. As water approaches the critical point, the solubility of salts approaches zero and the solubility of gas becomes practically infinite. Presumably this is because all gases are mutually soluble, and as liquid water approaches the critical point, it becomes more like a gas. Perhaps for the same reason it loses its solvent power for salts. This means that leaching and precipitation cannot be carried on at excessively high temperatures because the materials will not stay in solution and because excessively high temperatures require extremely high pressures. It is therefore conceivable that the chemical reactions that take place in pressure leaching are often quite complex.

The Relation Between Leaching Rate and Contact Time

The curves shown in Fig. 1 are typical of the curves obtained
when the laboratory data of extraction rate against leaching time
are plotted. The vertical coordinate is the per cent of the metal
dissolved and the horizontal coordinate is time. Such curves have
a characteristic shape - they rise rather rapidly from zero time
and then flatten off and approach the 100 per cent asymptotically.
In some cases the asymptote may be below 100 per cent if some of
the metal is in an insoluble form or completely encased in gangue
particles. When leaching is speeded up by using higher temperatures
or greater pressures, the curves rise more rapidly and approach the
limit more quickly, but they still have the same characteristic
shape. There are two main reasons for the high initial rate of
dissolution; the concentration of the solvent is usually at a
maximum, and the greatest possible surface of soluble mineral is
exposed. As dissolution proceeds the rate slows down because the
small minerals dissolve completely and thus greatly decreases the
active surface of contact, the strength of the solvent is 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 early. In practice
100 per cent extraction cannot be achieved. It is necessary to
determine the extraction time that will give the maximum economic
return.
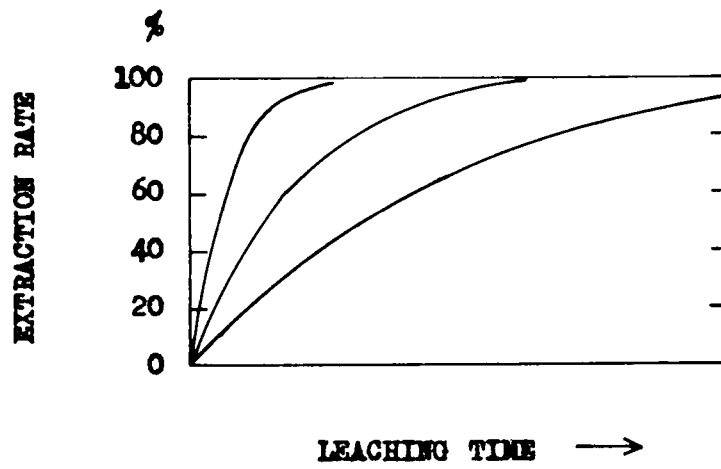
FIG. 1. TYPICAL LEACHING CURVES

Properties of Dilute Solutions

In this investigation, dilute sulfuric acid was used to leach copper and zinc contents from the roasted ore in an autoclave. It is therefore of interest to review the properties of dilute solutions.

There are four properties generally applicable to dilute solutions [25]:

A. Lowering of the vapor pressure.

B. Elevation of the boiling point.

C. Depression of the freezing point.

D. Osmotic pressure.

The first two properties are considered for the solutions of non-volatile solutes while the last two properties are considered for solutions in general. However, these four properties are closely related. Fig. 2 is a schematic diagram showing the relation between the elevation of the boiling point, lowering of the freezing point, and lowering of the vapor pressure caused by the addition of a non-volatile solute. It is noted that when a solution is separated from the solvent by a membrane which is permeable to the solvent but not to the solute, the solvent flows through the membrane into the solution where the chemical potential of the solvent is lower. This process is known as osmosis. An excess of pressure must be
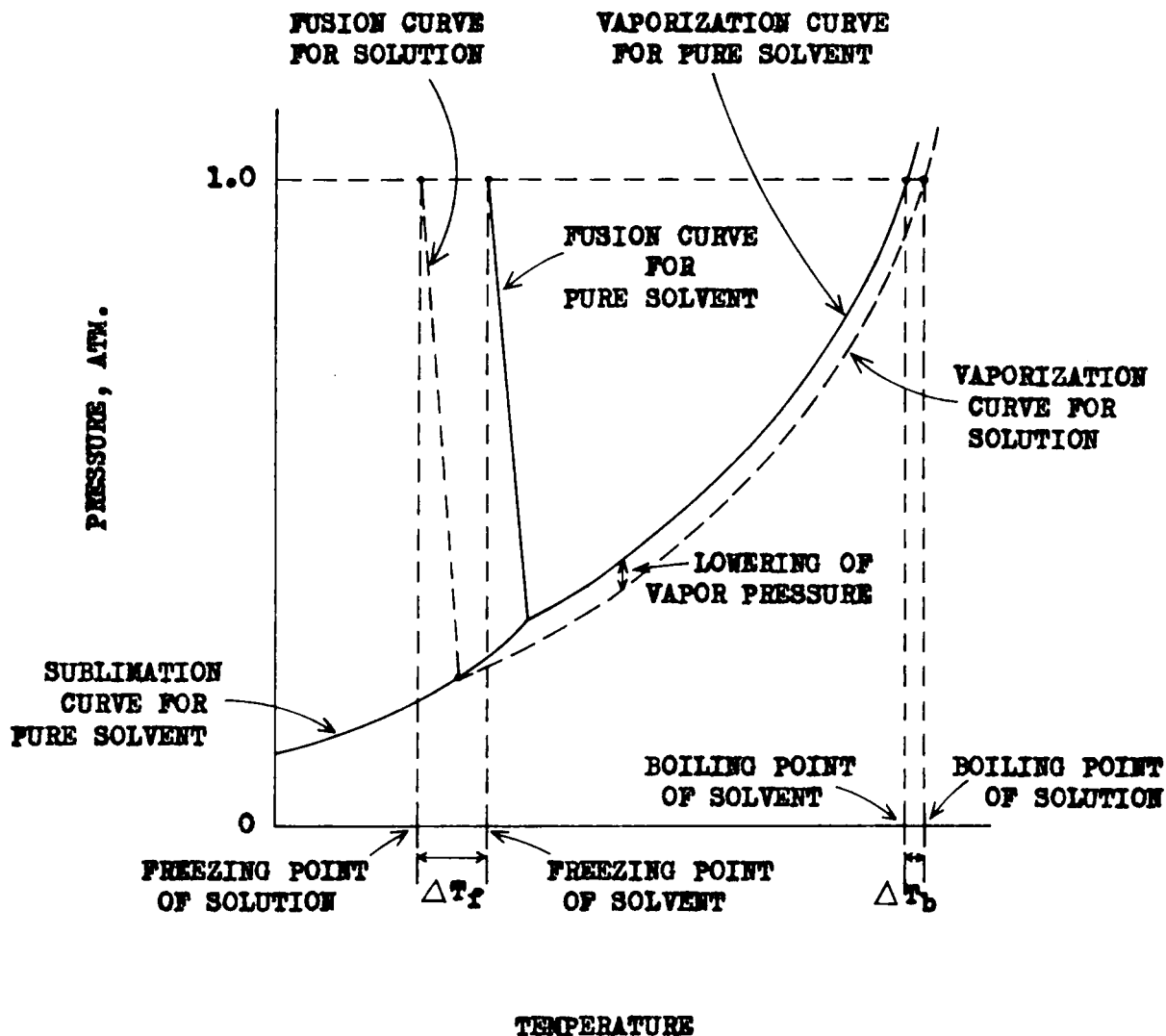
FIG. 2. SCHEMATIC DIAGRAM SHOWING THE RELATION BETWEEN THE
ELEVATION OF THE BOILING POINT, LOWERING OF THE FREEZING POINT,
AND LOWERING OF THE VAPOR PRESSURE CAUSED BY THE ADDITION OF A
NONVOLATILE SOLUTE. THE DIAGRAM IS NOT TO SCALE.

applied to the solution to prevent this flow of solvent through the membrane. The osmotic pressure is the pressure difference across the membrane required to prevent spontaneous flow in either direction across the membrane.

At equilibrium the chemical potential of pure solvent at 1 atm. pressure (u_1) is equal to the chemical potential of solvent in the compressed solution (u_2):

$$u_1 = u_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (28)$$

The chemical potential of the solvent in the solution is less than that of the pure solvent at the same pressure and temperature, but the chemical potential of the solvent in the solution can be raised by applying pressure. When the applied pressure is equal to the osmotic pressure, the two effects exactly counterbalance one another, so that the equation (28) is followed.

Chemical Kinetics

Chemical kinetics is greatly involved in this investigation. Chemical equilibria and thermodynamics involve only the initial and final states of the chemical reaction. However, we are interested in the intermediate steps which lead to final products.

The rate of a chemical reaction generally depends upon the concentrations of the reactants. The rate may also depend upon the concentrations of other substances not involved in the stoichiometric equation.

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 [26]. The first substantial treatment of the problem of reaction velocity at a solid-liquid interface, by Noyes and Whitney, led to the following relation:

$$\frac{dc}{dt} = m(c_s - c) \quad \dotsi (29)$$

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. The constant requires that the experimental conditions remain the same, specifically that the surface area of the solid and the thickness of the viscously flowing film adjacent to the solid do not change. It is convenient to express the change in concentration with time, dc/dt, in terms of the velocity constant (K) and the ratio of the volume of solution to the exposed interface ($\frac{V}{S}$) .

$$\frac{dc}{dt} = \frac{K}{V/S} (c_s - c) \quad \dotsi (30)$$

Rearrangement of variables and integration gives:

$$K = \frac{V}{S\theta} \ln \frac{c_s - c_1}{c_s - c_2} \quad \dotsi (31)$$

where,

K - the velocity constant, in centimeters per minute.

V - the volume of solution, in cubic centimeters.

S - the exposed interface, in square centimeters.

θ - the elapsed time, in minutes.

c_s - the saturation concentration, in any units as grams per liter.

c_1 - the initial concentration, in any units as grams per liter.

c_2 - the terminal concentration, in any units as grams per liter.

In a binary system consisting of solid and liquid phases, the rate of solution of solute in a solvent is greatly accelerated by pulverizing the material 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 crystals 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 [27].

Ore to be leached must be crushed and ground to such a size that the solvent can readily act on the soluble minerals. Grinding is usually unnecessary for porous oxidized ores.

For leaching purposes ore products are divided into two classes - slimes and sands. Slimes are ore products that are so finely ground that they tend to pack into a vat or tank and prevent the free circulation of liquid through the interstices of the bed of ore. Sands are products that are coarse enough to permit circulation of the solvent through the void spaces between the ore particles. These

two materials require different methods of attack. Slime leaching must be carried out by agitating the slime and solvent together in a suitable agitating tank. Sand leaching is done by allowing the solvent to percolate through the ore to be treated.

The Dissolution of Zinc Ferrite in Dilute Sulfuric Acid

As described previously, zinc ferrite is an undesirable material in the leaching process because it is practically insoluble in dilute sulfuric acid solution. In connection with the study on the formation of zinc ferrite, Nii and his associates [18] have investigated the dissolution of zinc ferrite in 9% dilute sulfuric acid under a temperature of 50 to 80°C. The maximum time of dissolution has been carried on as long as 1,215 minutes. The zinc ferrite, used in the tests, was formed by igniting a mixture of ferric oxide and zinc oxide. Their observations indicated that the rate of dissolution of zinc ferrite in dilute sulfuric acid was lowered by raising the preignition temperature of ferric oxide and the formation temperature of zinc ferrite. The dissolution rate was proportional to the surface area of ferrite particles, and the activation energies of dissolution were 15 to 18 kcal./mol.

It should be emphasized that one of the ultimate objectives of this investigation is to prepare the Great Gossan Lead complex sulfide ore as a commercial iron ore suitable for blast furnace feed. Zinc is a critical impurity since it will attack the refractory linings in the furnace with strong corrosive effects, and the fumes

formed by the vaporization of zinc will precipitate in the cooler sections of the furnace. Therefore elimination of the formation of zinc ferrite in the roasting process is important for obtaining a higher extraction of zinc in the subsequent leaching operation.

Elimination of Iron in the Pregnant Solution with Manganese Dioxide

Prevention or elimination of the dissolution of iron in the leaching solution is necessary in order to:

A. Maximize the recovery of iron when the leached residues are to be used as iron ore.

B. Eliminate the impurities in the electrolyte when electrolysis is used to precipitate copper, zinc and other valuable metals from the leach solution.

At the Kosaka Smelter, Dowa Mining Co. Ltd., Japan, manganese dioxide powder has been used to eliminate ferrous sulfate in the pregnant solution in the process of treating Cu-Zn concentrates with sulfatizing roasting, dilute sulfuric acid leaching, and electrolysis [28]. Through a correspondence with Mr. S. Tsunoda, the following principles were explained [29]:

A. Elimination of ferrous sulfate in the solution may normally be affected by converting ferrous sulfate into ferric sulfate and then neutralizing it to form a precipitate of ferric hydroxide.

$$2FeSO_4 + H_2SO_4 + \frac{1}{2} O_2 \longrightarrow Fe_2(SO_4)_3 + H_2O \quad \dots\dots\dots\dots\dots (32)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Fe(OH)_3 + 3CaSO_4 \quad \dots\dots\dots\dots (33)$$
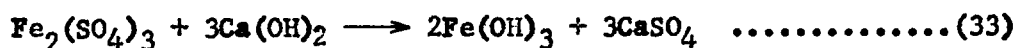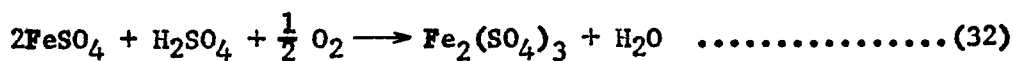
This process is not favored, however, because the fine precipitate of hydroxide will make filtration difficult, and the large volume of hydroxide precipitate will cause a considerable amount of loss of the valuable metals by adhesion.

B.   In solution with a proper amount of H_2SO_4, ferrous sulfate can be precipitated in the form of basic ferric sulfate by addition of manganese dioxide powder. The reaction is:

$$6FeSO_4 + 3MnO_2 + H_2SO_4 + nH_2O \longrightarrow 3Fe_2O_3 \cdot 4SO_3 \cdot nH_2O + 3MnSO_4 + H_2O$$

$$\dots\dots\dots\dots\dots(34)$$
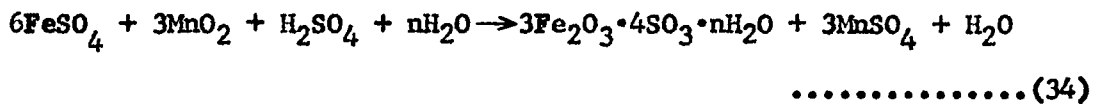
C.   If an excess amount of H_2SO_4 is present in the solution, the precipitation will not occur even though the ferrous sulfate will be oxidized to form ferric sulfate as the following reaction:

$$2FeSO_4 + MnO_2 + 2H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + 2H_2O \dots\dots\dots(35)$$
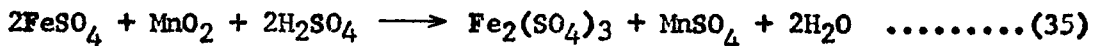
D.   If only a slight amount of H_2SO_4 is present, a precipitate of basic ferric sulfate may be formed:

$$10FeSO_4 + 5MnO_2 + H_2SO_4 + nH_2O \longrightarrow 5Fe_2O_3 \cdot 6SO_3 \cdot nH_2O + 5MnSO_4 + H_2O$$

$$\dots\dots\dots\dots(36)$$
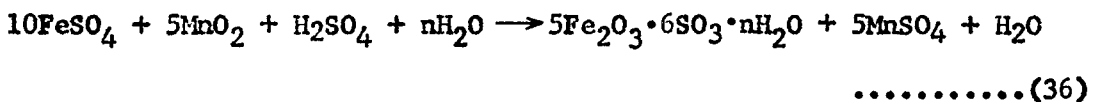
E.   Although the mechanism of these reactions is not clearly understood, the fact is that ferrous sulfate can be oxidized by manganese dioxide in an acidic solution and precipitated in the form of basic ferric sulfate, $x(Fe_2O_3) \cdot y(SO_3)$. Ferrous sulfate is then eliminated from the pregnant solution. By this process, the iron content in the pregnant solution is reduced from 5-6 grams per liter to 1.5-2 grams per liter.

