

OXIDATION OF COPPER CONCENTRATES
TO WATER-SOLUBLE COPPER

by

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ABSTRACT

The possibility of using a micro-fluidized bed system to obtain data for high temperature reactions has been investigated. The reaction chosen for this study was the selective oxidation of copper concentrates, containing copper primarily in the sulfide form, to the water-soluble copper sulfate.

The reaction was carried out in a microreactor which was immersed in a constant temperature fluidized sand bath. Preheated air was used to fluidize a 1.25 gram sample of copper concentrate contained in the microreactor. The volume of the microreactor was 4.28 cubic centimeters. The reaction was studied over a temperature range of 200 to 700 degrees Centigrade.

Eighty-eight percent conversion of the copper concentrate to water-soluble copper was obtained at 540 degrees Centigrade at a retention time of one-half hour under a fluidizing air rate. The air rate to the microreactor was fixed for all of the runs by the amount of air required to keep the bed in a well-fluidized condition. This air rate corresponded to a superficial velocity of 0.639 feet per second for a sample size of 1.25 grams. The total quantity of air which passed through the microreactor during

this time was two times the theoretical amount required to convert all of the copper to copper sulfate, all of the iron to ferric oxide, and all excess sulfur to sulfur dioxide. These results are in good agreement with previously published work. A retention time of two hours was found to be detrimental to the formation of water-soluble copper at temperatures above 500 degrees Centigrade.

The possibility of a recycle or sequential-type operation was also investigated and found to be promising. For this investigation the copper sulfate from two runs was leached from the respective concentrate samples and the remaining residues were used for an additional run at the same temperature. An increase in the total conversion from 85 to 91 percent was found for a recycle run at 555 degrees Centigrade.

Recommendations are included for future work in this area.

INTRODUCTION

The acquisition of precise data for high-temperature reactions has always been of utmost importance to the chemical process industries. A reaction which coincides with this interest is the possibility of selectively oxidizing copper concentrates, containing copper primarily in the sulfide form, to the water-soluble copper sulfate. Once the copper is rendered soluble, the sulfate form readily lends itself to the recovery of pure copper (R-20).

Traditional Processing Methods

In nature copper ore is found primarily in the form of oxides or sulfides with the oxide ore usually being accompanied by large quantities of iron sulfide. The processing of the oxide ore is traditionally handled by hydrometallurgical techniques. In this practice the ore is sprinkled with water and allowed sufficient time for the iron sulfide to be oxidized to iron sulfate. The water-soluble copper sulfate is then formed from the reaction between iron sulfate and copper oxide. Cement copper is produced by directing the copper sulfate stream over a bed of scrap iron. Pure copper is finally obtained by electrolytic purification.

The pyrometallurgical technique (R-5) for processing of the sulfide ores differs from the technique used for the oxide ores. The processes differ because the sulfide ores cannot be readily rendered water-soluble. Copper sulfide ores are generally very low grade (approximately one weight percent copper), therefore, they are first concentrated by a flotation process. For the flotation step the crude ore from the mine is crushed and ground until the copper-bearing minerals are substantially liberated from the gangue. The finely divided ore is agitated in water containing bubbles of air, frothing oils and minute quantities of other reagents, both organic and inorganic. Under these conditions the particles of floatable minerals tend to absorb a film of air, which enables them to be carried to the surface of the flotation machine, there to be delivered into a concentrate launder. The gangue minerals, which are difficult to float naturally or have been rendered so by the addition of suitable reagents, absorb a film of water. They become wetted and remain in suspension, thus passing through the flotation cell as tailing. The flotation process results in a concentration of the copper sulfides containing around 30 to 40 weight percent copper. The product of the flotation cell is referred to as copper concentrate.

The concentrates are then brought into the smelter by conveyor belt where they are fed to the sidewalls of a

reverberatory furnace and melted down into two products, matte and slag. The heavier matte primarily contains copper, iron, and sulfur, while the slag floats on top and contains the rock residues from the original ore that were retained during the concentration step.

The matte is tapped from a tap-hole, located at the bottom of the furnace, into ladles, and transferred to a converter. The slag is removed from a higher area in the wall of the furnace and transferred to a slag dump.

The converter or oxidizer is a horizontal, cylindrical, steel vessel lined with basic refractories with a row of air pipes arranged along the back wall. Mine ore is added to the blowing matte in order to form a slag of silica in the ore, plus oxidized iron from the matte. This slag is returned by ladle to the reverberatory furnace since it contains approximately two percent copper. It is finally disposed of with the reverberatory slag.

The conversion of matte to blister copper, as the product of the converter is called, is produced by adding ladles of matte periodically and removing the slag as it is formed. When a sufficient volume of copper sulfide accumulates in the converter, it is converted to the oxide without any further additions of fluxing ore and without the formation of any additional slag. The slagging portion of a charge requires about eight hours and the final

oxidation requires about three and one-half hours. The product of the converter is blister copper at approximately 98 weight percent copper.

The blister copper is then removed from the converter by ladle and placed in an anode vessel. This vessel is a furnace similar in construction to the converter but lacking the air pipes. Here, the copper is further oxidized by blowing with compressed air lances. The resulting slag is removed and fed to the converter. This small amount of slag contains most of the impurities to be found in the copper, now saturated with copper oxide. The charge is then reduced to remove the oxygen.

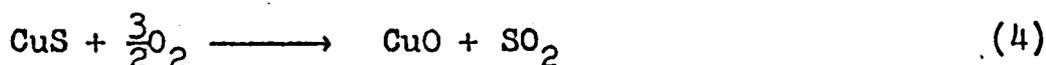
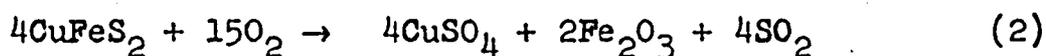
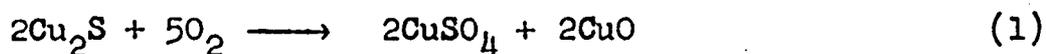
The copper is cast from the anode vessel into anode shapes for electrolytic refinement. The anode copper is approximately 99.8 weight percent copper. Further electrolytic purification produces copper with a purity of 99.99 weight percent.

Although the currently used processing methods for the production of copper are adequate, a sulfating roast of copper sulfide concentrates is particularly attractive for several reasons. If the copper is rendered water-soluble, it could be recovered from solution without going through the normal smelting stages with subsequent electrolytic refinement. Thus, greater economies could be realized since expensive furnaces and processing equipment, plus

the requirement of batch operation could be eliminated. Also, any oxide ore found in certain parts of the mine could be leached with sulfuric acid which could be produced from the copper sulfate solution and from the sulfur dioxide in the effluent gases from the roasting operation. Then too, since current copper smelting practice is best suited to large scale operations, many small to medium size mines with sulfide ore bodies are interested in alternative processes.

Principal Reactions

With the advent of a chemical processing technique for separating copper from a copper sulfate solution, the desire to convert copper sulfide concentrates directly to the water-soluble form has increased. The concentrates contain copper primarily in three sulfide forms, chalcocite, chalcopyrite, and covellite. Theoretically, air roasting of these sulfide minerals results in the formation of the sulfate according to the following reactions:

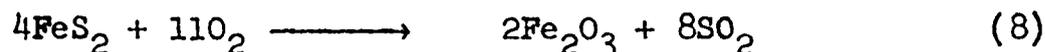
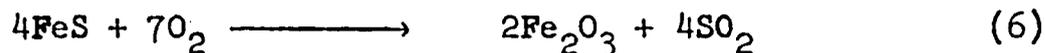


In the presence of sulfur dioxide and air, the following reaction applies for the roasting of oxide copper:



The source of sulfur dioxide for the reaction with copper oxide is not important. It can come from the burning of sulfides such as FeS or FeS₂, which are mixed with the ore, or it can be directly added to the inlet gas going to the reactor.

The most important side reactions involve the competition for oxygen by iron sulfide. The iron sulfide may be converted to the oxide or to the water-soluble sulfate according to the following reactions:



The most desirable situation is, of course, to selectively "sulfate" all of the copper without solubilizing any of the iron. This is desirable since the copper is more easily separated if it is in an essentially pure copper sulfate solution.

Fluidization Advantages

As a result of the timely introduction of the fluidization technique, renewed interest has been stimulated in the possibility of selectively sulfating copper sulfide concentrates to the water-soluble form. "Fluidization technique" is the term used to describe the partial suspension of solid particles in an upwardly moving stream of fluid. With this technique each individual partially suspended solid particle tends to be surrounded by a constantly changing fluid film. This condition provides the intimate contact which is necessary for solids-gaseous reactions.

