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A study of the deleading of zinc sulfide concentrates

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A STUDY OF THE DELEADING OF ZINC SULFIDE CONCENTRATES

BY

LARRY LEROY GIDLEY

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE, METALLURGICAL ENGINEERING

Rolla, Missouri

1956

Approved by - S. M. Morris

Professor of Metallurgical Engineering

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Dr. T. M. Morris, Professor of Metallurgical Engineering, and Dr. A. W. Schlechten, Chairman of the Metallurgical Engineering Department, served as advisors, and never failed to give freely of their time and advice throughout this research project.

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INTRODUCTION

The information submitted in this thesis is in partial fulfillment of the work required for the Degree of Master of Science, Metallurgical Engineering.

The problem was suggested and a fellowship was provided by the St. Joseph Lead Company, Zinc Smelting Division.

OBJECT

The object of this research was to study the basic principles and optimum conditions for the deleading of commercial zinc sulfide concentrates by sublimation of the lead in the form of a sulfide. Present commercial practice conducts this sublimation in hearth roasters. This research considered only the variables affecting sublimation of the lead sulfide, not the types of applicable equipment, or other possible processes. However, the laboratory conditions were at least partially similar to those that could be obtained in commercial practice.

REQUIREMENTS

Basic requirements for commercial application of the sublimation process are:

1.) Sufficient temperature
2.) Carrier gas and particle contact
3.) Removal of the lead sulfide vapors by the carrier gas

TEMPERATURE

Figure 1 (1) is a plot of vapor pressure versus temperature for the sulfides of lead and zinc, and the oxide of lead.

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(1) Kelly, K. K., Contributions to the Data on Theoretical Metallurgy, Bureau of Mines Bulletin 383, pp. 60-61, 1939.

(1) Hsiao, C. M., and Schlechten, A. W., Apparent Vapour Pressures of Several Metal Sulfides, J. Metals, Vol. 4, p. 65, 1952.

These curves show the substantial difference in vapor pressures of lead and zinc sulfides which permits separation of the two compounds at elevated temperatures by sublimation of the lead sulfide compound. Comparison between the sulfide and oxide curves of lead illustrates the need to retain lead as a sulfide since the sulfide has the higher vapor pressure.

The possibility of conversion of the oxide to the sulfide by reaction with zinc sulfide was studied thermodynamically. For the reaction

$$ZnS + PbO \longrightarrow ZnO + PbS$$

at 900°C, free energy versus temperature curves (2) result in an approximate ΔF° value of -6.5 kcal./mole which indicate that the reaction is possible.