Applications of Fluidized-Bed Roasting and

Dilute Sulfuric Acid Leaching

Okayama Smelter, Dowa Mining Co. Ltd., Japan [30]

This smelter has successfully applied the combined system of fluidized-bed roasting, dilute sulfuric acid leaching and precipitation processes to produce copper, iron ore and sulfuric acid from the complex pyrrhotite ore mined in the Yanahara mine of the company.

The Dorrco FluoSolids roaster is used for sulfatizing roasting of the raw ore, which is finely crushed and ground to a size range of 100 to 200-mesh and prepared into a feed slurry of 70-75% solids. The optimum range of roasting temperature is determined as 625-650°C., and the optimum SO_2 concentration of the roasting gas is determined as 7-8%. Rated capacity of the roaster is 115 tons per day.

The calcine is leached by dilute sulfuric acid solution (2% H_2SO_4) in quench tanks and agitators. The pregnant solution, which contains 2.5 grams per liter Cu, 20 grams per liter Fe and 5 grams per liter free H_2SO_4, goes to cementation troughs where the copper is precipitated on scrap iron. The leach residue is then sintered to produce 60% iron ore, containing less than 0.2% Cu, and sent to Amagasaki steel plant for treatment. Ninety-eight per cent sulfuric acid is produced from the exhaust gas of the roaster by a Monsanto contact system.

At present the approximate average copper analyses of feed, calcine, and leach residue are 0.80%, 1.00% and 0.14% respectively. Copper solubility is 85% and recovery is 82%. Overall iron recovery is 99.0%.

Kosaka Smelter, Dowa Mining Co. Ltd., Japan [28]

This smelter treats a complex mixture of copper and zinc sulfide concentrates produced from the Hanaoka mine of the company. The ore mined in the Hanaoka mine is an extremely complex sulfide ore, so-called "Black Ore," containing Au, Ag, Cu, Zn, Pb, Cd, etc., as the essential metallic components. Earlier tests on differential flotation of the ore indicated it would be very difficult to separate the copper and zinc sulfide minerals individually. However, application of the hydrometallurgical process combining sulfatizing roasting with the Dorrco FluoSolids roaster and leaching with aqueous solution of sulfuric acid and precipitation of valuable metals by electrolysis has made effective beneficiation of the ore possible. A mixture of bulk sulfide flotation of Cu-Zn concentrates, containing 8-10% Cu, 14-18% Zn, 20-25% Fe, and 35% S, is used as the roaster feed. The roasting conditions are:

A. Height of fluidizing layer .... 6.5 ft.

B. Roasting temperature .... 670°C.$\pm$ 5°C.

C. Ascending velocity of roasting gas...... 1.3 ft./sec.

D. Gas quantity .... 8000 ft.^{3}/min.

E. Gas composition .... SO_2 4-5%

O_2 8-10%

SO_3 0.4-0.5%

the remainder is N_2.

F. Air supply .... 8500 ft.^{3}/min.

G. Air pressure .... 4.5 psi.

H. Pulp density of the feed .... 70% solids.

The capacity of the system is 2500 tons of ore per month.
Since about 85% of the feed is minus 150-mesh, most of the over-
flow calcine is plus 150-mesh and most of the fine calcine carried
over the top of the roaster is minus 200-mesh. The calcines, in-
cluding overflow calcine and carried-over calcine, are leached by
a dilute sulfuric acid solution (5-6 grams per liter H_2SO_4) in a
series of quench tanks and agitators. At a temperature above 70°C.
manganese dioxide powder is added to the agitator to oxidize diva-
lent iron and precipitate it in the form of basic ferric sulfate
so that the iron content in the pregnant solution is reduced from
5-6 grams per liter to 1.5-2 grams per liter. Separation of the
pregnant solution and residue is affected by a series of thickeners.
The pregnant solution, containing 50 g/l Cu, 100 g/l Zn, 2 g/l Fe,
1 g/l H_2SO_4, is sent to the electrolysis plant to extract copper,
zinc, and cadmium step by step. The leach residue is about 45%
of the roaster feed. The residue contains 3 g/t Au, 350 g/t Ag,
1% Cu, 2% Zn, and 45% Fe. Among them, 30% of the Au, 50% of the
Ag, 40% of the Cu and 60% of the Zn are recovered by flotation

processes. It is reported that further utilization of the tailings, which contain 2 g/t Au, 120 g/t Ag, 0.6% Cu, 1-1.5% Zn, 4% Pb, and 45% Fe, is under investigation.

Luilu Metallurgical Plant, Union Minière Du Haut-Katanga, Katanga [31]

This is a modern hydrometallurgical plant in Katanga, Africa. Situated near the Kolwezi mines and concentrator of Union Minière du Haut-Katanga, the facilities occupy an area of one square kilometer. Yearly production is a little more than 100,000 tons of copper metal and 4,000 tons of electrolytic cobalt. Plant feed is composed of oxide concentrates mainly malachite, and sulfides, mainly chalcocite, associated with cobalt oxide and sulfide. The average composition of sulfide concentrates is 45% Cu, 2.5% Co while the composition of oxide concentrates is 25% Cu and 1.5% Co. The gangue is either siliceous or dolomitic and contains impurities as iron, nickel and zinc. Processing is by fluidized-bed roasting, dilute sulfuric acid leaching and electrolysis. Oxide concentrates can be dissolved directly, but insoluble sulfide concentrates are roasted to soluble sulfates by sulfatizing roasting in the Fluo-Solids-type reactors. Roasting temperature is maintained at 675°C. by an automatically regulated water spray. Approximately 98% of the copper and 96% of the cobalt is made soluble by this process. Sulfates and oxides are leached simultaneously with spent electrolyte from the copper electrolysis section. Leaching occurs in four rows of four 80-cubic meter Dorr agitators in a four-hour period.

After leaching, the solution contains 60 g/l of copper and 17 g/l of free sulfuric acid. Leaching of oxide concentrates requires the addition of sulfuric acid, a byproduct generated during electrolysis of copper sulfate from sulfide concentrates. Thus a proper balance of oxide and sulfide concentrates requires only moderate addition of fresh acid. Leached pulps are desanded and thickened. Waste gangue is washed counter-flow with fresh water in a series of washer thickeners before rejection as tailings. The pregnant solution is clarified just before electrolysis. During electrolysis copper is deposited while cobalt and associated minor elements stay in solution. Cathodes, containing 99.7% Cu, are collected after six days, and the spent electrolyte containing 25 g/l of copper with 70 g/l of sulfuric acid goes back to the leaching plant. A part of the spent electrolyte of copper processing circuit is bled to the cobalt processing circuit to extract cobalt.

III. EXPERIMENTAL APPROACH

Purposes

The purposes of this investigation were concentrated on investigating the following effects in the process of treating the Great Gossan Lead complex sulfide ore with oxidizing and sulfatizing roasting in a fluidized-bed kiln and dilute sulfuric acid leaching in an autoclave:

A. The size effect of solid particles in the fluidized-bed kiln.

B. The size effect of solid particles in the autoclave.

C. The effect of pulp density in the autoclave.

The ultimate objective of the whole series of investigations concerning the Great Gossan Lead ore deposit is to produce commercial iron ore from the complex sulfide ore, namely pyrrhotite.

Dr. G. C. McBride of the United States Steel Corporation has suggested a specification for the composition of an iron ore suitable for blast furnace feed as follows [32].

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

Assuming that a 58% iron ore could be produced, this specification would permit the following amounts of impurities:

Copper	0.058%
Zinc	0.006%
Sulfur	0.058%
Lead	0.058% or 0.006%

Experimental Procedure

Principal Experimental Stages

The investigation included five principal stages:

A. Preparation of ore sample.

B. Screen analysis.

C. Roasting.

D. Leaching.

E. Quantitative chemical analysis.

The flow diagram of the experimental procedures is shown in Fig. 3.

Descriptions of the Principal Procedures and Apparatus

A. Preparation of Ore Sample. The raw ore used in this investigation was obtained from the Betty Baker area of the Great Gossan Lead, about 6.5 miles north of Hillsville, Virginia.

Chemical analysis of the head sample shows its composition as: 35.52% Fe, 25.37% S, 1.96% Zn, 0.63% Cu, 0.34% Pb, and 36.18% gangue material.

The raw ore, as received for testing, was first crushed to minus 14-mesh. A size separation was made with the Raymond pneumatic

classifier. The undersize (-65 mesh) from the classifier was con-centrated by bulk sulfide flotation with a Wemco batch flotator while the oversize (+ 65 mesh) was treated by flowing-film concentration with a Wilfley table. The bulk sulfide flotation concentrates and the table concentrates together with middlings were then combined to make up the fluidized-bed kiln feed.

The bulk sulfide batch flotation was conducted with the follow-ing specifications:

1. Pulp density: 33% solids, that is, 1 kg. of sample plus two liters of tap water.

2. Reagents:

    a. Concentrated sulfuric acid: 3.5 ml.

    b. Sodium ethyl xanthate (AC 325): 0.2 g. (Dissolve 1 gram of the reagent in 50 ml. of distilled water, and use 10 ml. of the solution for each batch.)

    c. Pine oil: a few drops.

    d. Frother AC 77: a few drops.

    e. Froth collection time: about 30 minutes.

By these specifications 67% of the ore was recovered as concentrate while 33% of the ore was rejected as tailings.

B. Screen Analysis. Samples of the fluidized-bed kiln feed and calcines, both of the overflow calcine and cyclone calcine, were taken for screen analyses. The Tyler standard 8-inch diameter

ORE SAMPLE
(5-12 INCH)

JAW CRUSHER

ROLL CRUSHER

+14 MESH ———— < ——— VIBRATING SCREEN

-14 MESH

RAYMOND CLASSIFIER

+65 MESH   -65 MESH

GRAVITY CONCENTRATION   BULK SULFIED FLOTATION
WILFLEY TABLE   WEMCO FLOTATOR

TAILINGS   MIDDLINGS   CONCENTRATES   CONCENTRATES   TAILINGS
(WASTE)   (WASTE)

COMBINED SULFIDE CONCENTRATES

SCREEN ANALYSIS

FLUIDIZED-BED ROASTING

OVERFLOW CALCINES   CYCLONE CALCINES

SCREEN ANALYSIS   SCREEN ANALYSIS

COMBINED CALCINES

SIZING

-10 - +35 MESH   -35 - +65 MESH   -65 - +150 MESH   -150 MESH

AUTOCLAVE LEACHING

FILTRATION

PREGNANT SOLUTIONS   RESIDUES
(RESERVE SAMPLES)   (PROSPECTIVE IRON ORE)
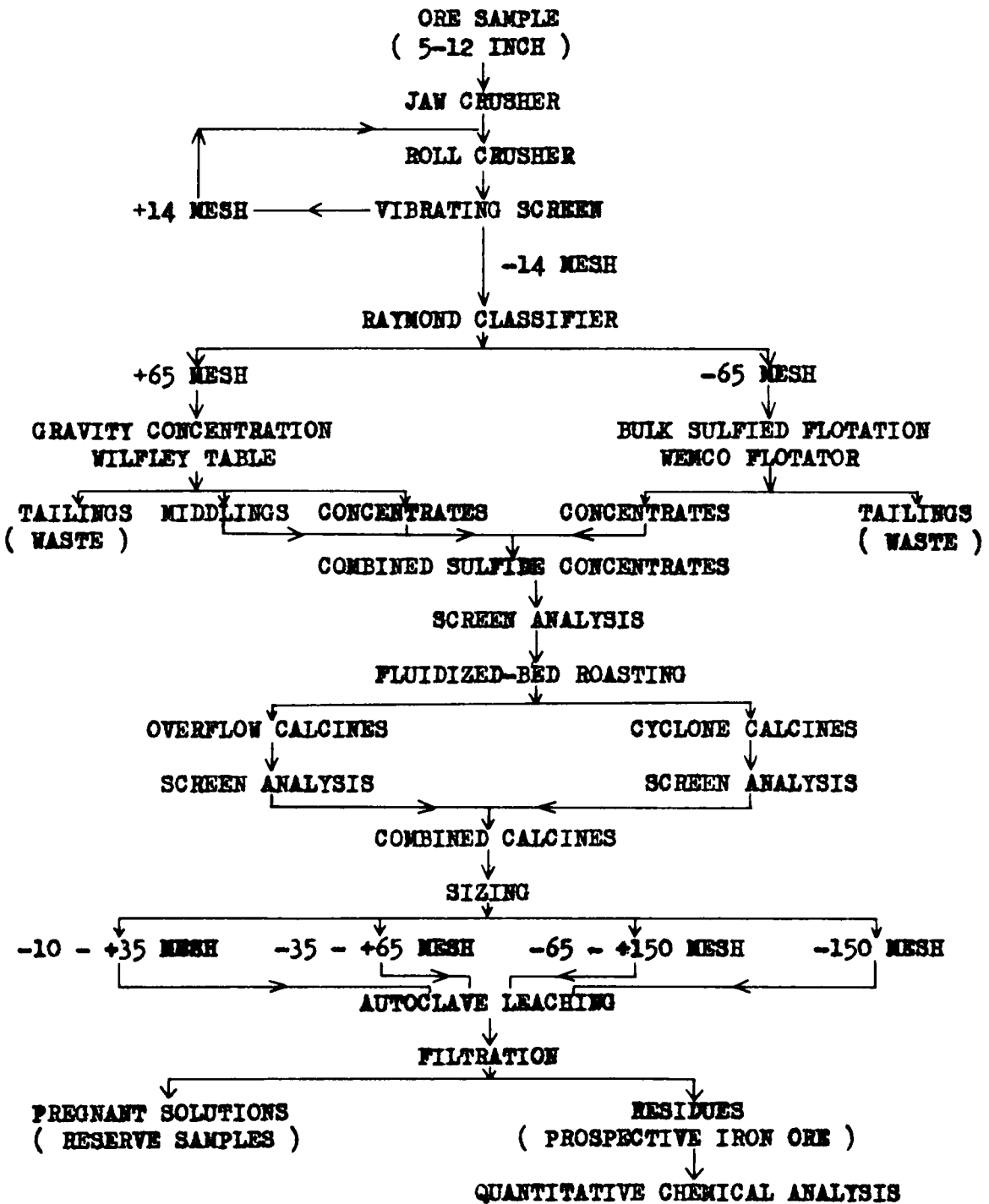
QUANTITATIVE CHEMICAL ANALYSIS

FIG. 3.   FLOWSHEET OF EXPERIMENTAL PROCEDURES

testing sieves and the Ro-Tap testing sieve shaker were used to perform the screen analyses.

C. Roasting. Roasting was conducted with a specially designed fluidized-bed kiln. The kiln was constructed of No. 316 stainless steel, 4-inch inside diameter. Heat was supplied to the kiln by two electric heating coils which were capable of approximately 1750°F. and rheostat controlled. The kiln was insulated with magnesia, which is efficient to a working temperature of 1850°F. Close temperature monitoring was made possible by using a Leeds & Northrup potentiometer and a chromel-alumel thermocouple inserted in a sealed thermocouple well. The temperature of the fluidized-bed was controlled by varying the voltage applied to the heating coils. The kiln was also fitted with a water injection system which made it possible to regulate the temperature of the reaction chamber within the operating range. In order to permit the air to enter the kiln and also support the bed, a No. 304 stainless steel plate perforated with 1/32-inch holes on 1/4-inch centers was placed between the reaction chamber and the air chamber. Air supply was controlled by a needle valve. Ore was fed into the kiln through a variable speed screw feeder. The coarser calcines were collected from the overflow outlet while the finer calcines were collected by the cyclone. The exhaust roasting gas was discharged through the flue. Fig. 4 illustrates the construction of the fluidized-bed kiln.