The ability of the fluidized bed to maintain an isothermal condition is the outstanding advantage of this method over other methods of carrying out reactions. Since this factor is vital to nearly all applications of the fluidized bed technique, the other advantages are generally of far less importance. Close control of chemical reaction variables is well known to be important in obtaining maximum yields of desired products. Of the many reaction variables, temperature is commonly the most important since reaction rates change exponentially with temperature. In the most general case in which several competing reactions may occur, a temperature change of a few degrees may shift the balance

between the several rates from a desirable one to an undesirable one. The unusually close control of temperature which is possible in a fluidized bed is due to a combination of the following three factors (R-15):

1. Turbulence Within the Fluidized Mass. The turbulent condition within the fluidized mass serves to break and disperse any hot or cold spots throughout the bed before they can grow to any significant size. However, it should not be inferred from this statement that the temperature of each solid particle in a given fluidized bed is the same. The reaction rate will differ somewhat from particle to particle, and those with greater activity will react faster. Consequently, their temperature will be different from that of the surrounding particles of lower activity. However, the departure of the individual particle temperature from the mean value of the bed will be much less than in a fixed bed, because of the turbulent mixing, plus the factors discussed in the following paragraphs.
2. High Heat Capacity of the Bed. The factor which stabilizes the temperature of the bed

is the high heat capacity of the bed relative to the gas within it. This permits the bed to absorb relatively large heat surges with only small temperature changes. For example, a bed of ordinary sand fluidized with air, at a solids concentration of about 70 pounds per cubic foot, would contain only around 0.05 pounds of air per cubic foot. This corresponds to a mass ratio of 1400 to 1.

3. High Heat-Transfer Rates. Relatively high heat-transfer rates are possible because of the large amount of transfer surface area per unit volume of the fluidized bed. The high transfer rates permit rapid leveling of any temperature surges either from the incoming gas or from the reaction within the bed. Although the heat transfer coefficients are not unusually high, the amount of surface per unit volume is very large. For example, the surface area of the sand cited in the previous paragraph would be in the range of 1000 to 5000 square feet per cubic foot of bed. The remarkable uniformity of temperature in a fluidized bed has been noted in many references. Temperature traverses

in large fluidized-catalyst beds indicate that the point-to-point variation is less than ten degrees Centigrade when the feed-gas temperature is not greatly different from that of the bed. Even if the temperature of the feed gas is considerably different from the bed, the high transfer rates possible commonly produce a close approach to thermal equilibrium within a few inches from the beginning of contact.

The ability to handle the fluidized solid like a liquid permits the technique to be easily adapted to many continuous operations, thereby obtaining the advantages of such operations, such as lower labor requirements, precise and automatic control of process variables, and uniformity of product quality.

For carrying out gas-solid reactions the advantages of the fluidization technique are the isothermal bed, the easily varied time of contact, the effective contact, the simple methods of handling solids and transferring heat, and the ease of continuous automatic operations. By properly controlling the fluidizing air or other gases admitted to the reactor, the composition of the gaseous atmosphere in the bed can be accurately controlled. Another inherent advantage of a fluidized system is the absence of moving

parts in the high temperature areas. This becomes important in an operating plant, since it contributes to low maintenance costs.

These characteristics strongly suggest the applicability of fluidization techniques to the selective sulfate roasting of copper concentrates.

Purpose

It was the purpose of this research to investigate the possibilities of using a micro-fluidized bed reactor to obtain data for high temperature reactions. Since the reaction between air and copper concentrates has become increasingly interesting, this reaction was chosen for investigation. Also, since some initial work has been done along these lines in macroscopic systems, a direct comparison of results was possible. Then too, the available data for this reaction in fluidized systems is extremely limited and any additional results should be very useful in extending the knowledge of gas-solid reactions.

LITERATURE REVIEW

Many studies concerning the roasting of copper sulfides have been reported in recent years. Ashcroft (R-1) studied the roasting of copper concentrates in pure oxygen. However, his paper gives neither data nor experimental details. Diev and others (R-3) investigated the roasting of chalcocite, Cu_2S , in air, and oxygen enriched air. Lewis and co-workers (R-16) also studied the oxidation of natural and synthetic chalcocite in air and oxygen atmospheres. The results of their work indicated that the maximum formation of water-soluble copper occurred at approximately 450 degrees Centigrade. Using air as the oxidant, the conversion at this temperature was around 32 weight percent. However, their results were obtained using a fixed bed reactor. It is a well known fact that local bed temperatures are subject to wide variations in a reactor of this type (R-14). It has been suggested by Stephens (R-21) that the primary reasons for failure of most of the sulfating operations has been the inability to maintain proper temperature and atmosphere control in the furnacing equipment. He maintains that hot spots frequently develop in the charge or within the individual ore particles, thus causing decomposition of the valuable metal sulfates.

Renewed interest in selective sulfation has been stimulated by the introduction of the fluidized bed reactor. Owing to the intense agitation in a well fluidized bed, local temperatures and solids distribution are almost perfectly uniform (R-14). Hence, precise control of temperature and atmosphere is now possible with this type reactor.

Several articles have appeared on the applications of fluidization techniques to the mineral industries (R-2, R-19, R-22). Whitehead and Urie (R-25) have studied the control roasting of copper concentrates to produce copper oxide. Their work describes the fluidized roasting of concentrates to produce copper oxide as a part of a technical evaluation of the hydrometallurgical recovery of copper from Australian chalcopyrite concentrates. Stephens (R-21) has studied the fluidized bed sulfate roasting of nonferrous metals. He used a two foot diameter reactor for the autogenous roasting of tonnage samples of chalcopyrite ore and concentrate. However, no specific results are given for the oxidation of copper concentrates to water-soluble copper. Howell (R-12) has also reported on the sulfating of copper sulfides, but, here again, no specific results are presented.

A better understanding of the events which occur during a sulfating roast should be realized when the

mechanism of sulfate formation is more fully understood. Some investigation has been done on the sulfation of chalcocite and covellite (R-17, R-18, R-23); however, no information on the rates of reaction and reaction mechanisms involved in sulfate roasting is available at this time.

Since temperature and gas compositions are relatively constant in fluidized bed roasting, a knowledge of the thermodynamics of the reactions may be applied with some success to roasting problems using the fluidization technique. Kellogg (R-23) has presented some of the principles concerned with sulfate roasting and has indicated convenient methods for calculating the relevant equilibrium gas compositions. Fisher (R-6) has also presented some of the reactions involved in sulfation and has indicated methods for the simple determination of the possibilities of selective sulfation of different metals. However, the thermodynamics of reactions merely show the direction in which they will proceed, but give no information about the rate. Before the phenomena involved in sulfation reactions is completely understood, the thermodynamic approach must be coupled with information on the rates of processes. One of the major difficulties today in many operating plants, however, is the variable nature of the minerals being fed to the roasting plant.

For instance, the concentrate material at the Rhokana Corporation cobalt plant contains a mixture of varying proportions of chalcopyrite, bornite, carrollite, cobaltiferous pyrite and pure pyrite, in addition to gangue which is predominantly siliceous (R-6). The cobaltiferous pyrite is of variable composition, with a cobalt content which varies from a trace amount to around 12 weight percent. Carrollite is nominally CO_2CuS_4 , but the copper may be replaced by cobalt up to the composition of linnaeite, Co_3S_4 . These variations in mineral composition must affect rates of reaction, and also reaction mechanisms. Therefore, it is rarely possible to relate reaction rates determined on pure mineral specimens quantitatively with plant practice.

THEORY

Fluidization Considerations

There are two types of reactors which are primarily used today: a fixed bed reactor and a fluidized bed reactor. In a fixed bed reactor the particles contained in the bed are motionless and are supported by contact with each other. Past experience has indicated that fixed bed roasting of sulfide ores or concentrates is unsatisfactory for the formation of a water-soluble metal sulfate. This has been attributed to the development of hot spots in the ore or within the individual ore particles, resulting in the decomposition of the valuable metal sulfates. With the introduction of the fluidized bed reactor renewed interest in the selective sulfation of sulfide minerals has been revived since local temperatures and solids distribution approach near uniform conditions in a reactor of this type.

In conventional fluidized beds of constant cross-sectional area it is a well known fact that as the gas flow is gradually increased the bed slowly passes from the fixed bed to the fluidized bed condition with fluidization first occurring in the uppermost part of the bed. A further increase in the gas flow causes the fluidization of the bed to move downward until the bed is completely fluidized.

Since the bed has liquid-like properties, the pressure difference between the top and bottom of the bed is proportional to the product of the height of the bed and the bed density. For a shallow bed of low density particles, this pressure difference will be small, thus the change in gas density will be negligible. Hence, the average linear velocity of the gas throughout the bed will be almost constant, thus ensuring uniform fluidization throughout the bed (R-4).

Associated with fluidized bed sulfate roasting are several terms which need to be described. The first of these is a dead roast. This refers to the roasting condition in which only one hundred percent of the theoretical air requirements is allowed to react with the feed. As a result of this, the products are completely oxidized, but not sulfated to any degree. Dead roasting prior to pyrometallurgical treatment has the advantage of a very high sulfur yield in the form of sulfur dioxide gas. A sulfating roast is the term used to describe the condition in which a substantial excess of air is available so as to provide an opportunity for sulfur values in the feed to be recombined in the calcine as sulfates. A partial roast is one in which insufficient air is provided to carry the chemical reactions involved to completion. This is sometimes desirable in order to retain a portion of the

sulfur content in the calcine as a requirement for further treatment.

If a sulfating roast is desirable, this necessarily dictates a well-fluidized bed. The air rate necessary to maintain a bed in a well fluidized condition may be determined by making a mass balance on the air flow through the bed. Consider the case depicted in Figure 1 below in which a fluid is flowing from section 1 to section 2.