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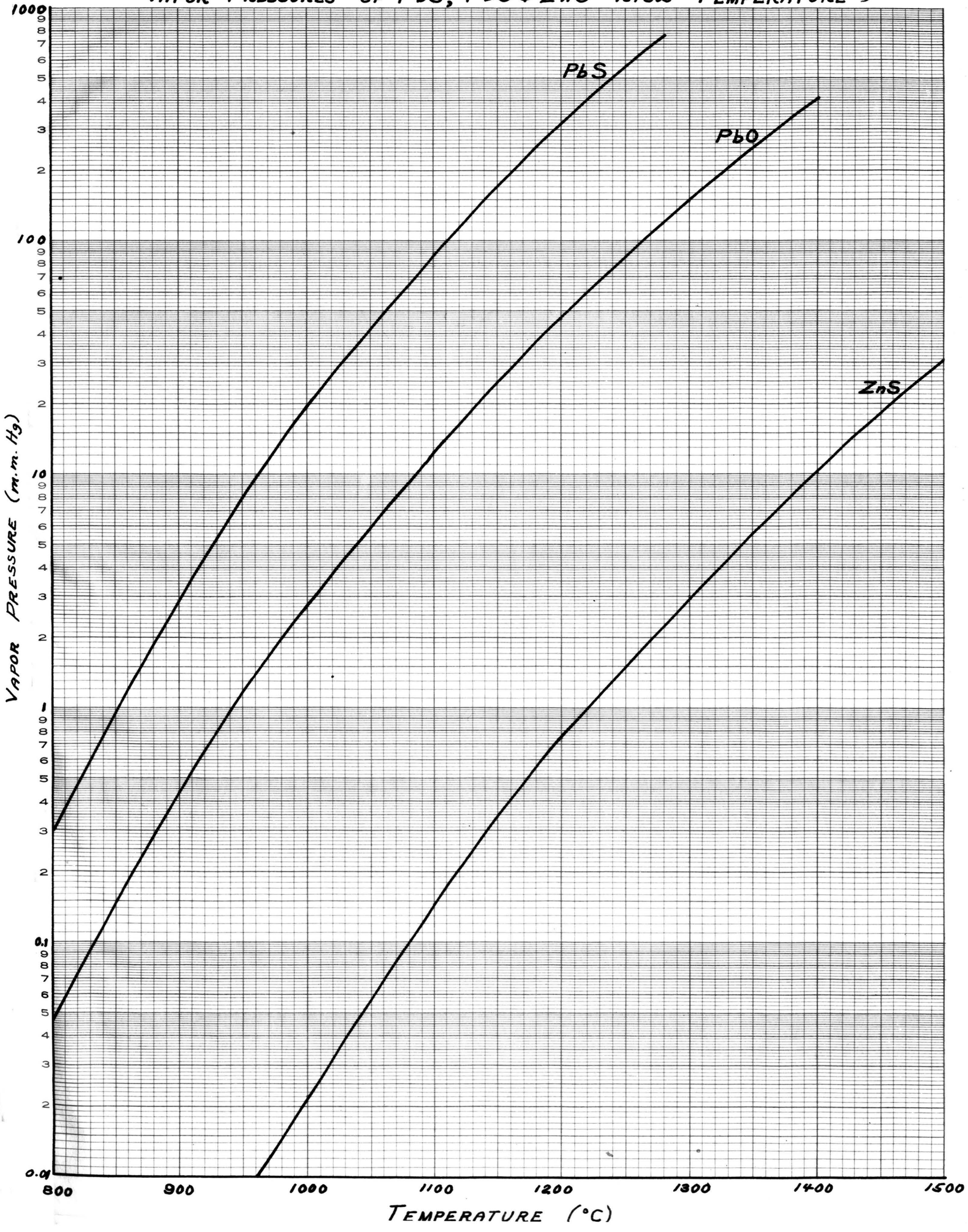
(2) Osborn, C. J., The Graphical Representation of Metallurgical Equilibria, J. of Metals, Vol. 188, p. 600, 1950.

Further examination of the graph indicates that the temperature range 800°C to 1100°C is suitable for investigation. The minimum temperature allowable for obtaining an appreciable lead sulfide vapor pressure is about 800°C. Above 1100°C the concentrate may become difficult to handle due to stickiness, and hearth roasters are not built

Figure 1

VAPOR PRESSURES OF PbS, PbO & ZnS versus TEMPERATURE 3



to operate at much higher temperatures. Temperature investigations were then limited to 800-1100°C.

CARRIER GAS AND PARTICLE CONTACT

Contact between the concentrate particles and the carrier gas permits diffusion of the lead sulfide vapor into the carrier gas. The best contact is obtained by surrounding each particle by the gas.

Retention of the lead as a sulfide requires the use of a non-oxidizing carrier gas. Nitrogen, a neutral gas, was selected for use in tests conducted for studying variables other than carrier gas composition.

REMOVAL OF THE LEAD SULFIDE VAPORS BY THE CARRIER GAS

Diffusion of the lead sulfide vapor into the carrier gas proceeds until all solid lead sulfide vaporizes, or until the equilibrium vapor pressure is reached. The rate of diffusion decreases as the vapor pressure approaches the equilibrium value, and becomes zero at equilibrium.

Possible equilibrium conditions between each separate particle and surrounding carrier gas must be eliminated or minimized. Continual replacement of the lead sulfide bearing carrier gas surrounding each particle prevents approaching equilibrium and thus maintains a maximum vaporization rate.

SELECTION OF THE EXPERIMENTAL DELEADING APPARATUS

Two different types of equipment were carefully considered. These were a typical laboratory tube furnace and a small scale fluidizer.

With regard to this deleading study, advantages of a tube furnace are: simplicity, compactness, ease of heating, good working conditions, and small quantities of nitrogen required. Disadvantages are: batch process only, poor contact between particles and carrier gas, small quantities of concentrate tested.

Advantages of a fluidizer are: best possible contact between solids and gas, excellent mixing, uniform temperature, possible batch or continuous tests, variable in size which in turn means variable quantity of concentrate that can be tested. Disadvantages are: loss of small particles due to dusting, bulky apparatus, more complicated design, minimum gas flow limited by the minimum required for fluidization, and large quantities of nitrogen required.