FIG. 4. CONSTRUCTION OF THE FLUIDIZED-BED KILN

(1) WATER INJECTION

(2) WATER GAUGE

(3) COOLING COIL

(4) PRESSURE TAPS
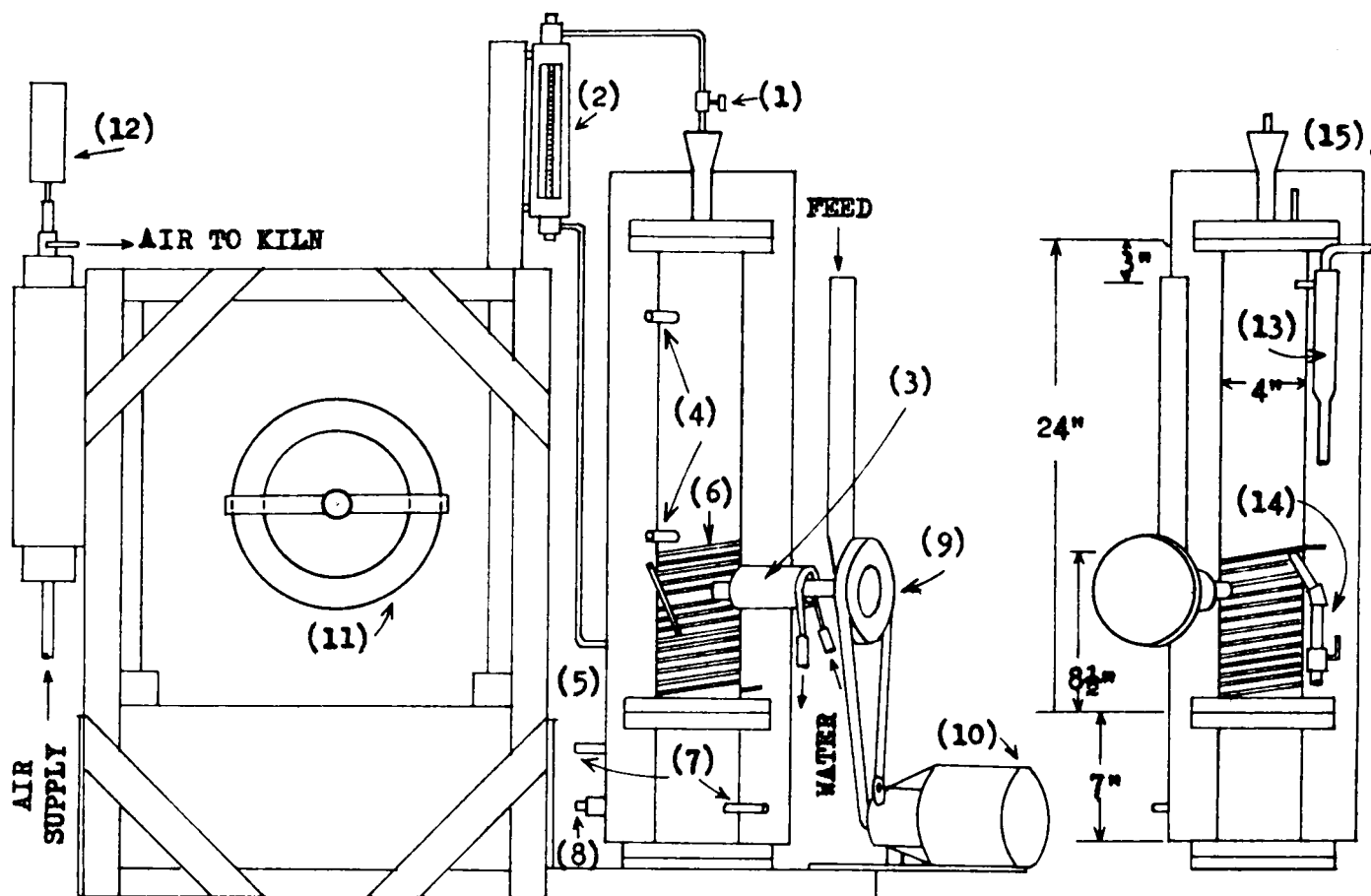
(5) THERMOCOUPLE WELL

(6) HEATING COIL

(7) PRESSURE TAPS

(8) AIR INLET

(9) SCREW FEEDER

(10) AC VARIABLE SPEED MOTOR

(11) VARIABLE TRANSFORMER

(12) AIR PRESSURE GAUGE

(13) CYCLONE

(14) BED OVERFLOW

(15) FLUE

After the roasting operation was finished, the overflow cal-
cines and the cyclone calcines were mixed together. For the subse-
quent leaching tests, the mixed calcines were then sized into four
ranges: + 35-mesh, -35 to + 65-mesh, -65 to + 150-mesh, and -150-
mesh.

D.   Leaching. The calcines obtained from the roasting stage
were treated by dilute sulfuric acid leaching with a one-gallon
stirred autoclave. The autoclave was made with all wetted parts
constructed from No. 316 stainless steel. It included heater,
cooling coil, sampling tube, safety head assembly, thermocouple
well, pressure gauge, charging openings, gas openings, turbine-
type agitator, vent valve, sample valve and electric drive motor.
The construction of the autoclave is shown in Fig. 5. This well-
equipped unit was capable of both high pressure and high temperature
up to a maximum of 3000 psi. and 650°F. respectively. Heat for the
autoclave was supplied by three 1000-watt electric heating elements
which were controlled with a variable transformer. The temperature
inside the autoclave was read with a Leeds & Northrup potentiometer
and a chromel-alumel thermocouple. The pressure in the vessel was
always indicated by the pressure gauge which was connected through
the oil cylinder to the autoclave. The turbine-type agitator pro-
vided with a hollow shaft was used in conjunction with the removable
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. The bubbles are broken up by the baffle bars. This type of agitation provides uniform suspension and insures constant circulation of the reactant gases through the liquid.

After leaching, the pulp was filtered with a vacuum pump and a porcelain funnel with No. 3 Whatman filter paper. The residual iron ore was washed into basins and dried in a steam heating room overnight. It was then allowed to naturally air-dry for two or three days and weighed repeatedly until a nearly constant weight was obtained. The air-dried residue was bottled, and samples were taken from the residue for chemical analysis. A sample of the pregnant solution was taken and reserved for further study.

E.   Quantitative Chemical Analysis. Quantitative chemical analyses were conducted to determine the moisture, ignition loss, insoluble matter, sulfur, iron, copper and zinc contents of the fluidized-bed kiln calcines and the leach residues.

The gravimetric method by precipitation of barium sulfate from hot solutions was followed to determine sulfur.

Titrimetric methods were used for the determinations of iron, copper and zinc. For determination of iron, the process of oxidation with potassium dichromate was followed. The iodide method was applied to determine copper. The determination of zinc was made by titration with potassium ferrocyanide in acid solution with uranium nitrate as an outside indicator.

PRESSURE GAUGE

OIL CYLINDER

GASKET - 316 SS.

CAP SCREWS

BODY - 316 SS.

THERMOWELL - 316 SS.

COOLING COIL - 316 SS.

SAMPLING TUBE - 316 SS.

AGITATOR SHAFT
    - 316 SS.

TURBINE AGITATOR
    - 316 SS.

BLOWPIPE - 316 SS.

ROTOR SEAL ASSEMBLY

FIXED PITCH
    SHEAVE

ELECTRIC MOTOR
    DRIVE
1/3 HP 110 VOLT
SINGLE PHASE

COVER - 316 SS.

SAFETY HEAD

12"

ELECTRIC HEATING
    JACKET

BAFFLE BAR
ASSEMBLY - 316 SS.

5"

6¼"
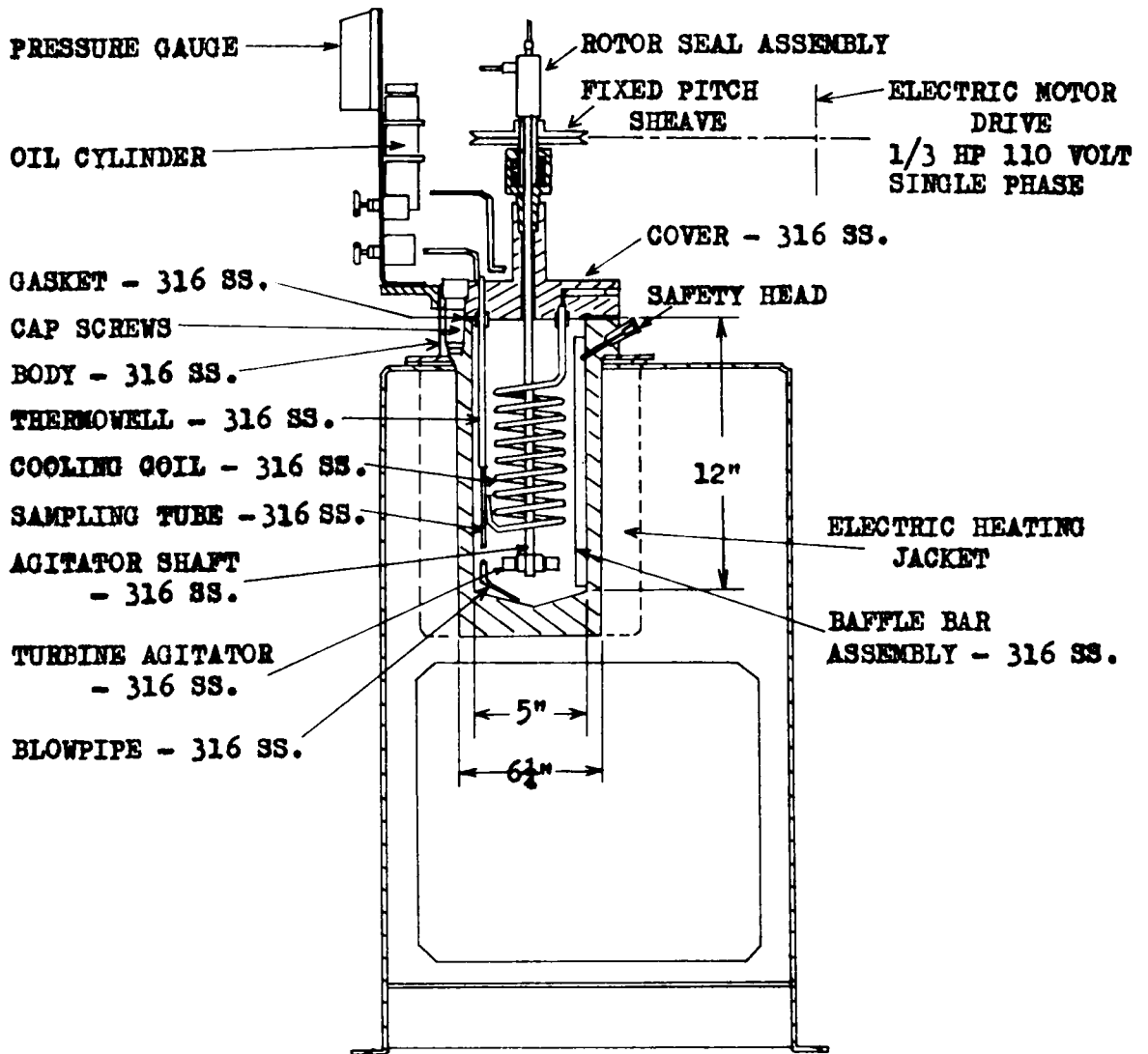
MAX. WORKING PRESSURE 3000 PSI.

MAX. WORKING TEMPERATURE 650°F.

FIG. 5.   CONSTRUCTION OF THE STANDARD
    ONE GALLON STIRRED AUTOCLAVE

Details of the chemical analysis methods used in this experi-
ment are presented in Appendices A through F [33,34,35,36].

Experimental Results

Data of Screen Analysis

The data of screen analyses on the samples of the fluidized-
bed roaster feed, overflow calcine and cyclone calcine are given
in Tables 1, 2 and 3. Table 4 shows the size distribution of the
mixed calcine, which is calculated from the data given in Tables 2,
3 and 5.

Figures 6 and 7 show the cumulative logarithmic diagrams and
the direct logarithmic diagrams of the screen analyses on roaster
feed and calcines. They are based on the data of Tables 1, 2, 3
and 4.

Roasting Performance

The fluidized-bed kiln was operated continuously for 37 hours
and 45 minutes. Feeding, air supply and heating were started at
the same time. At the beginning, it took two hours to heat the
fluidized-bed up to the proposed roasting temperature, 1450°Fahren-
heit. The kiln was then allowed to run at constant temperature for
one hour and a quarter before the collection of calcines was started.

The proposed roasting conditions were: feeding rate, 8 grams/
min.; air supply, 1.25 cu. ft./min.; air pressure, 2 psi.; and roast-
ing temperature, 1450° $\pm$ 50°F. However, the actual performance data,

calculated on the basis of the arithmetic means of the experimental records taken at 15 minute intervals throughout the whole operation time, indicated that an average feeding rate of only 6.8 grams/min. and an average roasting temperature of 1442°F. were obtained.

When the roasting was stopped and the kiln was cooled down to room temperature, the semi-roasted material remaining in the kiln was collected and weighed. This weight was assumed to be representing the amount of solid particles remaining and fluidizing constantly in the fluidized bed when the kiln was in operation. Therefore the average retention time of the solid particles in the fluidized-bed kiln could be estimated by dividing this weight with the actual average feeding rate. By this calculation, the average retention time of the solid particles in the fluidized-bed kiln was estimated to be 6.62 hours. The detailed performance data of the roasting experiment are listed in Table 5. The distribution of overflow and cyclone calcines obtained from the roasting stage is shown in Table 6.

Leaching Performance

As shown in Table 7, a factorial arrangement was adopted for the leaching stage. The factorial experiment dealt with two variable factors: size of the solid particles and pulp density. Four levels were chosen for each of the variable factors. The four levels of solid particle size were: (A) + 35-mesh, (B) -35 to + 65-mesh, (C) -65 to + 150-mesh, (D) - 150-mesh. Throughout this

experiment, pulp density was represented by the weight of solids treated in each leaching test. The quantity and quality of leaching solutions for each leaching test were kept constant. Two liters of distilled water plus 13 milliliters of 98% concentrated sulfuric acid were used as leaching solution for each test. The four levels of pulp density were therefore selected as: (1) 100 grams, (2) 150 grams, (3) 200 grams and (4) 250 grams of solids.

One test for each combination of the two variable factors was conducted. Totally, sixteen leaching tests were included in this leaching experiment.

Except the above-mentioned two variable factors and the concentration of dilute sulfuric acid leach solution, the following conditions were used for all of the sixteen tests:

A. Leaching temperature: 450°F.

B. Leaching pressure: no additional pressure except the increase of pressure in the autoclave due to the increase of temperature from room temperature to 450°F.

C. Leaching time: 2 hours, single leaching.

The leaching temperature and pressure were selected on the basis of a previous investigation record which indicated that a higher leaching efficiency of zinc was obtained at 450°F. than at 250°F. while no additional pressure was applied to the autoclave except the pressure increase due to the elevation of temperature[5, 37].

The pressure gauge of the autoclave was a 3 1/2-inch dial guage rated 0 to 5000 psi. and the smallest pressure value per dial division was 100 psi.. Because the pressure guage was not sensitive enough, no record of the actual leaching pressure could be obtained in this experiment from the gauge.

The performance data of the sixteen leaching tests are given in Table 8.