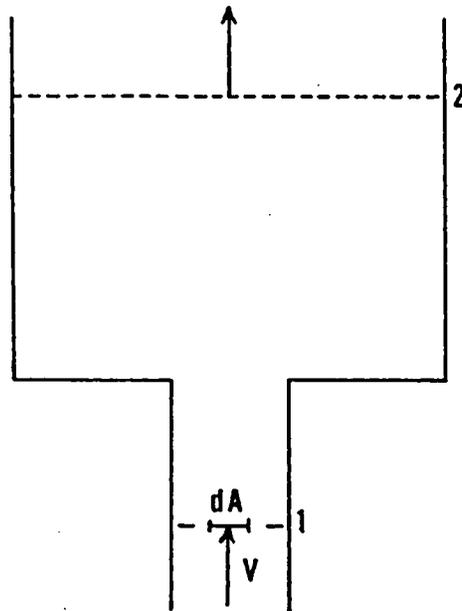


Figure 1

Fluid Flow Through a Tube

At section 1 the velocity at any point is V ; this velocity is normal to the area dA , and the density is ρ . The mass rate of flow through the area dA is given by $\rho V dA$. Since the velocity, V , may vary over section 1, the total mass rate of flow through section 1 is given by the integral

$$\int_1 \rho V dA \quad (1)$$

which is taken over the entire section 1. In a similar fashion, for section 2 the mass rate of flow through the entire section 2 is given by the integral

$$\int_2 \rho V dA \quad (2)$$

where ρ , V , and dA are taken at a point in section 2. For the case of steady flow, the mass rate of flow across section 1 equals the mass rate of flow through section 2, thus,

$$\int_1 \rho V dA = \int_2 \rho V dA = \text{constant.} \quad (3)$$

Consider the situation where V_1 is the uniform or average velocity across section 1, ρ_1 is the uniform density over section 1, and A_1 is the entire area of section 1 with the subscript 2 used similarly for the corresponding

factors at section 2. Then the equation of continuity takes the form

$$\rho_1 V_1 A_1 = \rho_2 V_2 A_2 = \text{constant.} \quad (4)$$

Section 2 corresponds to the cross-section of the fluidized bed while section 1 corresponds to the cross-section of the inlet gas line used to fluidize the bed. If section 2 is made of glass and filled with a bed of particles, the gas flow through section 1 can be adjusted until the bed is observed to be in a well fluidized condition. The corresponding superficial velocity, V_2 , can then be calculated with a knowledge of the cross-sectional areas and the gas densities at sections 1 and 2. The cross-sectional areas may be calculated directly by measuring the diameter of each circular section. If air is used as the fluidizing gas, the density may be calculated by assuming ideal gas behavior where the temperature and the density of the gas are related by the Ideal Gas Law:

$$T = \frac{pV}{nR} = \frac{MpV}{wR} = \frac{Mp}{\rho R} . \quad (5)$$

Figure 7 in the Appendix gives the density of air at one atmosphere pressure as a function of temperature over the temperature range investigated.

Admittedly, the mass balance approach is not entirely correct since some gas is given off in a sulfate roasting reaction. This evolved gas probably contributes somewhat to the required superficial velocity for fluidization; however, if the reactor bed is small, the amount of gas given off will be negligible in comparison with the amount of fluidizing air. Also, this approach does not account for any density changes which may occur in the bed particles themselves. But here again, these are small and may, for practical purposes, be neglected. This method of approach does give, however, a sound basis for predicting the necessary air flow for fluidization at high temperatures where direct observation of the bed condition is impossible.

Free-energy Considerations

Free energy is defined as the capacity of a reaction for doing work, and it is a measure of maximum available work which can be obtained from a reaction regardless of whether work is done or not. The size of the free-energy decrease is a quantitative measure of the driving force of the reaction.

At the present time there is no method known for the determination of absolute values for free energies of various substances. On the other hand changes in free energy can be measured, and from such measurements it is

possible to assign to a reacting substance a relative energy quantity called its free energy.

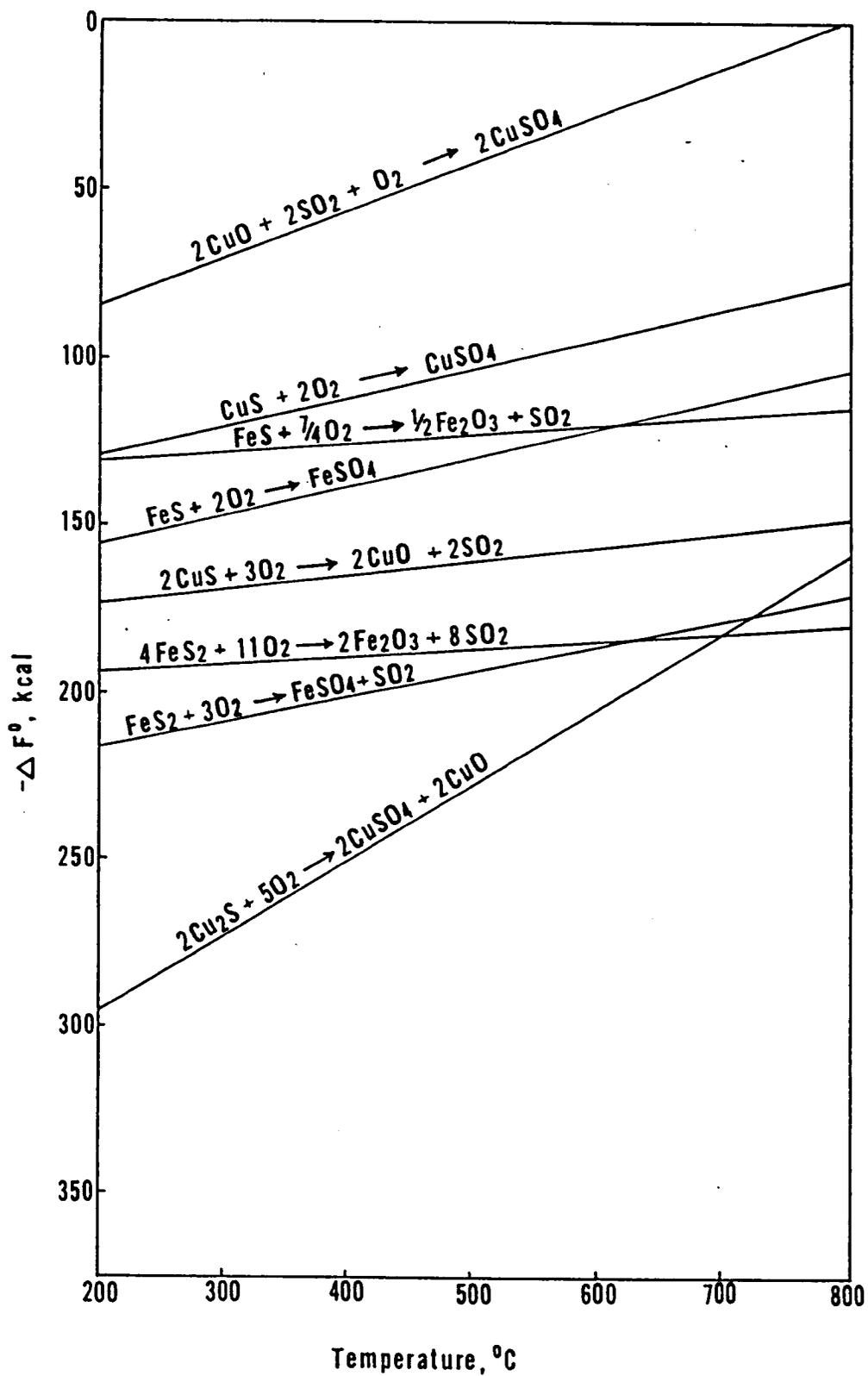
Inasmuch as change in free energy measures the tendency of a reaction to proceed, there are three possibilities for any given chemical reaction:

1. If the free-energy change is a negative value, the reaction is spontaneous and will proceed in the direction in which the equation is written.
2. If the free-energy change is a positive value, the reaction is not spontaneous in the direction of the written equation but will proceed in the reverse direction.
3. If the free-energy change is equal to zero, the system is in equilibrium and the reaction will not proceed in either direction.

Since the free-energy change of a chemical reaction is a quantitative measure of chemical affinity, such measurements are used to predict which chemical reactions can be expected to take place and which ones will not.

The principal reactions have already been presented in the Introduction and the changes in free energy for these reactions, calculated from the data of Kelley (R-23), are presented in Figure 2. It is readily apparent that the formation of copper sulfate from the copper sulfide minerals

FIGURE 2. Free-Energy Relationships for
the Principal Reactions



is indeed favorable over the temperature range considered. The most favorable reaction for the formation of copper sulfate is the oxidation of chalcocite. The change in free energy for the oxidation of chalcopyrite could not be calculated since the necessary thermodynamic data was not available. It should be pointed out that each of the free-energy curves were calculated with experimental data obtained over a fairly narrow temperature range, therefore, no great accuracy can be expected. Although the general picture is almost certainly correct, the individual plots should be regarded as close approximations only.