After carefully considering the inherent properties of the two types of equipment, the fluidizer was selected as the type best suited for the deleading tests.

DESIGN OF THE FLUIDIZING APPARATUS

The following outline served as a guide while designing the fluidizing apparatus.

1.) Fluidizer proper
2.) Cone design and accessibility
3.) Continuous operating possibilities
4.) Dust control
5.) Furnace construction
6.) Auxiliary equipment

FLUIDIZER PROPER

The usual basic construction of a laboratory fluidizer is in the form of a vertical cylinder whose diameter may vary from one inch to twelve inches. A four inch diameter is usually considered minimum for a study of fluidization due to the "wall effect". With smaller diameters, the ratio of wall area to cross sectional bed area becomes so great that representative fluidization is not obtained.

The cylinder is commonly made of metal pipe or ceramic tubing depending upon the temperature required, corrosiveness of the material handled, and accessories required beyond the basic fluidizer proper.

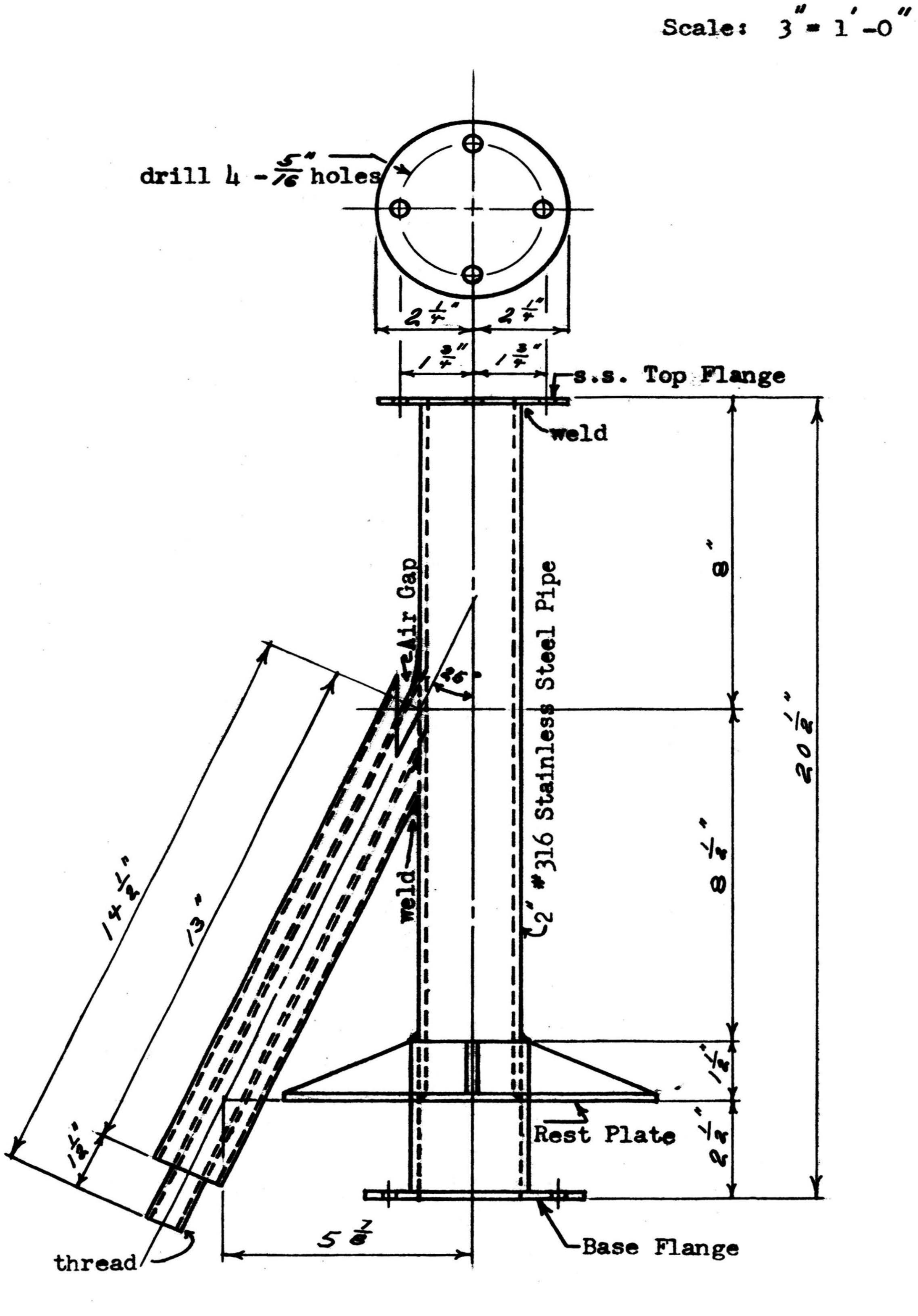
A two inch #316 stainless steel pipe was selected for the fluidizer proper. Metal was selected to permit greater ease for attaching accessories; stainless steel was selected because of the high temperatures; a two inch diameter was selected as a good size for experimental work and also to eliminate excessive nitrogen requirements. Two inches is below the minimum recommended for studying fluidization, but this research was conducted to study deleading, not fluidization.