Results of Quantitative Chemical Analysis

The roasted calcines of the four size ranges used in the leaching experiment and leach residues produced by the sixteen leaching tests were chemically analyzed. The results of analyses are given in Tables 9 and 10. The assay values of iron, copper and zinc are given on a moisture and ignition loss-free basis. The others are given on the natural air-dry basis.

Table 11 gives the recovery of iron which remained in the leach residues. Tables 12 and 13 give the extraction rates of copper and zinc which were dissolved and extracted by the leach solutions. The total sulfur content of the leach residue is given in Table 14. These tables are prepared in the form of the factorial arrangement to show the effects of solid particle size and pulp density in dilute sulfuric acid leaching.

Figures 8, 9, 10 and 11 are based on the data given in Tables 11, 12, 13 and 14 respectively. The effects of solid particle size and pulp density on the recovery of iron, the extraction rates of

copper and zinc, and the sulfur content in the residual iron ore
are clearly shown by the diagrams.

Example calculations for the recovery of iron and the extrac-
tion rates of copper and zinc are given in Appendix G.

Table 1. Size Distribution of the Roaster Feed.

Size, Tyler Mesh	Weight, Percent	Cumulative Weight, Percent
+ 14	0.1	0.1
- 14 + 20	2.0	2.1
- 20 + 28	18.8	20.9
- 28 + 35	24.7	45.6
- 35 + 48	16.5	62.1
- 48 + 65	6.6	68.7
- 65 + 100	6.4	75.1
- 100 + 150	5.8	80.9
- 150 + 200	7.4	88.3
- 200	11.7	100.0

Table 2. Size Distribution of the Overflow Calcine.

Size, Tyler Mesh	Weight, Percent	Cumulative Weight, Percent
+ 14	0.0	0.0
- 14 + 20	1.2	1.2
- 20 + 28	12.4	13.6
- 28 + 35	23.5	37.1
- 35 + 48	19.5	56.6
- 48 + 65	12.4	69.0
- 65 + 100	11.1	80.1
-100 + 150	7.5	87.6
-150 + 200	4.9	92.5
-200	7.5	100.0

Table 3. Size Distribution of the Cyclone Calcine.

Size, Tyler Mesh	Weight, Percent	Cumulative Weight, Percent
+ 14	0.4	0.4
- 14 + 20	0.7	1.1
- 20 + 20	0.5	1.6
- 28 + 35	0.4	2.0
- 35 + 48	0.3	2.3
- 48 + 65	0.9	3.2
- 65 + 100	1.7	4.9
- 100 + 150	4.2	9.1
- 150 + 200	16.8	25.9
- 200	74.1	100.0

Table 4. Size Distribution of the Mixed Calcine.

(Calculated)

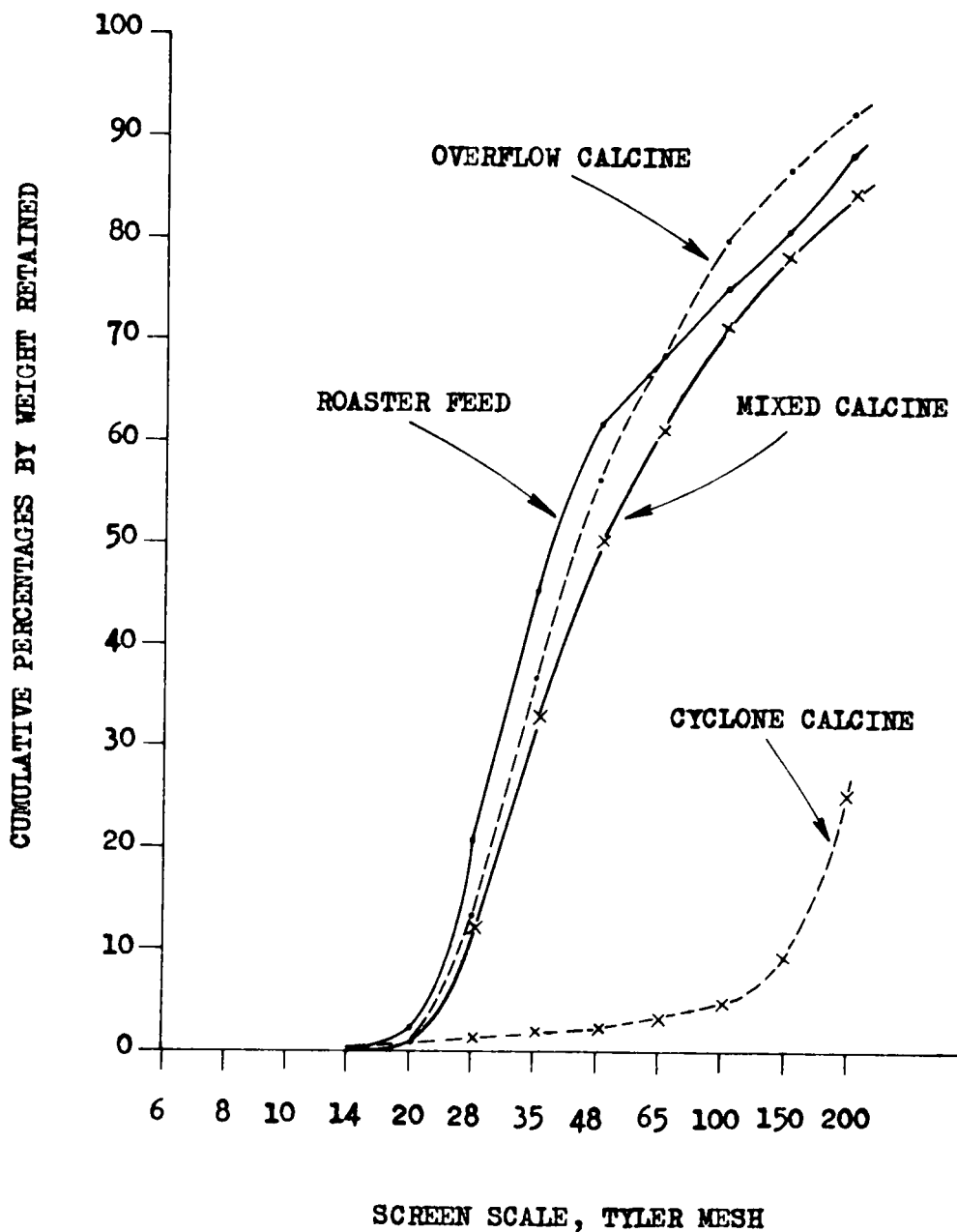| Size, Tyler Mesh	Weight, Percent	Cumulative Weight, Percent
+ 14	0.1	0.1
- 14 + 20	1.1	1.2
- 20 + 28	11.0	12.2
- 28 + 35	20.8	33.0
- 35 + 48	17.3	50.3
- 48 + 65	11.1	61.4
- 65 + 100	10.0	71.4
- 100 + 150	7.1	78.5
- 150 + 200	6.3	84.8
- 200	15.2	100.0

FIG. 6. CUMULATIVE LOGARITHMIC DIAGRAMS OF
SCREEN ANALYSES ON ROASTER FEED AND CALCINES
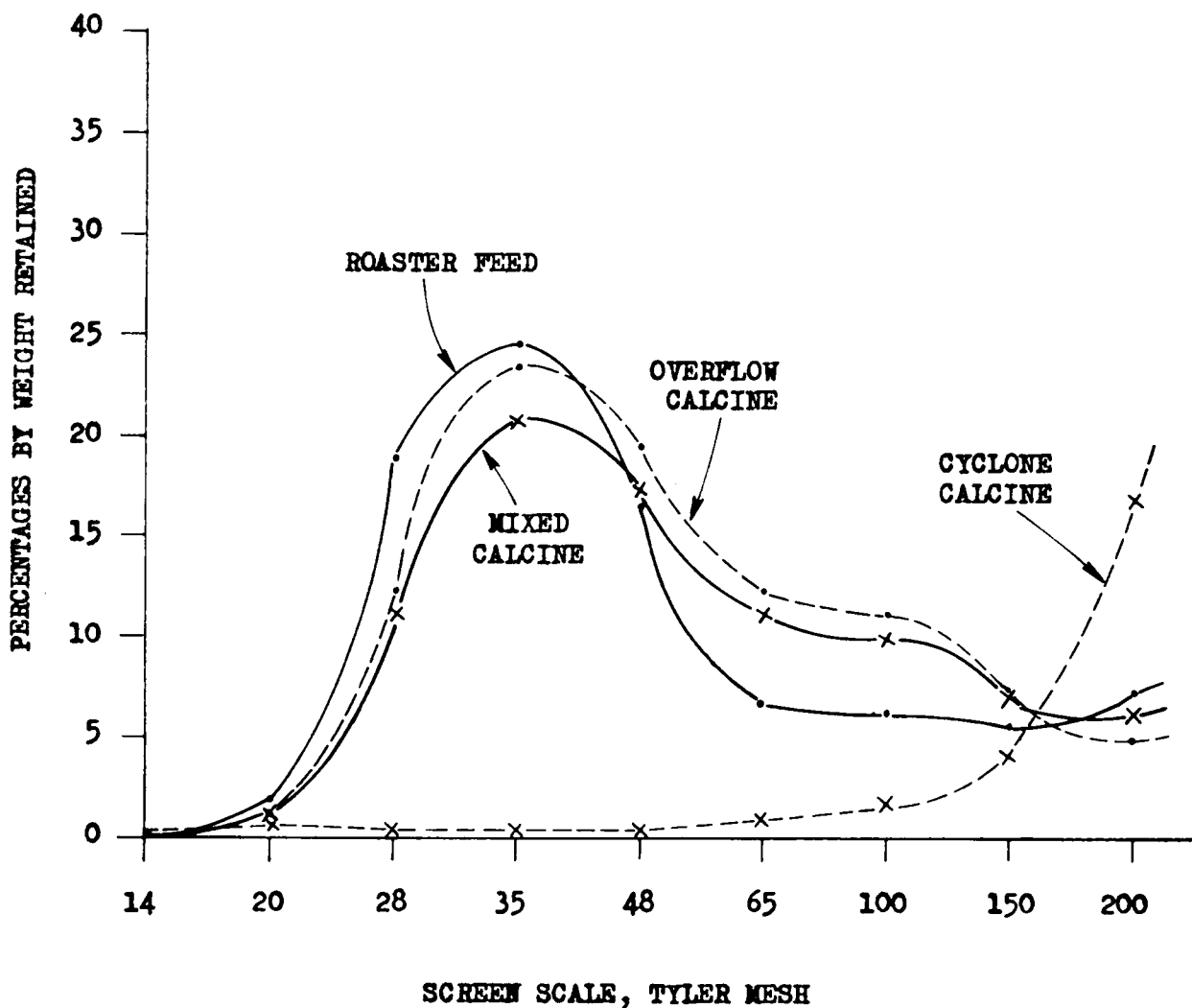
FIG. 7. DIRECT LOGARITHMIC DIAGRAMS OF
SCREEN ANALYSES ON ROASTER FEED
AND CALCINES

Table 5. Fluidized-Bed Roasting Conditions and Results.

Descriptions	Proposed Conditions	Actual * Performance
Feeding Rate	8 g./min.	6.8 g./min.
Air Supply	1.25 c.f.m.	1.25 c.f.m.
Air pressure	2 psi	2.02 psi
Roasting temperature	1450° $\pm$ 50°F.	1442°F.
Total operation time	-	37.75 hours.
Calcine collection time	-	34.50 hours.
Total feed	-	15.370 kg.(100%)
Calcine recovered:		
Overflow calcine	-	9.110 kg. (59.27%)
Cyclone calcine	-	1.188 kg. (7.73%)
Total	-	10.298 kg. (67.00%)
Semi-roasted ore remained in the fluidized-bed kiln	-	2.701 kg. (17.57%)
Roasting loss	-	2.371 kg. (15.43%)
Average retention time of solid particles in the kiln	-	6.62 hours

*The figures listed under Actual Performance are calculated on the basis of the arithmetic means of the experimental records taken at 15 minute intervals throughout the whole operation time.

Table 6. Distribution of Calcine

Product	Distribution, Percent
Overflow calcine	88.46
Cyclone calcine	11.54
Total	100.00

Table 7. Factorial Arrangement of the Leaching Tests.

Pulp Density, Represented by Weight of Solids.	Solid Particle Size			
	(A) + 35 Mesh	(B) -35 +65 Mesh	(C) -65 +150 Mesh	(D) -150 Mesh
(1) 100 G.	X_{A1}	X_{B1}	X_{C1}	X_{D1}
(2) 150 G.	X_{A2}	X_{B2}	X_{C2}	X_{D2}
(3) 200 G.	X_{A3}	X_{B3}	X_{C3}	X_{D3}
(4) 250 G.	X_{A4}	X_{B4}	X_{C4}	X_{D4}

(X) denotes the observation for each combination. The subscripts (A), (B), (C), and (D) denote the four levels of the factor, size of the solid particles; and (1), (2), (3) and (4) denotes the four levels of the factor, pulp density.

These notations are called test symbols and used to denote the specified leaching tests in all of the experimental data presented in this thesis.

Table 8. Autoclave Leaching Performance.

Test* Symbol	Calcine Leached g.	Leach Residue g.	Pregnant Solution ml.	Recovery of Residual Ore %
X_{A1}	100	89.90	1300**	89.80
X_{A2}	150	137.25	1800	91.50
X_{A3}	200	186.45	1310***	93.23
X_{A4}	250	232.40	1820	92.96
X_{B1}	100	88.50	1800	88.50
X_{B2}	150	137.80	1880	91.87
X_{B3}	200	187.00	1840	93.50
X_{B4}	250	239.65	1860	95.86
X_{C1}	100	87.75	1930	87.75
X_{C2}	150	133.00	1900	88.67
X_{C3}	200	188.90	1880	84.45
X_{C4}	250	231.10	1820	92.44
X_{D1}	100	73.75	1890	73.75
X_{D2}	150	116.90	1820	77.93
X_{D3}	200	161.80	1850	80.90
X_{D4}	250	202.70	1940	81.08

* See Table 7 for explanation of the test symbols.
** A little leakage of vapor from the gasket was observed.
***A little leakage of vapor from the safety head was observed.

Table 9. Chemical Analysis of Calcine

Assay No.	Test Symbol	Moisture %	Ig.Loss %	Moisture & Ig. Loss %	Insol %	S %	Fe %	Cu %	Zn %
1	A	0.11	7.68	7.79	9.85	1.85	51.02	0.72	2.64
2	B	0.06	2.19	2.25	10.77	1.80	48.21	0.72	2.25
3	C	0.18	3.94	4.12	8.87	1.87	50.52	0.82	3.05
4	D	0.62	9.86	10.48	6.12	7.52	50.73	1.06	3.92

All of the overflow calcine and cyclone calcine were mixed completely. The mixed calcine was then sized into four size ranges, A, B, C, and D. "A" denotes the range of + 35-mesh, "B" denotes the range of -35 to + 65-mesh, "C" denotes the range of -65 to + 150-mesh, and "D" denotes the range of -150-mesh. Samples were taken from each size range and analyzed individually.

The assay values of Fe, Cu, and Zn are given on a moisture and ignition loss-free basis. The others are given on the natural air-dry basis.

"Ig. Loss" denotes loss on ignition. "Insol" denotes insoluble matter.