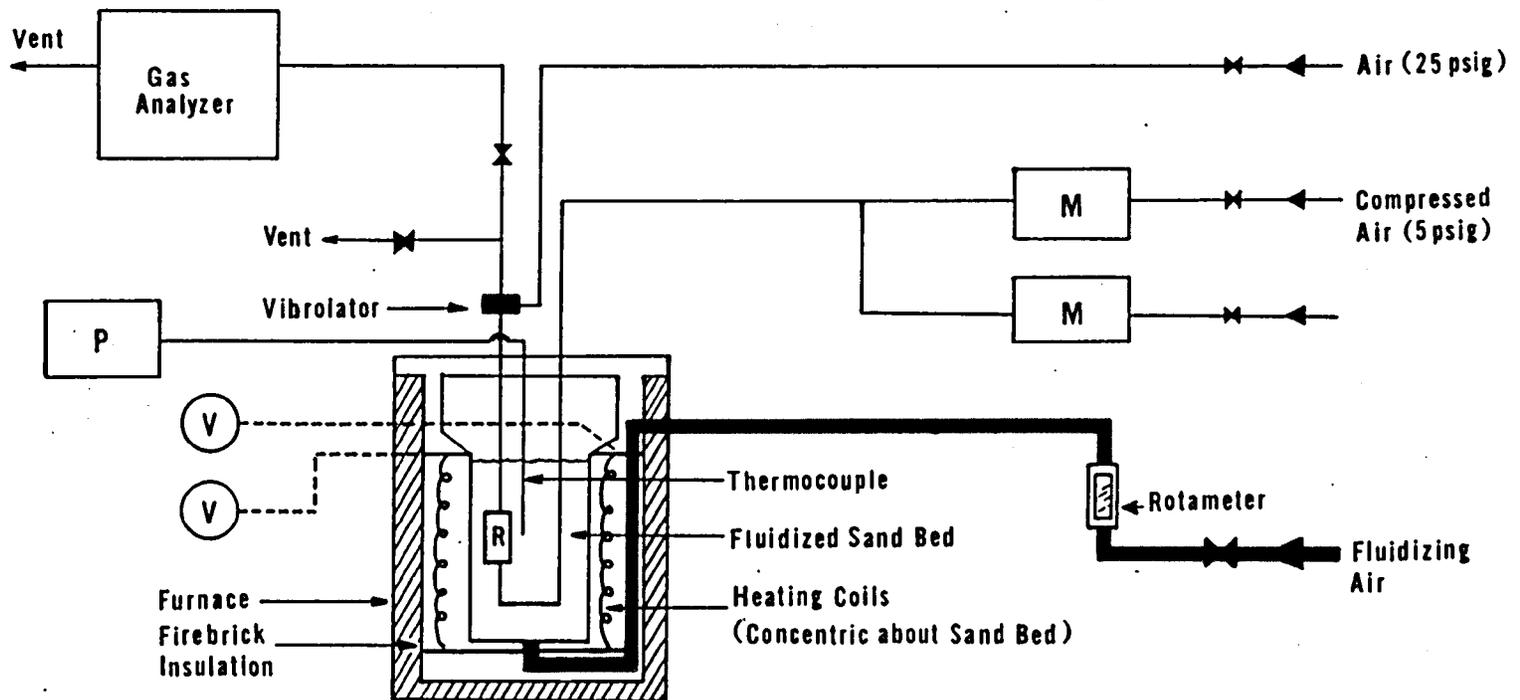
EXPERIMENTAL EQUIPMENT

General Arrangement

The general arrangement of the experimental equipment is shown in Figure 3. The major items in the apparatus consisted of two Hastings Mass Flowmeters, a constant temperature fluidized sand bed supplied with preheated air, a microreactor, a vibration inducer, and a Burrell Gas Analyzer.

Two Hastings Mass Flowmeters, Models LF-300, manufactured by Hastings-Raydist, Incorporated, Hampton, Virginia, were used to monitor the air feed to the microreactor. With 100 percent solid state circuitry and factory calibrated for air, the accuracy of these meters is claimed to be within one percent. The air feed to the microreactor passed through a 1/8 inch OD stainless steel tubing bayonet which supported the microreactor in the fluidized sand bed. In the early stages of experimentation a thermocouple was installed in the air stream at the inlet to the microreactor. This was done to make certain that the air feed reached the temperature of the sand bath before entering the microreactor under all temperature and flow conditions.

FIGURE 3. General Arrangement of Experimental
Equipment



P - Potentiometer
M - Mass Flowmeter
V - Variac, 130 volts
R - Microreactor

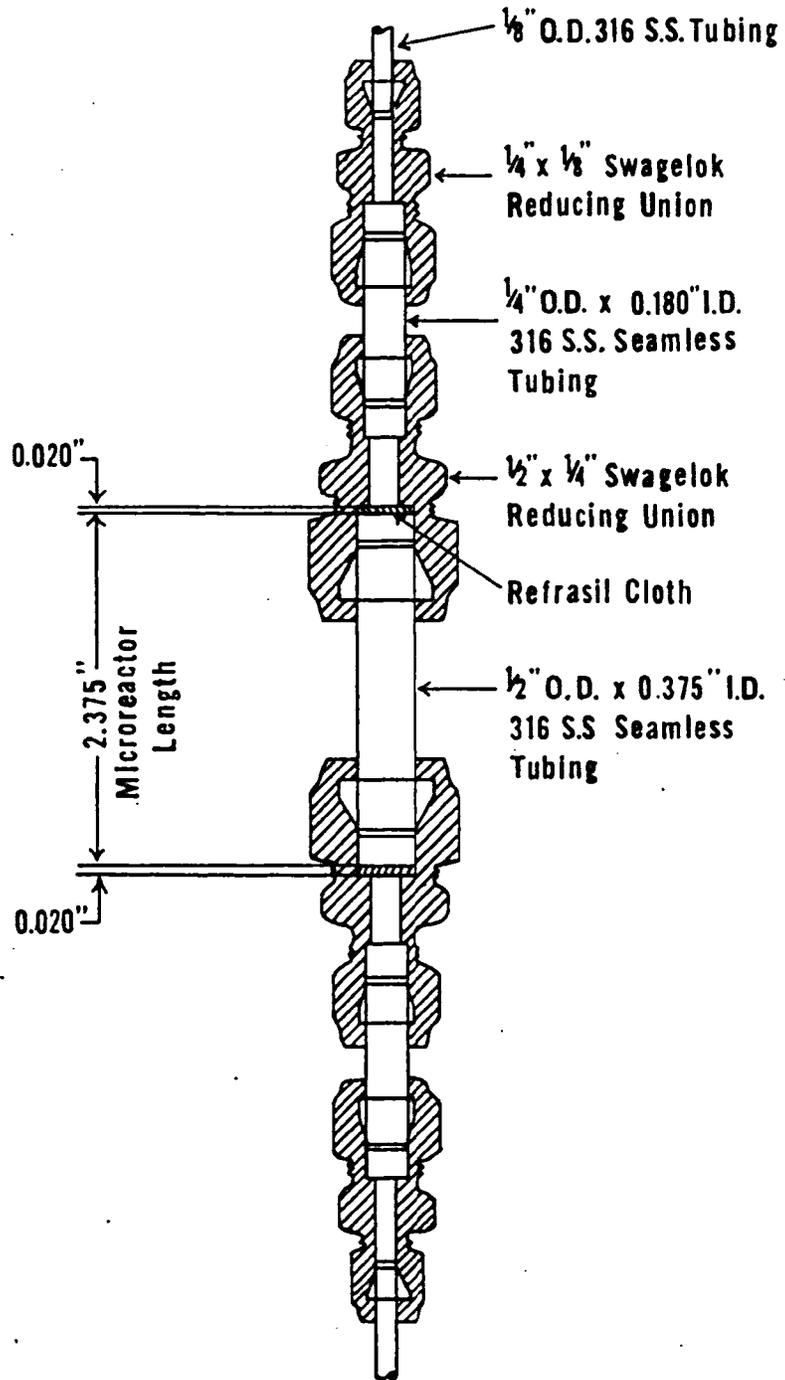
The effluent from the microreactor flowed through 1/8 inch OD stainless steel tubing and was directed to a Burrell Gas Analyzer or, by suitable valving, to a vent. The exit tubing was fitted with a Vibrolator Model BD, Size 10, vibration inducer which was used to keep the microreactor in a highly agitated state. The Vibrolator, an air driven vibration inducer, was used to decrease the possibility of channeling in the microreactor during the course of the reaction.

A Burrell Gas Analyzer was used to determine the sulfur dioxide and oxygen content of the effluent gas for the high temperature experiments.

Microreactor

The microreactor design used in this investigation was essentially the same as that employed by Hall (R-10) and is shown in Figure 4. The microreactor consisted of a 2.375-inch length of 1/2-inch O.D., 0.375-inch I.D. type 316 stainless steel tubing, with the volume defined by pieces of Refrasil cloth held in place by Swagelok fittings. Refrasil cloth, manufactured by the H. I. Thompson Fiber Glass Company, Los Angeles, California, is the trade name for their woven quartz. The use of this cloth as a retainer for the concentrate charge was desirable since it is inert and unaffected by high temperature exposure.