Table 10. Chemical Analysis of Leach Residue

Assay No.	Test Symbol	Moisture %	Ig. loss %	Moisture & Ig. Loss %	Insol %	S %	Fe %	Cu %	Zn %
5	X_{A1}	0.12	3.24	3.36	10.50	1.70	53.31	0.74	1.20
6	X_{A2}	0.42	3.19	3.61	10.16	1.40	52.96	0.74	1.27
7	X_{A3}	0.30	2.73	3.03	9.97	1.41	50.98	0.73	1.17
8	X_{A4}	0.31	2.44	2.75	9.33	1.43	51.26	0.73	1.28
9	X_{B1}	0.41	2.92	3.33	12.36	1.44	51.40	0.56	1.14
10	X_{B2}	0.35	2.78	3.13	12.05	1.47	50.97	0.58	1.20
11	X_{B3}	0.25	2.91	3.16	11.88	1.49	50.53	0.56	1.28
12	X_{B4}	0.21	1.86	2.07	11.08	0.95	48.22	0.74	2.05
13	X_{C1}	0.02	3.37	3.39	7.94	0.98	55.61	0.57	1.11
14	X_{C2}	0.01	2.65	2.66	8.63	1.23	54.75	0.63	1.12
15	X_{C3}	0.12	2.18	2.30	8.27	0.81	52.45	0.83	2.22
16	X_{C4}	0.28	2.53	2.81	8.54	1.41	53.73	0.70	1.27
17	X_{D1}	0.63	6.55	7.18	11.92	5.96	48.60	1.38	2.84

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Table 10. (Cont'd.) Chemical Analysis of Leach Residue

Assay No.	Test Symbol	Moisture %	Ig. Loss %	Moisture & Ig. Loss %	Insol %	S %	Fe %	Cu %	Zn %
18	X_{D2}	0.11	6.18	6.29	10.62	7.07	48.54	1.21	3.42
19	X_{D3}	0.12	5.81	5.93	9.07	6.75	49.23	1.23	3.58
20	X_{D4}	0.16	5.88	6.04	8.89	6.74	48.93	1.20	3.55

See Table 7 Factorial Arrangement of the Leaching Experiment for explanation of the test symbols. The subscripts, A, B, C, and D, denote the four levels of particle size, and the subscripts, 1, 2, 3, and 4, denote the four levels of pulp density.

The assay values of Fe, Cu, and Zn are given on a moisture and ignition loss-free basis. The others are given on the natural air-dry basis. "Ig. Loss" denotes loss on ignition. "Insol" denotes insoluble matter.

Table 11. The Effect of Particle Size and Pulp Density on the

Recovery of Iron in Dilute Sulfuric Acid Leaching.

Pulp Density, Represented by Weight of Solids	Solid Particle Size			
	(A) + 35 Mesh	(B) - 35 + 65 Mesh	(C) - 65 + 150 Mesh	(D) -150 Mesh
(1) 100 G.	98.34	93.32	97.33	73.26
(2) 150 G.	99.27	96.25	97.55	78.06
(3) 200 G.	97.96	97.09	99.92	82.49
(4) 250 G.	98.50	96.05	99.66	82.08

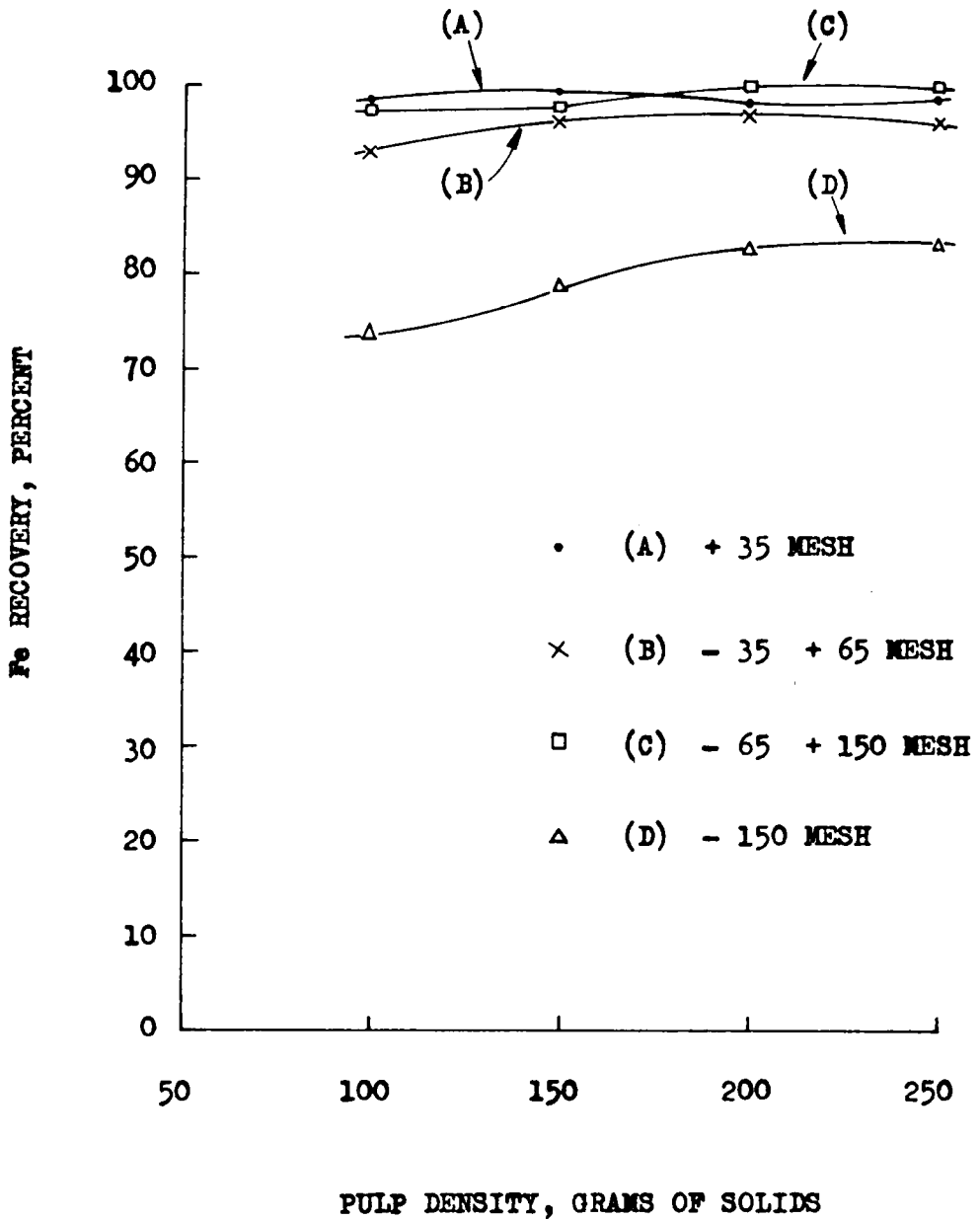The values of iron recovery are given in percent.

FIG. 8. THE EFFECTS OF PARTICLE SIZE AND PULP DENSITY
ON THE RECOVERY OF IRON IN DILUTE SULFURIC ACID LEACHING

Table 12. The Effect of Particle Size and Pulp Density on the

Extraction Rate of Copper in Dilute Sulfuric Acid

Leaching.

Pulp Density, Represented by Weight of Solids	Solid Particle Size			
	(A) + 35 Mesh	(B) - 35 + 65 Mesh	(C) - 65 + 150 Mesh	(D) - 150 Mesh
(1) 100 G.	3.27	31.92	38.54	0.44
(2) 150 G.	1.70	26.66	30.84	6.88
(3) 200 G.	0.60	27.95	2.59	1.35
(4) 250 G.	0.60	1.31	20.00	3.66

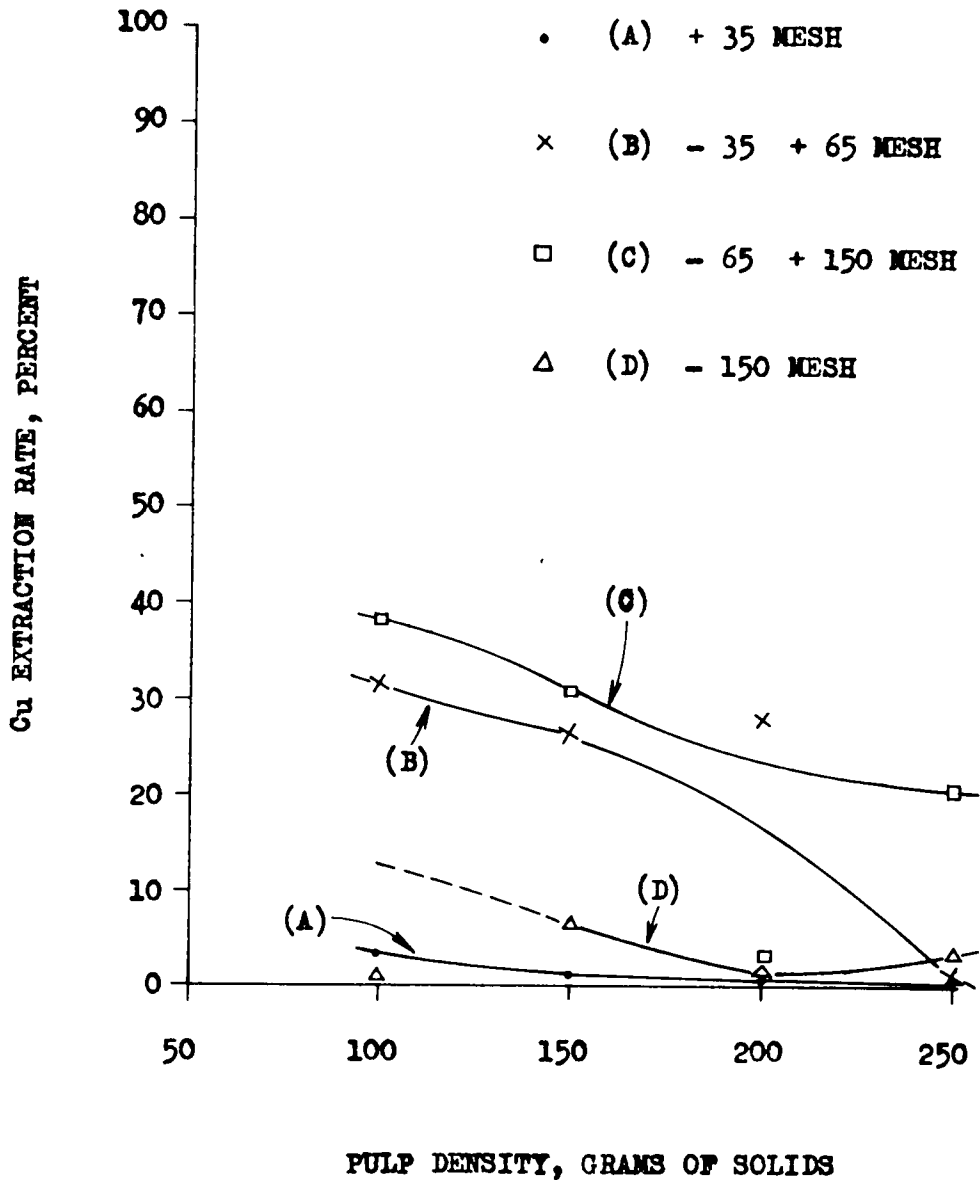The values of copper extraction rate are given in percent.

FIG. 9. THE EFFECTS OF PARTICLE SIZE AND PULP DENSITY ON
THE EXTRACTION RATE OF COPPER IN DILUTE SULFURIC ACID LEACHING

Table 13. The Effect of Particle Size and Pulp Density on the

Extraction Rate of Zinc in Dilute Sulfuric Acid Leaching.

Pulp Density, Represented by Weight of Solids	Solid Particle Size			
	(A) + 35 Mesh	(B) - 35 + 65 Mesh	(C) - 65 + 150 Mesh	(D) -150 Mesh
(1) 100 G.	57.23	55.65	67.82	44.60
(2) 150 G.	53.99	51.45	66.94	28.83
(3) 200 G.	56.55	47.30	29.95	22.36
(4) 250 G.	52.47	12.51	60.98	22.93

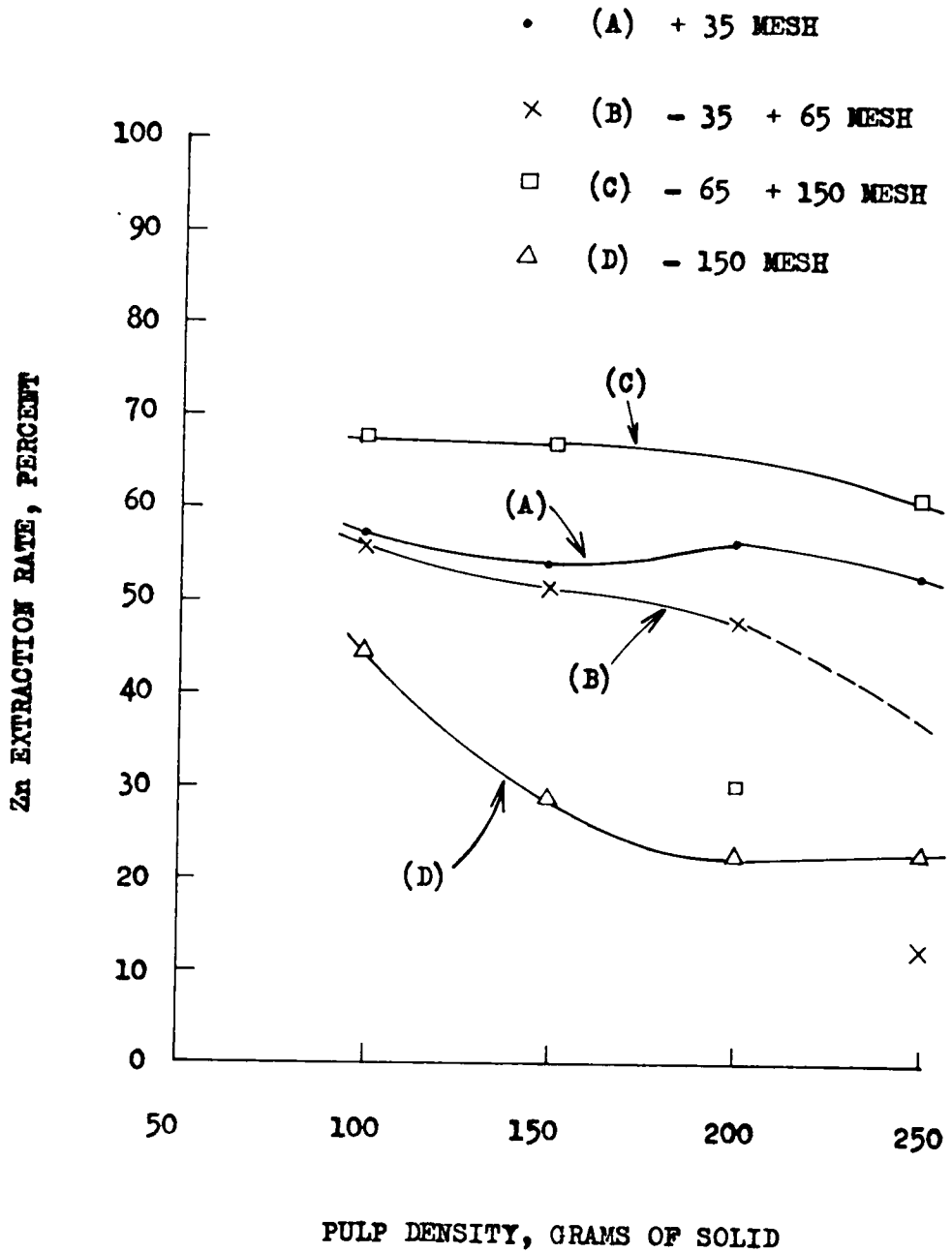The values of zinc extraction rate are given in percent.

FIG. 10. THE EFFECTS OF PARTICLE SIZE AND PULP DENSITY ON
THE EXTRACTION RATE OF ZINC IN DILUTE SULFURIC ACID LEACHING

Table 14. The Effect of Particle Size and Pulp Density on the
Sulfur Content of Leach Residue.