FIGURE 4. Microreactor Detail



The microreactor was prepared by first cutting a piece of 1/2-inch tubing to the desired length. The ends of the tubing were then machined so that they were perpendicular to the axis of the tube. A piece of shim stock 0.020 inches thick was then placed against the shoulder in the Swagelok fitting to act as a spacer for the Refrasil cloth. The microreactor tube was then inserted into the fitting against the shim stock and the nut on the fitting was tightened in order to set the ferrule. The ferrule was set by turning the nut one revolution after it had been made hand tight. This procedure left enough clearance between the shoulder of the fitting and the end of the tube to accommodate two pieces of Refrasil retaining cloth. Preliminary investigations indicated that two pieces of cloth did the best job of containing the fine concentrate particles. A number 7 cork bore was found to be of exactly the right size for cutting out the Refrasil cloth.

Air entered the bottom of the microreactor through a 1/8-inch O.D. stainless steel tube. Just before the air entered, it passed through a three-foot coil of tubing. Calculations showed that this length of tubing provided enough heat transfer surface to insure that the air was preheated to the same temperature as the microreactor. The effluent gas from the microreactor also passed through

a length of 1/8-inch O.D. stainless steel tubing and was finally exhausted to a vent.

Sand Bath

The container for the fluidized sand was constructed of 3-inch schedule 40 steel pipe. The bath was enclosed in a furnace lined with magnesia firebrick insulation as shown in Figure 3. The furnace was electrically heated with two sets of 16-gage Nichrome-IV heating coils. Each set contained eight coils of Nichrome wire suspended vertically from the top to the bottom of the furnace and spaced concentrically around the sand bed. The coils were connected with Nichrome-IV ribbon at the top and bottom of the furnace in order to complete the resistance circuit. Power to the coils was controlled by two 130-volt, 20-ampere Variacs.

A 3-inch by 6-inch schedule 40 concentric reducer welded to a 6-inch length of 6-inch schedule 40 steel pipe provided a sand disengaging space at the top of the fluidized sand bed. The bottom of the fluidized sand section was fitted with a flange which held a 100 mesh stainless steel screen. The screen allowed the fluidizing air to pass while retaining the sand.

The fluidizing air to the sand bed was delivered through a 1/2-inch schedule 40 steel pipe and controlled

by a rotameter. The best setting for the air flow was determined by observing the action of the fluidized sand in the bed. The air line entered the furnace at the top and was connected to a 1/2-inch reducer on the bottom of the sand bed. This arrangement allowed the air to be pre-heated as it flowed through the furnace atmosphere before it entered the sand bed.

Gas Analyzer

The sulfur dioxide and oxygen content of the effluent gas from the microreactor was determined with a Burrell Gas Analyzer, Model 39-540, manufactured by the Burrell Corporation, Pittsburgh, Pennsylvania. This piece of equipment corresponds exactly to the standard Orsat Analyzer and is described in detail by Furman (R-9). The procedure used for the gas analysis is presented in the Appendix.

EXPERIMENTAL PROCEDURE

Concentrate Preparation

The copper concentrate used in this investigation was obtained from the American Smelting and Refining Company. The material as received was dry but rather lumpy. In order to improve the physical consistency of the concentrate, the sample material was ground in a ball mill for 48 hours. This resulted in a concentrate size distribution as shown below in Table 1.

Table 1. Concentrate Screen Analysis

<u>Size, Mesh</u>	<u>Weight Percent</u>
Plus 100	6.72
Minus 100 Plus 150	1.49
Minus 150 Plus 200	3.95
Minus 200 Plus 270	20.08
Minus 270 Plus 325	39.74
Minus 325 Plus 400	13.66
Minus 400	14.36

Since the bulk of the material fell in the minus 200 size range, the last four size fractions shown above were

combined and used for this study. A partial chemical analysis of this combined concentrate is given in Table 2.

Table 2. Partial Chemical Analysis of Concentrate

<u>Constituent</u>	<u>Weight Percent</u>
Total Copper	29.55
Oxide Copper	3.58
Iron	31.80
Sulfur	32.60
Insolubles	3.00

Photomicrographic inspection of a sample of the concentrate revealed the presence of the following copper minerals: chalcopyrite, chalcocite, and covellite. Most of the copper was in the form of chalcopyrite and chalcocite, with very little covellite present.

Determination of Fluidizing Velocity

Since it was very important to accurately determine the air velocity necessary to fluidize the bed, it was decided that visible observation would be the most convincing evidence. This evidence was obtained with a Pyrex microreactor, which consisted of a piece of Pyrex tubing 2.375 inches long with an outside diameter of 0.500 inches and an inside diameter of 0.375 inches. These dimensions

corresponded exactly to those of the stainless steel microreactor used in the final analysis.

The glass microreactor was prepared by first cutting four circular portions of Refrasil cloth and placing two of the cloth portions inside each of two 1/2-inch Swagelok tube fittings. Both ends of the Pyrex tubing were wrapped with Teflon tape. One end of the tubing was then inserted into one of the fittings and the nut was carefully tightened until a snug fit was evident. The Teflon tape wrapping gave a good tight fit, thus preventing air leakage between the glass and the walls of the Swagelok fittings. A 1.25 gram sample of concentrate was then fed into the open end of the tubing with the aid of a small glass funnel. The other Swagelok fitting was then fitted onto the open end of the tubing. This resulted in a microreactor which exactly resembled the stainless steel microreactor with the additional benefit afforded by the glass.

The glass microreactor was used in the same manner as the stainless microreactor. The air pressure on the compressed air cylinder which fed the microreactor was adjusted to five psig and the air pressure to the Vibrolator was adjusted to 25 psig. The mass flowmeter was connected to the microreactor bayonet and the Vibrolator was attached to the exhaust line. The air flow through the microreactor was then adjusted until the bed was observed to be in an

intensely fluidized condition. A flow rate of 830 cubic centimeters per minute at 29 degrees Centigrade was found to be sufficient to maintain the bed, also at 29 degrees Centigrade, in a well fluidized state. This volumetric flow rate corresponded to a superficial velocity in the microreactor of 0.639 feet per second.

With the required superficial velocity for fluidization of the bed now determined, the equation of continuity was used to predict the necessary fluidization rates for each of the experimental runs. Figure 8 in the Appendix gives the required fluidization rates as a function of temperature. Assurance that the bed remained in a fluidized state throughout each run was evidenced by a "loose" bed condition when the microreactor was opened at the completion of a run. Initial investigation revealed that an improper fluidizing velocity resulted in a "fixed" bed condition. That is, the concentrate particles became agglomerated in a solid mass and consequently had to be chiseled from the microreactor.

Microreactor Procedure

The first step in making an experimental run was to adjust the fluidizing air flow to the sand bed. The desired reaction temperature in the sand bed was then obtained by adjusting the Variacs on the furnace. The

fluidizing air flow to the sand bed usually had to be decreased slightly after the bed had reached the desired temperature due to the increase in superficial velocity in the bed caused by the decrease in the density of air at higher temperatures. The sand bed was always allowed to reach the reaction temperature several hours before a run was started. The maximum temperature deviation between the top and bottom of the sand bed was about three degrees Centigrade. All temperatures were recorded with a Millivolt Potentiometer, Catalog number 8690, manufactured by the Leeds and Northrup Company using a chromel-alumel thermocouple. When the microreactor was installed in the bed it always occupied a position near the center of the bed. The temperature variation in the sand bed between the top and the bottom of the microreactor was measured and found to be negligible.

Using the heat of reaction data of Kelley (R-23), calculations revealed that the oxidation of covellite to cupric oxide is exothermic with an evolution of 97.1 kilocalories per mole at 700 degrees Centigrade. If all of the copper were in this form and the reaction went to completion, the maximum temperature rise of the sand bed for adiabatic operation of the microreactor would be about 0.3 degrees Centigrade if the reaction were instantaneous. Although this type of reaction is highly exothermic, there

are several reasons why the microreactor should remain in an isothermal condition. To begin with, the reactions studied in the investigation did not generally go to completion since the maximum degree of conversion of copper to the water-soluble form was found to be approximately 88 percent. Also, the rate of reaction for metal sulfides in general is not instantaneous but depends on several factors such as temperature, partial pressure of oxygen at the particle surface, surface area of the particles, and the presence of suitable catalysts (R-6). Since the reactions did not generally go to completion, the actual amount of heat given off during reaction was smaller than the calculated theoretical value plus the fact that the heat evolved from the incomplete reaction was distributed over the total time the reactor remained in the reaction zone. Then too, due to the dissipation qualities of both the fluidized sand bed and the fluidized microreactor bed, the microreactor should remain in an isothermal condition.

Before each run the microreactor was thoroughly cleaned with soap and water, washed with acetone, and dried with blasts of compressed air. New Refrasil cloths were cut and installed on the shoulders of the Swagelok fittings and the microreactor was charged with a 1.25 gram sample of concentrate. With the furnace at the desired reaction temperature, the microreactor was placed in the

sand bath and connected to the air lines as shown in Figure 3. At the completion of an experimental run, the microreactor was disconnected and removed from the sand bath and brought to room temperature with forced convection air cooling.

Leaching Procedure

The microreactor was carefully disassembled after it had cooled to room temperature and the contents were accurately weighed on a Mettler Analytical Balance made by the Mettler Instrument Company, Hightstown, New Jersey. The sample was then transferred to a 600 milliliter beaker containing 100 milliliters of water at 100 degrees Centigrade. Hot water was used since the solubility of copper sulfate greatly increases with temperature as shown below in Table 3 (R-11).