Pulp Density, Represented by Weight of Solids	Solid Particle Size			
	(A) + 35 Mesh	(B) -35 + 65 Mesh	(C) - 65 + 150 Mesh	(D) - 150 Mesh
(1) 100 G.	1.70	1.44	0.98	5.96
(2) 150 G.	1.40	1.47	1.23	7.07
(3) 200 G.	1.41	1.49	0.81	6.75
(4) 250 G.	1.43	0.95	1.41	6.74

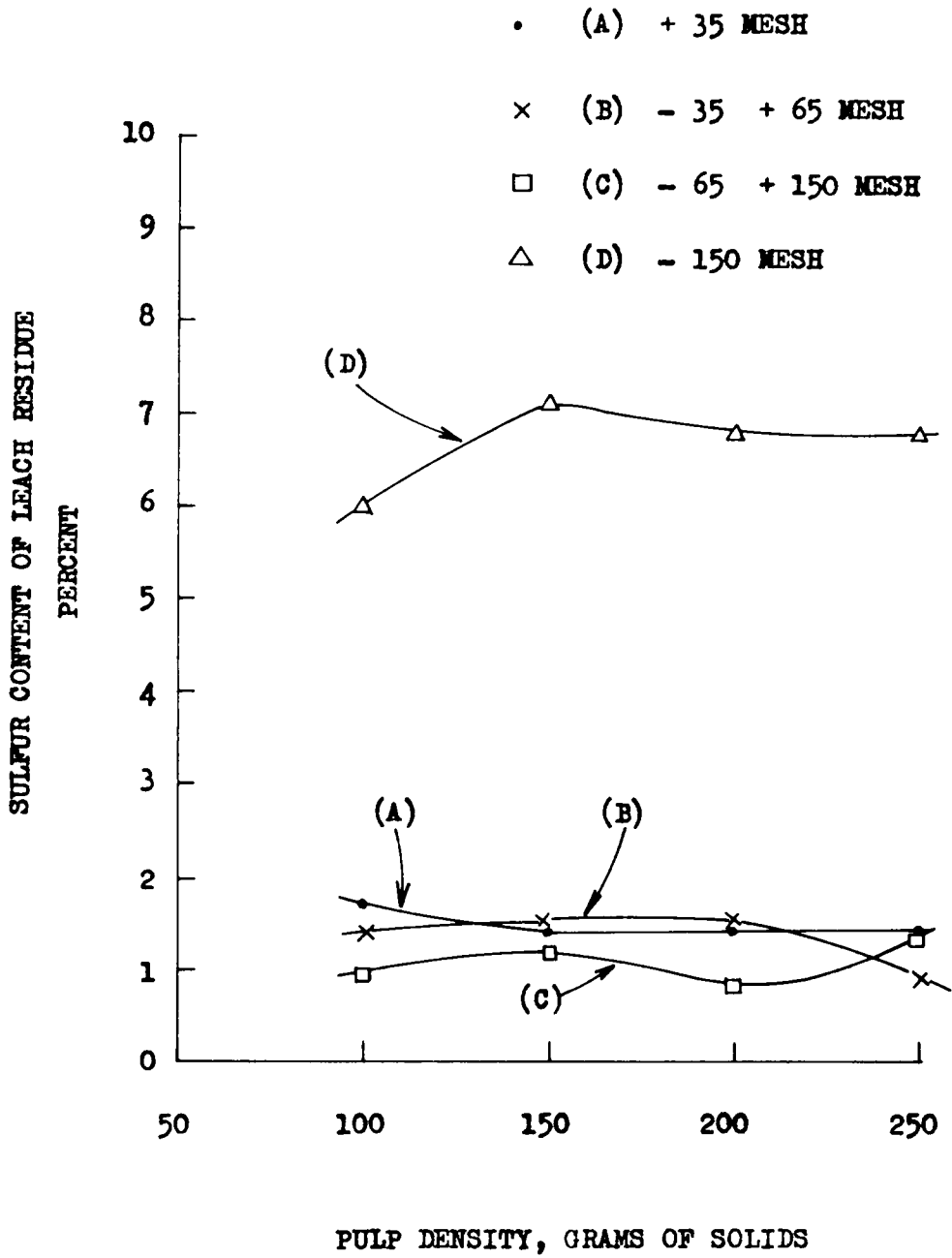The values of sulfur content of leach residue are given in percent.

FIG. 11. THE EFFECTS OF PARTICLE SIZE AND PULP DENSITY ON
THE SULFUR CONTENT OF LEACH RESIDUE

IV. STATISTICAL ANALYSIS OF EXPERIMENTAL RESULTS

Description

Since zinc is the critical impurity in iron ore, the data of zinc extraction rates obtained from the factorial leaching experiment are analyzed statistically to determine the significance of solid particle size and pulp density in the leaching process.

The statistical model used in this analysis is the mixed effects model of two-way analysis of variance, one observation per combination. The principles and test procedures given by Bowker and Lieberman in their work, Engineering Statistics, are followed to carry out this analysis.(38)

The factor of solid particle sizes is considered as a random effect, whereas the factor of pulp densities is considered as a fixed effect. This implies that the experimental results will lead to conclusions about the distribution of solid particle sizes. But the conclusions about pulp densities will extend only to the four fixed levels used in this experiment.

The data of the factorial experiment on zinc extraction rates, and the analysis of variance table are given in Tables 15 and 16.

The level of significance is chosen as 0.05. From the manner in which the model is developed, it is necessary to assume that the interaction is nonexistent in testing for the random effects, whereas the test for the fixed effects does not depend on any assumption about the interaction.

Table 15. Data of the Factorial Experiment on Zinc Extraction Rate.

Pulp Density, Represented by Weight of Solids	Solid Particle Size				Totals	Average
	+ 35 Mesh	- 35 + 65 Mesh	- 65 + 150 Mesh	- 150 Mesh		
(1) 100 G.	57.23	55.65	67.82	44.60	225.30	56.33
(2) 150 G.	53.99	51.45	66.94	28.83	201.21	50.30
(3) 200 G.	56.55	47.30	29.95	22.36	156.16	39.04
(4) 250 G.	52.47	12.51	60.98	22.93	148.89	37.22
Totals	220.24	166.91	225.69	118.72	731.56	
Average	55.06	41.73	56.42	29.68		

The values of zinc extraction rate are given in percent.

Table 16. Analysis of Variance Table for Zinc Extraction Rate.

Source of Variance	Sum of Squares	Degrees of Freedom	Mean Square	Test
Between particle sizes	1900.01	3	633.34	$F = 3.87$
Between pulp densities	1001.18	3	333.73	$F = 2.04$
Residual	1471.21	9	163.47	
Total	4372.40	15	291.49	

Test for the Particle Size Effects (Random Effects)

Hypothesis about the Homogeneity of Particle Size Effects

$$H : \sigma^2 = 0$$

where σ^2 is the variance of the particle size effects.

Rejection Area

Reject the hypothesis if,

$$F = \frac{\text{Mean square between particle sizes}}{\text{Mean square residual}} \geq F_{0.05(3,9)}$$

where the value of $F_{0.05(3,9)}$ is obtained from the table of F distribution,

$$F_{0.05(3,9)} = 3.86$$

Test

$$F = \frac{633.34}{163.47} = 3.87$$

Since, $F > F_{0.05(3,9)}$

Therefore, reject the hypothesis $H : \sigma^2 = 0$

Conclusion

At a significance level of 5%, there is significant difference in zinc extraction rate due to the difference of solid particle sizes.

Test for the Pulp Density Effects (Fixed Effects)

Hypothesis about the Homogeneity of Pulp Density Effects

$$H : \emptyset_1 = \emptyset_2 = \emptyset_3 = \emptyset_4 = 0$$

where $\emptyset_1$, $\emptyset_2$, $\emptyset_3$ and $\emptyset_4$ are the effects of level (1), level (2), level (3) and level (4) respectively.

Rejection Area

Reject the hypothesis if,

$$F = \frac{\text{Mean square between pulp densities}}{\text{Mean square residual}} \geq F_{0.05(3,9)}$$

where the value of $F_{0.05(3,9)}$ is obtained from the table of F distribution,

$$F_{0.05(3,9)} = 3.86$$

Test

$$F = \frac{333.73}{163.47} = 2.04$$

Since, $F < F_{0.05(3,9)}$

Therefore, accept the hypothesis $H : \emptyset_1 = \emptyset_2 = \emptyset_3 = \emptyset_4 = 0.$

Conclusion

At a significance level of 5%, there is no significant difference in zinc extraction rate due to the difference of the four levels of pulp density tested in this experiment.

V. DISCUSSION

Effect of Particle Size on the Roasting Process

It is evident that the degree of roasting is directly propor-
tional to the roasting time. In fluidized-bed roasting, the roast-
ing time is the retention time of solid particles in the kiln. In
this experiment, the average retention time of solid particles in the
kiln was estimated as 6.62 hours. However, the finer particles are
easily carried through the bed by the ascending roasting gas and dis-
charged from the kiln rapidly through the cyclone or the flue. The
retention time of fine particles is shorter than the retention time
of coarse particles, and the fine particles may not have sufficient
roasting time to allow complete conversion of sulfides to oxides or
sulfates. Therefore overflow calcine is more desirable than cyclone
calcine.

Table 2 indicated that 87.6% of the overflow calcine was plus
150-mesh and 12.4% of it was minus 150-mesh; while Table 3 indicated
that 9.1% of the cyclone calcine was plus 150-mesh and 90.9% of it
was minus 150-mesh.

It is interesting to note the size distribution diagrams shown
in Figures 6 and 7. From Figure 7, it is found that the overflow
calcine curve intersects the roaster feed curve at a point between
35-mesh and 48-mesh, and at another point between 150-mesh and 200-
mesh. Between these two intersections, the overflow curve lies above
the roaster feed curve. This may be explained by the overflow rate

of the solid particles within the size range of minus 35 to plus 150-mesh, which is comparatively higher than the overflow rates of particles in the range of plus 35 mesh and the range of minus 150-mesh. The vertical distance between the curve of overflow calcine and the curve of roaster feed is largest at the point of 65-mesh, which is the intermediate size of the range of minus 35 to plus 150 mesh. This is identical to the fact that, in Figure 6, the cumulative size distribution curves of overflow calcine and roaster feed intersect at the point of 65-mesh. At this point the slope of the overflow calcine curve surpasses the slope of the roaster feed curve. It may be explained that, among the solid particles of the roaster feed, the particles around 65-mesh have the highest overflowing rate.

Based on these data, it seems reasonable to determine an optimum size range of minus 35 to plus 150-mesh, and a best size of around 65-mesh for the standard of solid particle size in the fluidized-bed roasting process. But this inference might be effective only when the roasting is conducted under the same roasting conditions which were performed in this investigation.

Particle Size Effect in the Leaching Process

It has been confirmed by the statistical analysis that the variance of the particle size effects on the extraction rate of zinc is significant at a significant level of five percent. Comparing this statistical result with the evidences revealed in Figures 8, 9, 10 and 11, it is easily found that the inference derived from the

statistical analysis on zinc extraction rate can be extended to the
iron recovery, copper extraction rate as well as the sulfur content
of the residual iron ore.

In Figure 8, which shows the iron recovery in the dilute sul-
furic acid leaching, the curves (A), (B) and (C) indicate that the
iron recoveries for all the plus 150-mesh particles closely approach
100 percent while the (D) curve indicates that the iron recovery for
minus 150-mesh particles lies between 73.26 and 82.08 percent. This
implies that about 20 to 30 percent of the iron content in the minus
150-mesh calcine was dissolved into the pregnant solutions. In a
beneficiation process combining leaching and electrolysis for recovery
of copper or zinc, the iron dissolved in the leach solution is a crit-
ical impurity that will affect the efficiency of copper or zinc elec-
trolysis. During the roasting process, SO_3 gas is formed in the
roaster. Because of the cooling action of the cyclone and the flue,
a relatively large amount of iron dust entering the hot cyclone may
be sulfated. This iron sulfate, which is collected as the cyclone
calcine, will dissolve in the dilute sulfuric acid solution during
subsequent leaching process. This general trend has been proved by
the (D) curve. It is also interesting to see the trend of (C) curve,
which shows that the highest iron recovery has been reached by the
solid particles within the size range of minus 65 to plus 150-mesh.

This experiment did not attain a favorable extraction rate of
copper. It can be found from Table 12 and Figure 9 that the copper
extraction rates of the sixteen leaching tests were lower than 40

percent. However, the effects of solid particle size in the copper leaching can be reviewed clearly from Figure 9. In this chart the (C) curve again indicates the best copper extraction rate, whereas the (D) curve and (A) curve show the worst copper extraction rate. It could be explained that in the fluidized-bed roasting, the finest particles might not have had sufficient roasting time to convert their copper sulfide into cupric oxide or copper sulfate completely. Previous microscopic studies on the ore indicated that the discrete particles of chalcopyrite in the ore average less than 10 microns and the chalcopyrite is usually finer than the marmatite. Therefore, both in the roasting process and in the leaching process, the largest particles might not have had sufficient surface exposures for complete chemical reactions. This could be the reason that the plus 35-mesh particles presented a poor copper extraction rate in Figure 9.

A consistent evidence for the highest extraction rate of zinc for minus 65 to plus 150-mesh particles is presented by the (C) curve in Figure 10. The (D) curve in this figure also indicates the lowest zinc extraction rate for the minus 150-mesh particles. It is evident that the effect of surfaces becomes greater as the degree of subdivision of matter is increased. In the fluidized bed, the zinc oxide and the iron oxide of finer grains would have higher possibility to contact each other and form the insoluble zinc ferrite at somewhat above 650 degrees Centigrade (equivalent to 1200 degrees Fahrenheit). This might be the reason that caused the lowest extraction rate of zinc for the finest particles in the leaching process.

In a hydrometallurgical process with roasting and leaching, a by-product of sulfuric acid can be produced by recovering the sulfur content of the sulfide ore. As roasting process is applied to prepare sulfide ore, there is no difficulty to oxidize the sulfur content with air at high temperature as completely as desired. However, some of the sulfur is usually remaining in the calcines, both in the forms of sulfates or sulfides due to incomplete roasting, when the roasting is not aimed at complete oxidation of sulfur. As discussed above, sulfates are easily formed in the cyclone and the flue because of the formation of SO_3 gas in the roaster and the cooling action of the cyclone and flue. The sulfate sulfur is therefore accumulated in the cyclone calcine. Again, the cyclone calcine may contain a lot of sulfide sulfur because it may not have had sufficient roasting time to convert all of its sulfides into sulfate or oxides. These phenomena can be found in Table 9, which indicates that the total sulfur content of minus 150-mesh calcine, that is the major component of the cyclone calcine, is 7.52% while those of the calcines belonging to the other three size ranges are 1.80 to 1.87%. Sulfur content of the solid material may be reduced slightly in the dilute sulfuric acid leaching. This tendency can be observed from the analytical data of sulfur shown in Table 9 and 10. Figure 11 shows the distribution of sulfur content in the leach residues. Iron ore is required to have a low sulfur content. In this figure, the (D) curve lies far above the (A), (B) and (C) curves. It is notable that the

(C) curve indicates the particles within the size range of minus 65 to plus 150-mesh have the lowest sulfur content. This is also identical to the above-mentioned evidences of highest iron recovery and highest copper and zinc extraction rates for the minus 65 to plus 150-mesh particles.

From these experimental results, it can be concluded that the solid particles within the size range of minus 65 to plus 150-mesh would have the highest iron recovery, the highest extraction rates of copper and zinc, and the lowest sulfur content in the leach residue.