Table 3. Solubility of Copper Sulfate in Water

<u>Temperature, °C</u>	<u>Solubility*</u>
0	14.3
10	17.4
20	20.7
30	25
40	28.5
50	33.3
60	40
70	--
80	55
90	--
100	75.4

* Grams of copper sulfate per 100 grams of water at the temperature given.

The solution was stirred thoroughly for five minutes and vacuum filtered through Whatman Number 42 filter paper, followed by generous washings with distilled water. All of the copper sulfate was said to be extracted when no blue color resulted in the wash water on the addition of ammonium hydroxide (R-7). The beaker containing the copper sulfate solution was then placed on a hot plate and brought to dryness. The concentrate residue remaining on the filter paper was saved and allowed to dry. Both the copper sulfate residue, containing the water-soluble copper, and the concentrate residue, containing the remaining total copper, were analyzed in order to accurately determine the percentage conversion. This same procedure was used to determine the amount of water-soluble copper initially present in the concentrate. Three samples were analyzed and no initial water-soluble copper was found in any of the tests. The analytical procedure used for the copper determinations is presented in the Appendix.

EXPERIMENTAL RESULTS

The experimental results obtained in this investigation are tabulated in Table 4. The amount of air used as a fluidizing medium in this test work was recorded as a multiple of the air theoretically required to convert all of the copper to copper sulfate, all of the iron to ferric oxide, and all excess sulfur to sulfur dioxide. The theoretical air required for a 1.25 gram sample of concentrate was calculated and found to be 0.115 gram-moles. Since the required air rate for fluidization was fixed for each of the runs, the amount of air used was also directly related to the time of reaction. This time of reaction will be referred to as the retention time. The quantity of air used for each of the runs is tabulated in the Excess Air column.

The sulfur dioxide and oxygen percentages for some of the high temperature runs are presented in Table 5. The initial gas analysis was taken approximately four minutes after the microreactor was plunged into the fluidized sand bath. Approximately one minute before a run was terminated, the final gas analysis was taken. Vacancies in the gas analysis data on some of the high temperature runs was due to the development of leaks in the gas analyzer during the course of a run.

For Runs 5-2, 6-1, 6-6, and 7-1 a commercial analysis was performed by Hawley and Hawley Assayers and Chemists, Incorporated, Tucson, Arizona in order to determine the amount of copper and iron which had been rendered water-soluble.

Figure 5 shows the effect of roasting temperature on the solubilization of copper at a retention time of approximately two hours under a fluidizing air flow. The runs which correspond to this amount are Runs 2-1 through 4-1, inclusive, plus Runs 5-1, 5-2, 6-1, 6-6, and 7-1.

The effect of roasting temperature on the solubilization of copper at a retention time of approximately one-half hour in the high temperature regions under a fluidizing air flow is shown in Figure 6. Included in this plot are Runs 2-1 through 5-5, inclusive, and Runs 6-2 through 6-5, inclusive.

Table 4. Experimental Results

Run	Temp., °C	Excess Air	$\%H_2O$ -Soluble Copper	$\%H_2O$ -Soluble Iron
2-1	200	22.2x	2.0	--
2-2	270	13.5x	15.5	--
3-1	300	18.3x	25.0	--
4-1	400	15.6x	51.7	--
4-2	458	6.7x	70.5	--
5-1	500	13.6x	84.5	--
5-2	500	13.6x	76.5	8.2
5-3	522	2.0x	87.0	--
5-4	555	2.0x	85.0	--
5-5	580	2.0x	62.5	--
6-1	600	12.1x	20.7	0.73
6-2	613	2.0x	54.6	--
6-3	628	2.0x	27.0	--
6-4	641	2.0x	11.2	--
6-5	648	2.0x	10.3	--
6-6	650	11.4x	3.2	0.0
7-1	700	10.8x	2.0	0.0
R*	522	2.0x	1.0	--
R*	555	2.0x	6.4	--
D**	589	9.1x	15.2	--
D**	622	8.7x	0.9	--

* Recycle run

** Dilution run

Table 5. Gas Analysis on Some of the High Temperature Runs

Run	Temp., °C	<u>% SO₂</u>		<u>% O₂</u>	
		Initial	Final	Initial	Final
5-3	522	3.2	2.4	9.3	11.7
6-2	613	3.0	0.4	12.9	16.5
6-3	628	9.6	1.6	5.0	18.3
6-5	648	12.0	2.0	3.2	15.2
6-6	650	11.4	3.4	3.8	10.2
7-1	700	11.8	7.4	---	---

FIGURE 5. Effect of Roasting Temperature on the Solubilization of Copper at a Retention Time of Approximately Two Hours Under a Fluidizing Air Flow

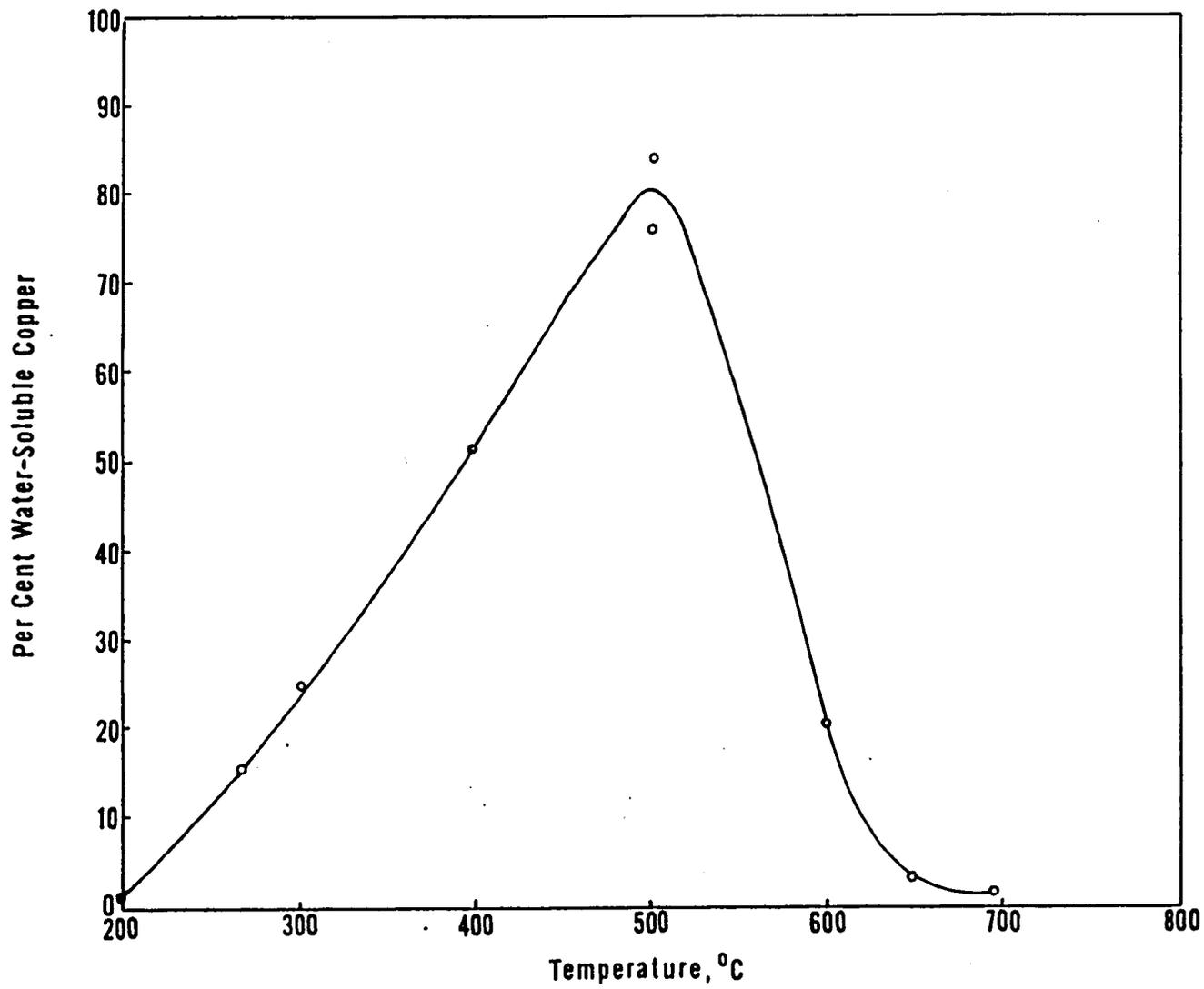
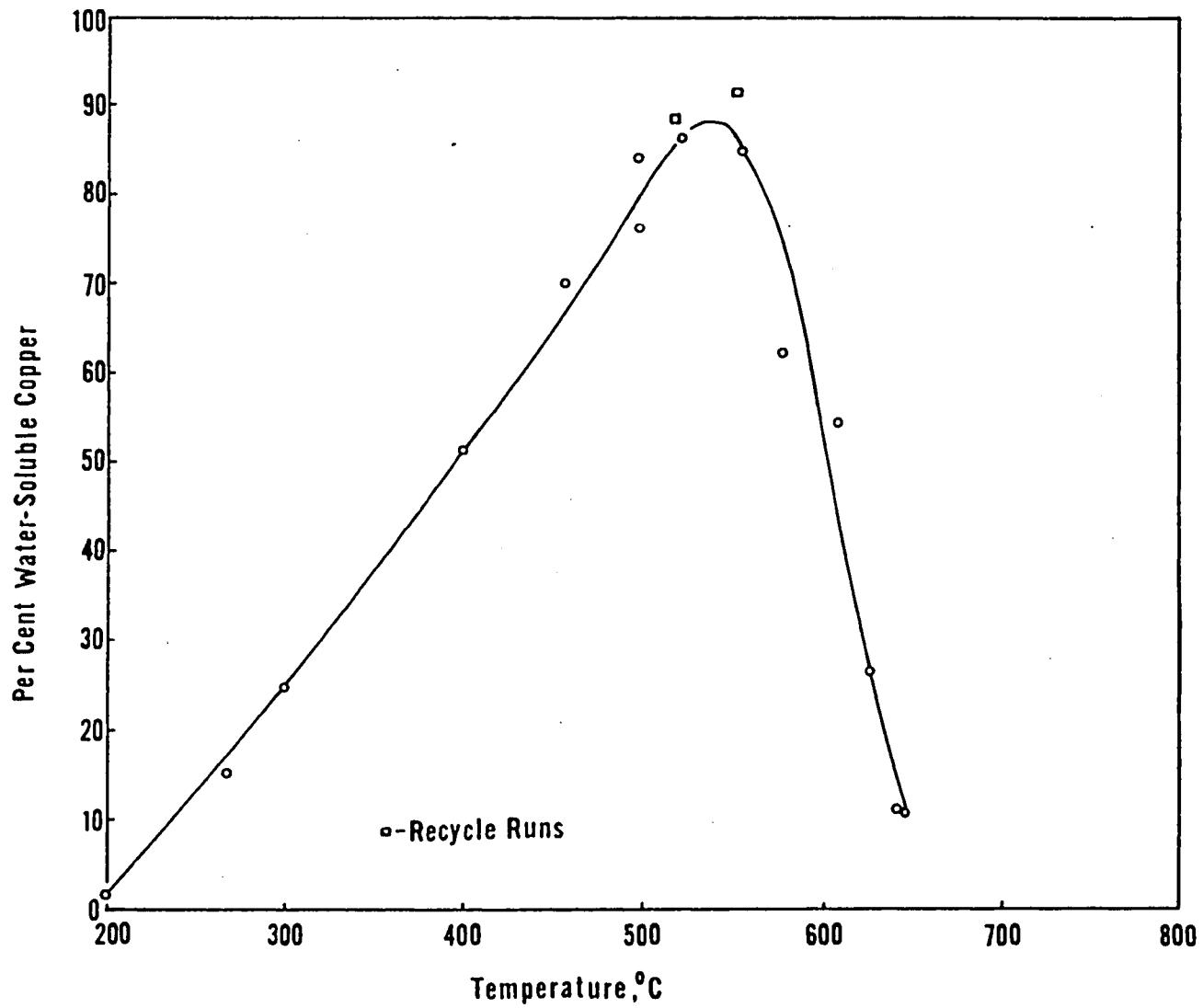