The effects of particle size in both roasting process and leaching process are closely related. The optimum size range (minus 65 to plus 150-mesh) for leaching process is within the optimum size range (minus 35 to plus 150-mesh) for higher overflowing rate in the fluidized-bed roasting process. The (B) curves in Figures 8, 9, 10 and 11 indicate a medium preference for the particles within the size range of minus 35 to plus 65-mesh. For practical purposes, an optimum size range of minus 35 to plus 150-mesh could be applied to both the fluidized-bed roasting process and the dilute sulfuric acid leaching process.

Pulp Density Effect in the Leaching Process

In this experiment, an aqueous solution of sulfuric acid, consisting of 2 liters of distilled water and 13 milliliters of concentrated sulfuric acid, was used for each leaching test. The amount of calcine used in each test varied within the four levels, 100 grams,

150 grams, 200 grams and 250 grams. It had been estimated stoichiometrically that the concentration of sulfuric acid in the leach solution was sufficient enough to dissolve the copper and zinc contents in 250 grams of the calcine.

The statistical analysis for the pulp density effects on the extraction rate of zinc has concluded that, at a significance level of 5 percent, there is no significant difference in zinc extraction rate due to the difference of the four levels of pulp density tested in this experiment. Because there is a stoichiometric relationship between the sulfuric acid concentration of the leach solution and the amount of acid soluble compounds in the calcine to be leached, it is logical to consider that the inferences drawn from this experiment can only extend to the four specified levels of pulp density used in this experiment.

By comparing the diagrams of Figures 8, 9, 10 and 11, it can be understood that the conclusion of the statistical analysis for the pulp density effects on zinc extraction rate can be applied to the pulp density effects on iron recovery, copper extraction rate and sulfur content in the leach residue. Almost all of the curves show a moderate slope or even become nearly horizontal. These phenomena indicate that, within the range of pulp density from 100 grams to 250 grams of solids per 2 liters of distilled water plus 13 milliliters of concentrated sulfuric acid, there is no significant difference in iron recovery, copper extraction rate, zinc extraction rate and sulfur content of the leach residue due to the difference of pulp densities.

However, some general trends of the diagrams must be noted. In Figure 8, the general trends of the curves show that the iron recovery decreases as the pulp density decreases. In Figure 9, the curves indicate that the extraction rate of copper decreases as the pulp density increases. The curves in Figure 10 also indicate that the extraction rate of zinc decreases with the increase of pulp density. The curves in Figure 11 are all nearly horizontal. It implies that almost no pulp density effect on the sulfur content of leach residue within the specified range of pulp density.

Significance of the Pressure Effect in the Autoclave Leaching

The autoclave is a pressure vessel where leaching process can be conducted under high pressure and high temperature. But the leaching process can not be carried on at an excessively high temperature without a corresponding high pressure to overcome the vapor pressure of leach solution. The critical point of water is 374°C. and 218 atmospheres (about 705°F. and 3200 psi.). As water approaches the critical point, it becomes more like a gas and loses its solvent power for salts.

Since the autoclave was introduced to the investigation on beneficiation of the Great Gossan Lead complex sulfide ore at the Virginia Polytechnic Institute, the pressure effect on the autoclave leaching has not been studied and no record of the leaching pressure has been reported in the previous work. Nevertheless, a previous experimental record indicated that a higher leaching efficiency for the extraction

of zinc was obtained at 450°F. than at 250°F. while no additional
pressure was applied to the autoclave except the pressure increase in
the autoclave due to the elevation of temperature from room tempera-
ture to the leaching temperature. Following the previous experimental
results, the leaching experiment of this investigation was conducted
at 450°F. without applying additional pressure to the autoclave except
the pressure increase in the autoclave due to the elevation of temper-
ature from room temperature (about 80°F.) to the leaching tempera-
ture. Consequently, the leaching experimental results, as they were
presented in the preceding sections, did not appear to be favorable
to the extraction of zinc and the extraction of copper. The highest
zinc extraction rate attained in this experiment is 67.82 percent.
The highest copper extraction rate is only 38.54 percent. And none
of the final products, leach residues, meets the specifications of
a commercial iron ore.

A table of vapor pressure of water is given in Appendix H of
this paper. From this table, it can be found that the vapor pressure
of water at 428°F. is 336 psi· (equivalent to 22.86 atm.). Since
the pressure gauge of the autoclave was not sensitive enough, no
record of the actual leaching pressure could be obtained in this
experiment from the gauge. Theoretically it can be inferred that
a part of the aqueous leach solution must have vaporized in the auto-
clave and lost its solvent power for salts under the leaching con-
ditions. However, leaching has also occurred at the beginning before
the temperature was raised up to 450°F., and at the end during the

time of cooling the autoclave. For each leaching test, it was normally

necessary to have an hour to heat up the autoclave to 450°F. at the

beginning and another one hour to cool the vessel down to room tem-

perature at the end before the vessel could be opened. But some of

the solutes dissolved into the solution during the beginning might

dissociate from the solvent when the solution vaporized. Furthermore,

the effect of the osmotic pressure of the leach solution may also

have an important role in the complicated pressure conditions of the

autoclave. The effect of leaching pressure on the experimental

results could be very important. A careful study on the pressure

effect is necessary before making a final conclusion on the appli-

cability of autoclave leaching in the beneficiation of the Great

Gossan Lead complex sulfide ore.

IV. CONCLUSIONS

A.   An optimum size range of minus 35 to plus 150-mesh and an
average size of around 65-mesh for the standard of the solid particle
size in the fluidized-bed roasting process for the complex sulfide
ore was determined. The solid particles within this size range have
a comparatively higher overflowing rate from the fluidized bed. But
this inference might be effective only when the roasting is conducted
under the same conditions which were performed in this investigation.
The average roasting conditions were: feeding rate, 6.8 g./min.;
air supply, 1.25 c.f.m.; air pressure, 2.02 psi.; and roasting tempera-
ture, 1442°F.

B.   In the dilute sulfuric acid leaching of the roasted calcine
with autoclave, the variance of the particle size effects on the re-
covery of iron, the extraction rate of copper, the extraction rate
of zinc and the sulfur content of the leach residue is significant.
The solid particles within the size range of minus 65 to plus 150-
mesh would have the highest recovery of iron, the highest extraction
rate of copper, the highest extraction rate of zinc and the lowest
sulfur content of the leach residue. This optimum particle size range
for the leaching process is within the optimum particle size range
of minus 35 to plus 150-mesh for higher overflowing rate in the
fluidized-bed roasting process. For practical purposes, a broad
optimum particle size range of minus 35 to plus 150-mesh could be
applied to both the fluidized-bed roasting process and the dilute
sulfuric acid leaching process.

C. In the dilute sulfuric acid leaching of the roasted calcine with the autoclave, within the range of pulp density from 100 to 250 grams of the calcine per 2 liters of distilled water plus 13 milliliters of concentrated sulfuric acid, there is no significant difference in the recovery of iron, the extraction rate of copper, the extraction rate of zinc and the sulfur content of the leach residue due to the difference of pulp densities. However, within the tested range of pulp density, the general trends are: The iron recovery decreases as the pulp density decreases, the copper extraction rate decreases as the pulp density increases, the zinc extraction rate decreases as the pulp density increases, and there is almost no pulp density effect on the sulfur content of leach residue.

D. The pressure effect could be a significant factor in the autoclave leaching process. It should not be disregarded. A careful study on the pressure effect is necessary before making a final conclusion on the applicability of autoclave leaching to the beneficiation process for the complex sulfide ore.

VII. SUMMARY

As a continuation of a series of investigations on exploring
an applicable beneficiation process for the Great Gossan Lead com-
plex sulfide ore, this investigation has been conducted for the pur-
pose of studying the effect of solute size distribution on the roast-
ing and leaching of the ore. The pulp density effect in the leach-
ing process has also been studied.

The combined sulfide concentrates prepared by bulk sulfide flo-
tation and tabling were used for roasting. The oxidizing roasting
was conducted in a 4-inch diameter fluidized-bed kiln. Sulfatizing
reactions were allowed to occur together with the oxidation reactions
in the roaster. The roasting operation was carried on for 37 hours
and 45 minutes under the following average conditions: feeding rate,
6.8 grams/minute; air supply, 1.25 cu. ft./minute; air pressure 2.02
psi.; roasting temperature 1442°F.

The screen analyses on the roaster feed and calcines led to a
conclusion that, for a higher overflowing rate from the fluidized
bed, the optimum solid particle size range would be minus 35 to plus
150-mesh and the best size would be around 65-mesh. However, this
inference might be effective only when the roasting is conducted
under the same conditions performed in this investigation.

The overflow and cyclone calcines obtained from the fluidized-
bed roasting were mixed together and sized into four size ranges for
leaching tests.

Sixteen leaching tests were conducted by dilute sulfuric acid leaching with a one-gallon stirred autoclave. The leaching tests were arranged in a factorial design which dealt with two factors, solid particle size and pulp density. Four levels for each of the two factors were selected. The four levels of particle size were: (A) plus 35-mesh, (B) minus 35 to plus 65-mesh, (C) minus 65 to plus 150-mesh, (D) minus 150-mesh. And the four levels of pulp density were: (1) 100 grams (2) 150 grams, (3) 200 grams and (4) 250 grams of solids per 2 liters of distilled water plus 13 milliliters of concentrated sulfuric acid. The leaching tests were conducted at 450°F. without applying additional pressure to the autoclave except the pressure increase due to the elevation of temperature from room temperature to the leaching temperature.

The calcines and the leach residues were chemically analyzed to determine their moisture, loss on ignition, sulfur, iron, copper and zinc contents. Interpretations of the leaching results were based on the iron recovery, copper extraction rate, zinc extraction rate and the sulfur content of the leach residue.

Statistical analysis of the particle size effects and the pulp density effects on the extraction rate of zinc was performed. The inferences drawn from the statistical analysis on the zinc extraction rate are considered to be applicable to the recovery of iron, the extraction rate of copper and the sulfur content of leach residue.

From the results of the leaching tests, chemical analyses and statistical analysis, the following conclusions have been reached:

A. The variance of the solid particle size effects on the iron recovery, the extraction rates of copper and zinc, and the sulfur content of leach residue is significant. The solid particles within the size range of minus 65 to plus 150-mesh would have the highest iron recovery, the highest copper extraction rate, the highest zinc extraction rate and the lowest sulfur content of leach residue. Practically, an optimum particle size range of minus 35 to plus 150-mesh could be applied to both the fluidized-bed roasting process and the dilute sulfuric acid leaching process.

B. Within the range of pulp density tested in this investigation, there is no significant difference in the iron recovery, the extraction rates of copper and zinc, and the sulfur content of leach residue due to the difference of pulp densities. However, the general trends are the iron recovery decreases as the pulp density decreases, the copper extraction rate decreases as the pulp density increases, the zinc extraction rate decreases as the pulp density increases, and there is almost no pulp density effect on the sulfur content of leach residue.

The purposes of this investigation, to explore the solid particle size effect on roasting and leaching and the pulp density effect on leaching, have been attained. But none of the final products, the leach residues, meets the specifications of a commercial iron ore.

The pressure effect could be a significant factor in the autoclave leaching process. A careful study on the effect of leaching pressure is recommended.

VIII. RECOMMENDATIONS FOR FUTURE WORK

Some modifications of the process and new topics of study are recommended.

Sulfatizing Roasting without Oxidizing Roasting

For the roasting of complex sulfide ores, oxidizing roasting at higher temperatures will present difficulties in the prevention of zinc ferrite formation. By sulfatizing roasting at a relatively lower temperature near 650°C., it is possible to eliminate the formation of zinc ferrite. The oxides formed by oxidizing roasting require a considerable amount of acid for dissolution in the subsequent leaching process, while the sulfates formed by sulfatizing roasting are water soluble and do not require large quantities of sulfuric acid. The sulfatizing roasting of complex sulfide ores with the fluidized-bed kiln has been successfully practiced in many mines. It is preferable to oxidizing roasting.

Open Vat Leaching for the Roasted Calcines without Pressure Leaching

For practical purposes, the open vat leaching process is simpler and more economical than autoclave leaching. The feasibility of the open vat leaching process for treating roasted calcines has been demonstrated by its application in many mines. It is not necessary to use the complicated and power-consuming autoclave to treat the roasted calcines.

Oxygen Pressure Leaching with Autoclave bypassing Roasting

Recent investigations have indicated the possibility of leaching sulfide ores directly in the autoclave by introducing sufficient amounts of oxygen under high pressure and temperature. This process will bypass the roasting stage normally required to prepare the sulfide ores for leaching. The application of the autoclave would be justified economically if this process could be successfully developed. This approach should be investigated.

Study of the Pressure Effect in Autoclave Leaching

The autoclave is a pressure leaching vessel. Whenever it is applied, the pressure effect should not be disregarded. In this study the effect of pressure on the leaching results could be very important. A careful study of the effect of pressure on the leaching process is necessary before a final conclusion concerning the applicability of autoclaves to the beneficiation of the Great Gossan Lead can be drawn.

Study of Elimination of Iron Dissolution by using
Manganese Dioxide in the Leaching Process

To develop a beneficiation process for the complex sulfide ore, it is necessary to study the method of eliminating iron dissolusion in the leaching process. Manganese dioxide has been proven to be applicable for this purpose at the Kosaka smelter of Japan. It could be applicable to the beneficiation process for the Great Gossan Lead ore.

The author believes that hydrometallurgy is a promising technique for developing an applicable beneficiation process for the Great Gossan Lead sulfide ore.

IX. ACKNOWLEDGEMENTS

The author is obliged to his mother and family in his home country. They have given him every support and encouragement to study abroad, and are waiting for his return.

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XII. APPENDICES

A. Method for Determination of Moisture and Loss on Ignition

Procedure

1. Weigh about 1 gram of sample into a previously ignited and weighed crucible.

2. Heat in an air-drying oven at 110°C. for 30 minutes.

3. Cool in a desiccator.

4. Weigh. The loss in weight represents the amount of moisture.

5. Ignite in a muffle furnace at 1000°C. for about 30 minutes.

6. Cool in the desiccator.

7. Weigh. The loss in weight represents the amount of loss on ignition.

B. Method for Determination of Insoluble Matter

Procedure

1. Weigh about 1 gram of sample into a 400-ml. beaker.

2. Dissolve it by adding 20 times its weight of concentrated HCl with a few drops of 5% $SnCl_2$ solution.

3. Add 4 or 5 drops of HF.

4. Cover with a watch-glass and heat to 80° or 90°C. until solution is complete.

5. Add a little more $SnCl_2$ solution to assist solution.

6. Filter off the residue.

7. Wash the residue 3 times with water.

8. Ignite the residue in a muffle furnace for 30 minutes.

9. Cool in a desiccator.

10. Weigh. The weight of residue represents the amount of insoluble matter.

C. Method for Determination of Sulfur

<u>Reagents</u>

1. <u>Bromine-Potassium Bromide Solution</u>

    a. Dissolve 80 grams of potassium bromide in just sufficient water.

    b. Pour 50 ml. of bromine into the saturated solution.

    c. Mix well and dilute the solution to 500 ml.

2. <u>10% Barium Chloride Solution</u>

    a. Dissolve 100 grams of $BaCl_2 \cdot 2H_2O$ in 1000 ml. of water.

<u>Procedure</u>

1. Weigh about 1.374 gram of sample into a 400-ml. beaker.

2. Add 10 ml. of bromine-potassium bromide mixture.

3. Cover the beaker with a dry watch-glass.

4. Let it stand 15 minutes in a cold bath with occasional shaking of the beaker.

5. Add 15 ml. of concentrated HNO_3 and allow the mixture stand 15 minutes longer at room temperature.

6. Warm on an asbestos board on the steam bath until the reaction has apparently ceased and the bromine has been vaporized.

7. Evaporate to dryness. The cover of the beaker is raised above the rim by means of riders.

8. Add 10 ml. of concentrated HCl.

9. Evaporate to dryness to expel the nitric acid.

10. Dehydrate the silica by heating in the air oven at 100°C. for 1 hour.

11. Add 4 ml. of concentrated HCl.

12. 5 minutes later, add 100 ml. of hot water. Rinse the sides of the beaker and the cover into the solution.