FIGURE 6. Effect of Roasting Temperature on the Solubilization of Copper at a Retention Time of Approximately One-Half Hour in the High Temperature Regions Under a Fluidizing Air Flow



DISCUSSION OF RESULTS

The effect of temperature on the solubilization of copper at a retention time of approximately two hours under a fluidizing air flow can be seen in Figure 5. The total quantity of air used in these runs, recorded as "excess air," corresponded to more than ten times the theoretical air. The term "excess air" is perhaps a misnomer, but, due to the lack of a better descriptive term, this phrase was used to describe the total amount of air passing through the microreactor during a run. Also, since previous investigators used this term to report their results, "excess air" was reported in this work so that the experimental results could be compared on a common basis. Confusion should not arise if it is recalled that the ratio of the volume of concentrate to the air feed rate was maintained at a constant value for all runs, therefore, the only way to change the total amount of air for any run was to vary the time of reaction. Good results were obtained up to and including the experiments at 500 degrees Centigrade. However, for the higher temperature runs the conversion to water-soluble copper decreased rapidly with increasing temperature. By decreasing the retention time to approximately one-half hour

improved conversion to the desirable sulfate was obtained in the higher temperature regions. This decrease in retention time corresponded to a decrease in the total amount of air to approximately two times the theoretical amount. The results of this effort can best be seen by reference to Figure 6, where a conversion of approximately 88 percent was obtained at 540 degrees Centigrade. These results are in good agreement with the work reported by Stephens (R-21). At two times the theoretical air flow, he reported a 94 percent conversion to water-soluble copper for the roasting of copper ore at 600 degrees Centigrade. However, an exact comparison of results is difficult since the chemical composition of the ore used in his work was not specified.

The formation of water-soluble copper was found to be more favorable at the lower retention time in the high temperature regions (500 degrees Centigrade and above). At the higher retention time some of the copper sulfate that was formed probably decomposed due to the high temperature exposure over the two hour time period. The decomposition temperature of copper sulfate in a mixture is not well defined and has been reported by Kellogg (R-13) to be dependent on the stoichiometry of the system and the total pressure.

In all of the runs at 500 degrees Centigrade and above, the concentrate bed was in a semi-fluid condition

when the microreactor was opened, e. g., the bottom portion of the bed was somewhat agglomerated while the top portion of the bed was in a relatively loose condition. In all of the results obtained, the loose portion of the bed was used for the analysis. Even at a relatively high superficial velocity of 1.57 feet per second, Whitehead and Urie (R-25) also experienced agglomeration tendencies. An attempt to decrease the agglomeration tendency of the bed was tried by making two dilution runs at 589 and 622 degrees Centigrade. For these two runs the concentrate was diluted with sand which had been screened through a 270 mesh sieve. The total weight of the two mixtures was maintained at 1.25 grams each with a distribution of one part of concentrate to 5 parts of sand. The bed condition at the completion of these two runs, although relatively loose throughout, still contained small lumps of concentrate material. Even though these runs did not completely eliminate the agglomeration tendency of the bed, they did seem to substantiate the tendency of low conversions at long retention times as shown in Table 4.

To investigate the possibility of a multi-pass or sequential-type oxidation procedure, two recycle runs were performed at 522 and 555 degrees Centigrade. The products from Runs 5-3 and 5-4, which were carried out at 522 and 555 degrees Centigrade, respectively, were leached to remove

the water-soluble copper sulfate and the respective residues were used in the microreactor for the recycle runs. The additional conversion to water-soluble copper obtained in these runs is shown in Figure 6. The recycle effort resulted in an additional six percent conversion of the total copper to the water-soluble form at 555 degrees Centigrade. This type of recycle operation might be desirable, especially at slightly higher temperatures (600 degrees Centigrade or more) where the soluble iron decreases. Another advantage at the higher temperatures is the increased evolution of sulfur dioxide as shown in Table 5. This gas analysis was made in order to verify the availability of sulfur dioxide. Since copper oxide may be converted to copper sulfate in the presence of sulfur dioxide and air, this gas could be added to the incoming fluidizing air for additional conversion possibilities.

CONCLUSIONS AND RECOMMENDATIONS

The results of this work indicate that a microfluidized bed system can be used successfully to obtain data for high temperature reactions. Also, since the results obtained in this investigation were comparable to those obtained by Stephens (R-21), the data obtained with the microreactor appear to be directly applicable to pilot size equipment. Eighty-eight percent conversion of the copper concentrates to water-soluble copper was obtained at 540 degrees Centigrade at a retention time of one-half hour which corresponded to two times the theoretical air. These results are in good agreement with previously published work. A retention time of two hours, corresponding to approximately ten times the theoretical air, was found to be detrimental to the formation of water-soluble copper at temperatures above 500 degrees Centigrade.

On the basis of two runs the possibility of a recycle or sequential type operation seems promising with an increase in conversion from 85 to 91 percent at 555 degrees Centigrade. A recycling procedure might prove to be commercially advantageous since operation could be carried out at a temperature (perhaps 600 degrees Centigrade or more)

which favored only the solubilization of copper with the iron converted to the insoluble form. Then too, at these high temperatures the concentrate would surrender most of its sulfur in the form of sulfur dioxide which could, in turn, be added to the incoming fluidizing air for increased conversion possibilities.

An extension of the work reported here could include the effect of sulfur dioxide additions to the incoming air feed on the conversion to water-soluble copper. Also, additional data in the higher temperature areas might further substantiate the possibility of a recycle operation. Along these same lines, a study of the effect of composition of the concentrates on the rates of reaction would be helpful in extending the knowledge of sulfating reactions. An investigation of this type might be performed with a differential thermal analyzer. In terms of reducing the agglomerating tendency of the concentrate bed, it seems possible that the organic materials and oils picked up by the concentrate in the flotation step could have some effect on the fluidized bed condition, especially at high temperatures. Leaching of these oils from the concentrate prior to the fluidized bed sulfating roast should prove or disprove this possibility. Since the data reported here was collected at approximately one atmosphere pressure, a study of the effect of pressures other than atmospheric is in order.

Another interesting possibility for further work in this area would be a study of the effect of particle size on the conversion to water-soluble copper. Smaller particle sizes might be more susceptible to reaction especially if diffusional effects are important.

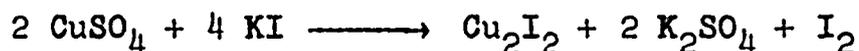
APPENDIX

Nomenclature

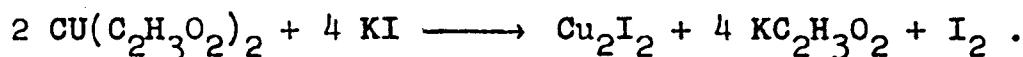
A	=	Cross-sectional area, ft ²
M	=	Molecular weight of gas, lb/lb-mole
n	=	number of moles of gas, lb-moles
p	=	Pressure, atm
R	=	Molar gas constant, ft ³ -atm/lb-mole °R
T	=	Temperature, °F
V	=	Average velocity, ft/sec
v	=	Molar volume of gas, ft ³
w	=	Weight of gas, lb
ΔF°	=	Standard free-energy change for a chemical reaction, Kcal
ρ	=	Density, lb/ft ³

Analytical Procedure

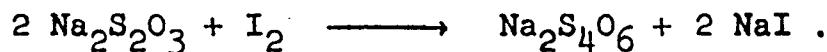
The Short Iodide Method (R-7) was used to determine the percentage of copper which had been converted to the water-soluble sulfate. This procedure depends on the fact that cupric salts, when treated with potassium iodide, liberate iodine, the cuprous iodide formed being insoluble in dilute acetic acid and soluble in excess of potassium iodide. The chemical reactions to be considered are:



or



The liberated iodine is titrated with standard thiosulfate solution according to the following reaction:



The standard thiosulfate solution is standardized with pure metallic copper. This method gives accuracy on the order of plus or minus 0.2 percent.

Gas Analysis Procedure

For the high temperature runs (over 500 degrees Centigrade) the effluent gas from the microreactor was directed into the Burrell Gas Analyzer. A 100 milliliter sample of the gas was collected approximately four minutes after the microreactor was plunged into the sand bath. The sulfur dioxide was absorbed first with standard iodine solution (R-8). The oxygen content of the gas was then determined by absorption in a pyrogallol solution (R-8). Another sample of the gas was collected and analyzed just before the completion of a run. The operating procedure for the Burrell Gas Analyzer is vividly described by Furman (R-9).

FIGURE 7. Variation of Air Density with
Temperature at 1 Atmosphere
Pressure

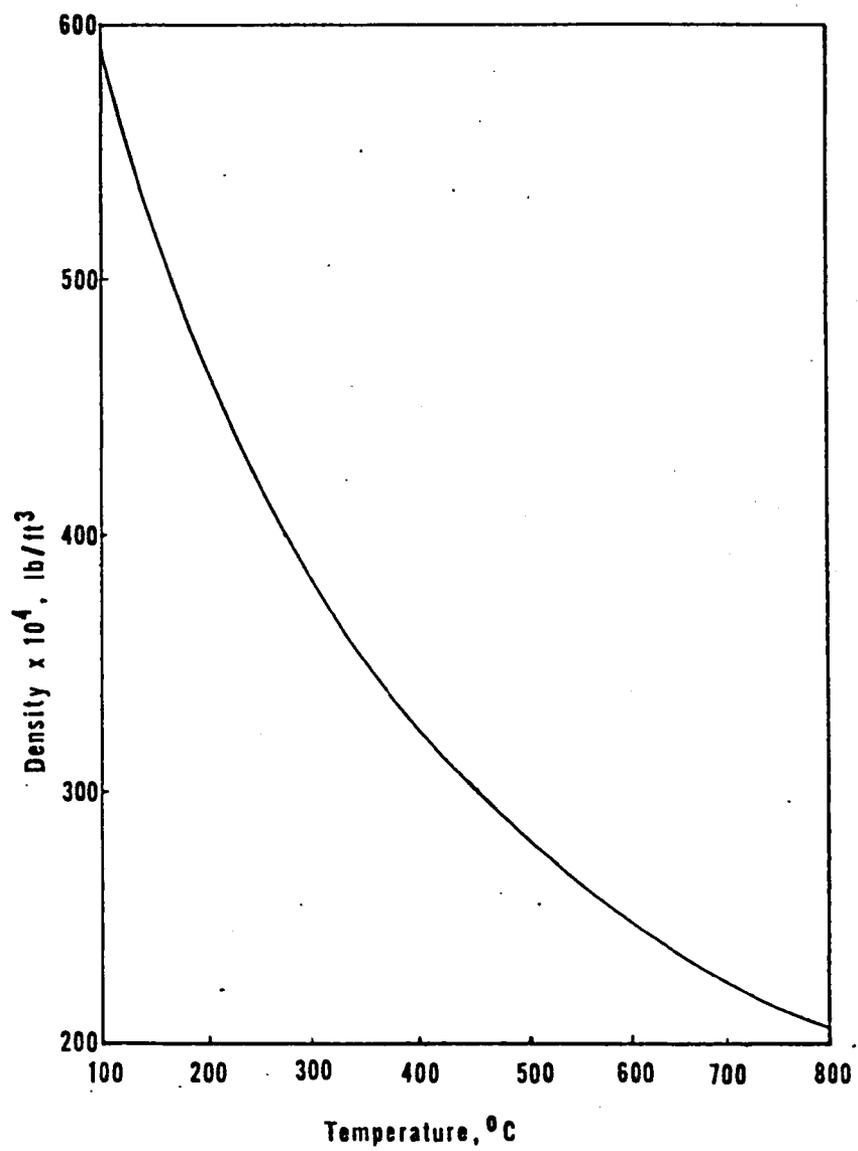
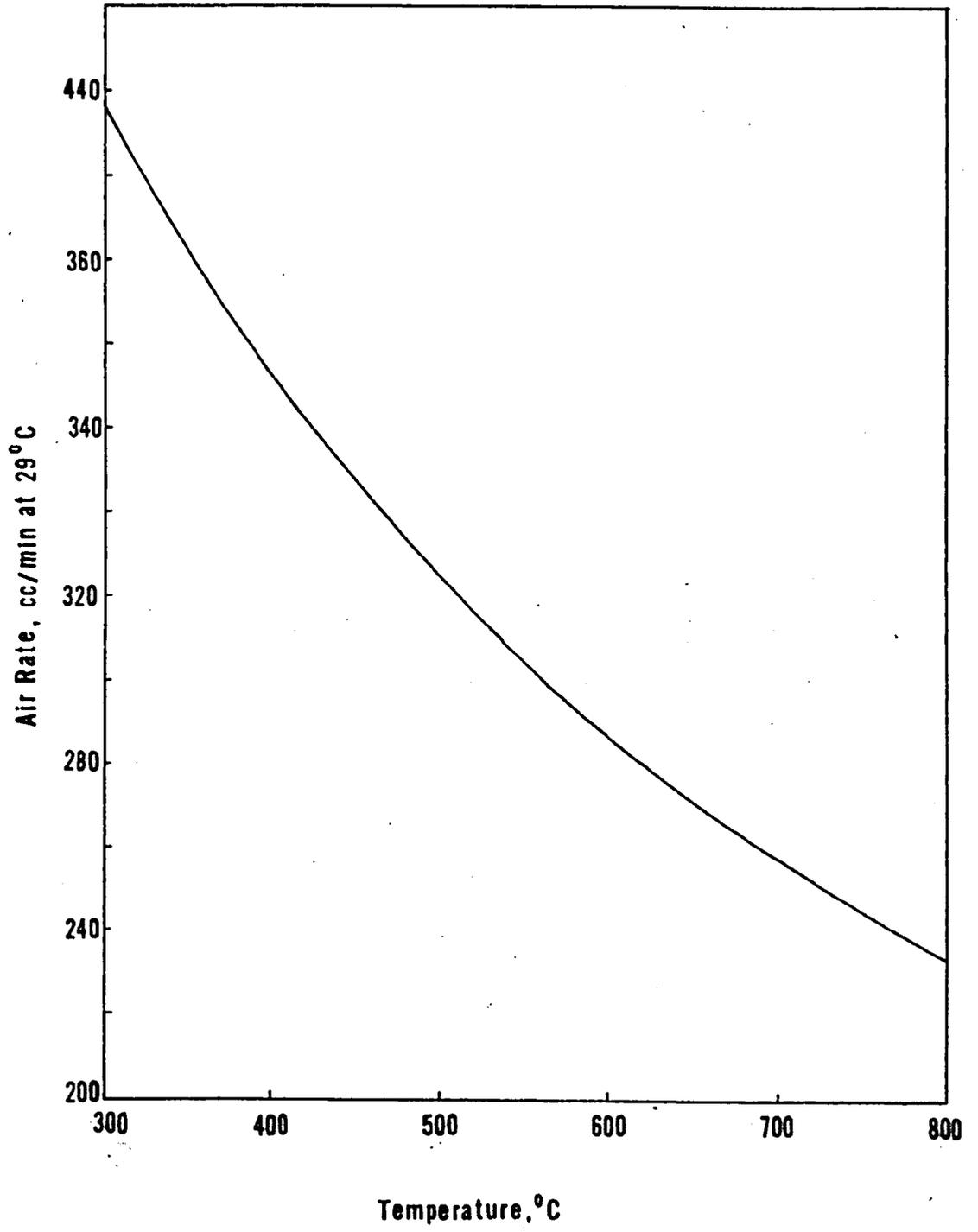


FIGURE 8. Variation of the Required Air
Fluidization Rate with
Temperature



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