13. Remove the riders of the cover. Boil the sample for 5 minutes.

14. Cool for about 5 minutes.

15. Stir about 0.2 gram of aluminum powder into the solution. Keep the beaker covered during the intervals between stirring.

16. When the iron has been reduced, the solution becoming color-less, the sample is filtered into a 600-ml. beaker.

17. Wash the residue on the filter 9 times with hot water.

18. Make the solution acid by addition of HCl, using phenol-phthalein indicator.

19. Add 4 ml. of HCl (sp. gr. 1.2) in excess.

20. Dilute to 400 ml. with hot water.

21. Heat to boiling.

22. Add a 10% solution of barium chloride in a fine stream from a burette at the rate of 10 ml. in 2 to 10 minutes. The reagent is added in slight excess of that required to react with the sulfuric acid or sulfate. (10 ml. of 10% $BaCl_2 \cdot 2H_2O$ solution will precipitate about 0.13 gram of sulfur.)

23. Place the beaker on a steam bath and allow the precipitate to settle for about an hour.

24. Filter the solution through a fine grade filter paper.

25. Wash the precipitate 10 times with hot water.

26. Dry, and ignite the precipitate in a muffle furnace for 30 minutes.

27. Cool the white $BaSO_4$ precipitate in a desiccator.

28. Weigh the precipitate.

29. Calculate the amount of sulfur as follows:

$BaSO_4$ x 0.1374 = gram S.

D. Method for Determination of Iron

Reagents

1. 0.2 N Standard Potassium Dichromate

   a. Dissolve 9.807 grams of the recrystallized dehydrated salt of $K_2Cr_2O_7$ in water and make up to 1 liter.

   1 ml. of the 0.2 N standard solution is equivalent to 0.0112 gram of Fe.

2. Stannous Chloride

   a. Dissolve 60 grams of the crystallized salt of $SnCl_2$ in 600 ml. of concentrated HCl.

   b. Make up to 1 liter with water.

3. Phosphoric Acid - Sulfuric Acid Mixture

   a. Mix 150 ml. of concentrated H_2SO_4 and 150 ml. of concentrated H_3PO_4.

   b. Dilute to 1 liter with water.

4. Mercuric Chloride

   a. Dissolve 60 - 70 grams of $HgCl_2$ in 1 liter of water.

5. Barium Diphenylamine Sulfonate Indicator

   a. Dissolve 0.5 gram of the reagent in 100 ml. of water and filter the solution.

Procedure

1. Weigh about 1 gram of sample into a 400-ml. beaker.

2. Dissolve it by adding 20 times its weight of concentrated HCl with a few drops of 5% $SnCl_2$ solution.

3. Add 4 or 5 drops of hydrofluoric acid.

4. Cover with a watch-glass and heat to 80° or 90°C. until solution is complete.

5. Add a little more $SnCl_2$ solution, but do not exceed the amount sufficient to decolorize the solution completely.

6. Filter the solution, and wash the residue on the filter 3 times with water.

7. Treat the residue as insoluble matter. (See the method for determination of insoluble matter in Appendix B.)

8. Add sufficient test lead to the solution to cover the bottom of the beaker completely.

9. Cover the solution and boil it vigorously until the yellow color has completely disappeared and the solution is colorless.

10. Cool and decant the solution into a 600-ml. beaker.

11. Wash out the remaining iron from the lead mat by several de-cantations with water. (Two or three 50-ml. portions of water should be sufficient, the washings are added to the main solution.)

12. If the solution becomes slightly colored, a few drops of $SnCl_2$ solution are added, followed by 10 ml. of $HgCl_2$ solution.

13. Add 15 ml. of H_2SO_4-H_3PO_4 mixture and 3 to 4 drops of barium diphenylamine sulfonate indicator.

14. Titrate with the standard potassium dichromate solution. The green-colored solution changes sharply to a deep violet at the end point.

15. Calculate the amount of iron as follows:

Wt. Fe in sample = (Volume $K_2Cr_2O_7$ solution in ml.) X (Fe value per ml.)

E. Method for Determination of Copper

Reagents

1. Sodium Thiosulfate Standard Solution

a. Dissolve 4 grams of $Na_2S_2O_3 \cdot 5H_2O$ in water.

b. Add 1 gram of NaOH and dilute to 1 liter.

c. Standardize the thiosulfate solution as follows:

(1) Weigh about 0.1 gram of copper foil into a 250-ml.
     beaker, dissolve it in 10 ml. of HNO_3.

(2) Dilute to 25 ml. and boil off the red fumes.

(3) Add 5 ml. of bromine water and boil about
     10 minutes.

(4) Dilute to 75 ml., and add NH_4OH until the solution
     becomes just alkaline but not more.

(5) Add acetic acid until the solution becomes acid,
     then 2 ml. more of acetic acid.

(6) Cool to room temperature.

(7) Add 3 grams of potassium iodide dissolved in 15
     ml. of water.

(8) Stir a moment.

(9) Run in the thiosulfate solution from a burette
     until the yellow color of free iodine has nearly
     gone.

(10) Add 5 ml. of starch solution. This should produce
      a marked blue color.

(11) Continue the titration until on the addition of another drop the blue color of starch iodide disappears.

(12) 1 ml. of the thiosulfate solution should be equal to about 0.001 gram of copper.

2. Starch Solution

a. Stable starch indicator solution prepared by the Fisher Scientific Company can be used.

3. Potassium Iodide Solution

a. Dissolve 125 grams of potassium iodide in water and dilute to 500 ml.

4. Bromine Water

a. Dilute 50 ml. of bromine to 500 ml. with water.

Procedure

1. Weigh about 2 grams of sample into a 250-ml. beaker.

2. Add 7 ml. of HCl.

3. Warm.

4. Add 10 ml. of HNO_3.

5. Heat gently until the ore is decomposed.

6. Add 7 ml. of H_2SO_4.

7. Heat until fumes of H_2SO_4 are given off.

8. Cool.

9. Add 30 ml. of water.

10. Warm until soluble salts are dissolved.

11. Cool, and add 4 grams of granulated zinc.

12. Shake for 5 - 10 minutes.

13. Heat until zinc is gone.

14. Add 25 ml. of H_2S water.

15. Filter, wash the residue with feebly acidulated H_2S water until iron is removed.

16. Wash the copper (i.e. the residue) back into the beaker with as little water as possible.

17. Add 7 ml. of HNO_3.

18. Heat to dissolve the copper, and boil to expel oxides of nitrogen.

19. Filter the hot solution.

20. Wash the filter paper with a few ml. of bromine water.

21. Wash the beaker and filter paper with hot water.

22. Boil the filtrate until all bromine is expelled.

23. Cool, and add NH_4OH until the solution just turns blue.

24. Acidify with acetic acid, and then add 3 to 4 ml. of 80% acetic acid in excess.

25. Cool to room temperature.

26. Add 15 ml. of potassium iodide solution, stir well.

27. Immediately titrate with the thiosulfate standard solution.

28. When the brown tints have nearly disappeared, add 5 ml. of starch solution, and continue the titration until one drop changes the color from blue to yellowish-white.

29. Calculate the amount of copper as follows:

Wt. Cu in sample = (Vol. of the thio solution in ml.) X (Cu value per ml.)

F. Method for Determination of Zinc

1. Ammonia Wash Solution

    a. Dissolve 100 grams of NH_4Cl (C.P.) in 1000 mL of

    water.

    b. Add 100 ml. of NH_4OH (sp. gr. 0.90).

2. Sulfuric Acid (1:1)

    a. Mix 500 ml. of H_2SO_4 (sp. gr. 1.84)

    with 500 ml. of water.

3. Uranium Nitrate

    a. Dissolve 5 grams of the reagent in 100 ml. of water.

4. 3% Hydrogen Peroxide Solution

    a. Dilute 10 ml. of 30% H_2O_2 solution to 100 ml. with

    water.

5. Potassium Ferrocyanide Standard Solution

    a. Dissolve 21.12 grams of the crystallized $K_4Fe(CN)_6 \cdot 3H_2O$

    in water and make up 1 liter. One ml. of the solution

    is equivalent to about 0.005 gram of zinc.

    b. Standardize the solution as follows:

    (1) Weigh 0.2 gram of zinc (C.P.) into a 600-ml. beaker.

    (2) Dissolve in 50 ml. of water and 15 ml. of HCl

        (sp. gr. 1.19).

(3) Add 25 grams of NH_4Cl.

(4) Dilute to 300 ml.

(5) Neutralized with NH_4OH, using litmus paper as an indicator.

(6) Acidify with HCl, and add 1 gram of granuated test lead.

(7) Boil for 30 minutes.

(8) Add 10 ml. of HCl (sp. gr. 1.19) and heat to boiling.

(9) Pour about 100 ml. into a small beaker.

(10) Add $K_4Fe(CN)_6$ solution to the remaining portion until a drop added to uranium nitrate test solution on a spot plate gives a brown color.

(11) Add most of zinc solution in the small beaker to the main portion and continue addition of $K_4Fe(CN)_6$ solution until the end point is just passed.

(12) Wash all remaining solution from the small beaker into the 600-ml. beaker and finish the titration 2 drops at a time.

Procedure

1. Weigh about 2 grams of sample into a 400-ml. beaker.

2. Moisten with water.

3. Add 30 ml. of HCl (sp. gr. 1.19).

4. Boil gently for 10 minutes with the beaker covered.

5. Add 20 ml. of HNO_3 (sp. gr. 1.42) and continue the boiling
    for 10 minutes more.

6. Wash the cover and the sides of the beaker.

7. Add 15 ml. of H_2SO_4 (1:1) and evaporate to dryness.

8. Cool, and add 5 ml. of HCl.

9. Add 10 grams of NH_4Cl and dilute to 50 ml. with water.

10. Warm until all salts are in solution.

11. Cool, and add 1 ml. of liquid bromine.

12. Neutralize with NH_4OH (sp. gr. 0.90), and add 20 ml.
    in excess.

13. Heat to boiling and boil for 1 minute.

14. Filter the solution into a 600-ml. beaker.

15. Wash the precipitate 3 times with ammonia wash solution.

16. Wash the precipitate from the paper into the original beaker.

17. Add 5 ml. of HCl and 5 ml. of 3% H_2O_2 to dissolve the manga-
    nese in the precipitate.

18. Cool, and add 1 ml. of liquid bromine, neutralize with NH_4OH
    and add 20 ml. in excess.

19. Filter and wash as before, catching the filtrate and washings
    in the 600-ml. beaker containing the first filtrate and
    washings.

20. Add 1 gram of test lead to the combined filtrates.

21. Boil for 20 minutes.

22. Acidify with HCl, and boil for 10 minutes more.

23. Add 10 ml. of HCl, dilute to 450 ml. with water.

24. Heat to boiling and titrate with the standard solution of $K_4Fe(CN)_6$ as described under the standardization steps (9) through (12).

Blank Determination

1. Dissolve 25 grams of NH_4Cl in 300 ml. of distilled water in a 600-ml. beaker.

2. Acidify with HCl.

3. Add 1 gram of granulated test lead.

4. Boil for 30 minutes.

5. Add 10 ml. of HCl.

6. Titrate to the end point with the standard solution.

Calculations

1. Calculate the factor as follows:

$$F = \frac{W}{A - B}$$

where A = ml. of $K_4Fe(CN)_6$ solution required for the standard zinc solution

B = ml. of $K_4Fe(CN)_6$ solution required for the blank.

W = weight of zinc in the standard zinc solution.

F = grams of zinc per ml. of $K_4Fe(CN)_6$ solution.

2. Calculate the percentage of zinc in sample as follows:

$$\%Zn = \frac{(A - B) \; X \; F \; X \; 100}{W}$$

where A = ml. of $K_4Fe(CN)_6$ solution required for the sample.

B = ml. of $K_4Fe(CN)_6$ solution required for the blank.

F = grams of zinc per ml. of $K_4Fe(CN)_6$ solution.

W = weight of the sample in grams.

G. Example Calculations for the Recovery of Fe, and the Extraction Rates of Cu and Zn

The following experimental data of the leaching test X_{Al} were given by Tables 8, 9 and 10:

Weight of calcine leached = 100 g.

Weight of leach residue = 89.80 g.

Recovery of residual ore = 89.80 %

Chemical analysis of calcine A:

Moisture and Ig. Loss = 7.79 %

Fe = 51.02 %

Cu = 0.72 %

Zn = 2.64 %

Chemical analysis of leach residue:

Moisture and Ig. Loss = 3.36 %

Fe = 53.31 %

Cu = 0.74 %

Zn = 1.20 %

The assay value of Fe, Cu and Zn were given on a moisture and ignition loss-free basis. Calculate the recovery of Fe, and the extraction rates of Cu and Zn respectively.

Solution:

$$Fe \text{ recovery } \% = \frac{89.80 \times (1 - 0.0336) \times 0.5331}{100.00 \times (1 - 0.0779) \times 0.5102} \times 100$$

$$= 0.8980 \times 1.0480 \times 1.0449 \times 100 = 98.34\%$$

$$Cu \text{ extraction rate } \% = 100 - \left[\frac{89.80 \times (1 - 0.0336) \times 0.0074}{100.00 \times (1 - 0.0779) \times 0.0072} \times 100 \right]$$

$$= 100 - \left[0.8980 \times 1.0430 \times 1.0278 \times 100 \right]$$

$$= 100 - 96.73 = 3.27\%$$

$$Zn \text{ extraction rate } \% = 100 - \left[\frac{89.30 \times (1 - 0.0336) \times 0.120}{100.00 \times (1 - 0.0779) \times 0.0264} \times 100 \right]$$

$$= 100 - \left[0.8980 \times 1.0480 \times 0.4545 \times 100 \right]$$

$$= 100 - 42.77 = 57.23\%$$

H. Table of Absolute Vapor Pressure of Water *

Temperature	Vapor Pressure		Temperature
°C.	m.m. of mercury	lb./in.^{2}	°F.
0	4.58	0.0886	32
5	6.51	0.126	41
10	8.94	0.173	50
15	12.67	0.245	59
20	17.5	0.339	68
40	55.1	1.07	104
60	149	2.89	140
80	355	6.87	176
100	760	14.7	212
120	1490	28.8	248
140	2710	52.4	284
160	4630	89.6	320
180	7510	145	356
200	11650	225	392
220	17390	336	428

* Abstracted from COLLEGE PHYSICS by Sears, F. W. and Zemansky, M. W.,
Addison - Wesley Publishing Co., Reading, Massachusetts, 1960,
3rd ed., p. 371.

ABSTRACT

This investigation has been carried out for the purpose of determining the effect of solid particle size distribution on the roasting and leaching of a complex sulfide ore. The effect of pulp density in the leaching process has also been studied.

The oxidizing roast of the combined sulfide concentrates, prepared by bulk sulfide flotation and tabling, was conducted with a fluidized-bed kiln. The calcines were leached by dilute sulfuric acid in an autoclave. The following conclusions have been reached:

1. In the fluidized-bed roasting, the solid particles within the size range of minus 35 to plus 150-mesh would have a higher overflow rate from the fluidized bed. This inference might be effective only when the roasting is conducted under the conditions performed in this investigation.

2. In the process combining fluidized-bed roasting and dilute sulfuric acid leaching, the effect of solid particle size is significant. The solid particles within the size range of minus 65 to plus 150-mesh have the highest iron recovery, the highest copper and zinc extraction rates and the lowest sulfur content of leach residue.

3. In dilute sulfuric acid leaching there is no significant effect of pulp density within the range tested in this investigation. The general trends are: iron recovery decreases as the pulp density decreases, extraction rates of copper and zinc decrease as pulp density increases, and there is little pulp density effect on the sulfur content of leach residue.