An expected bed depth of ten inches, and a free board height for splashing of eight inches, resulted in a total fluidizer proper length of eighteen inches.

A stainless steel plate, the circular rest plate, was welded to the base of the two inch pipe. This plate served as a support for the fluidizer proper.

Figure 2 is a detailed drawing of the fluidizer proper. Figures 3 and 4 are photographs of the same. Note the presence of other addi-

Figure 2. Fluidizer Proper



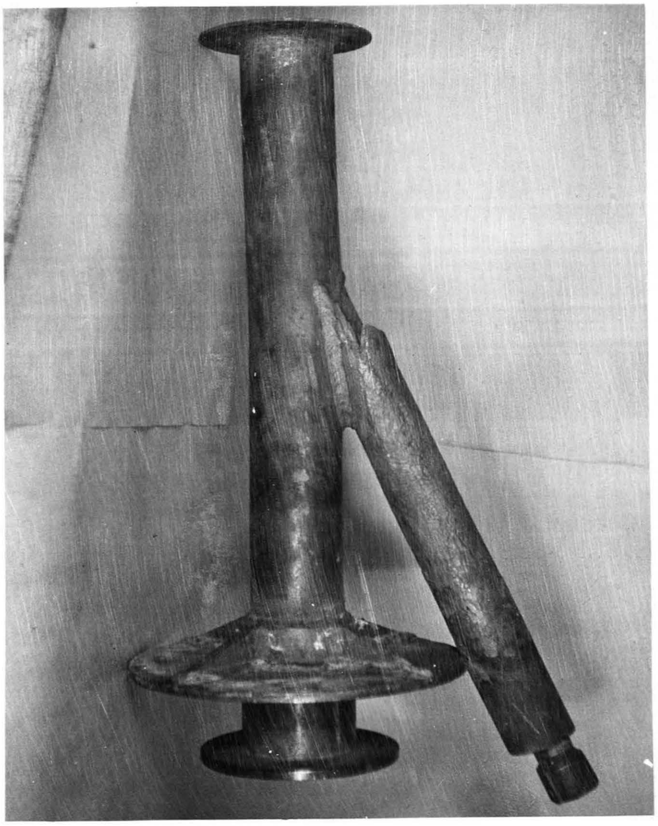


Figure 3. Fluidizer Proper

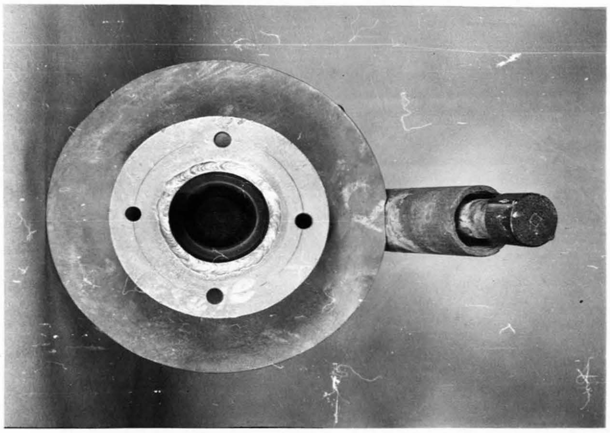


Figure 4. Bottom view Fluidizer Proper

tions to the two inch pipe. These additions will be discussed later under their proper headings.

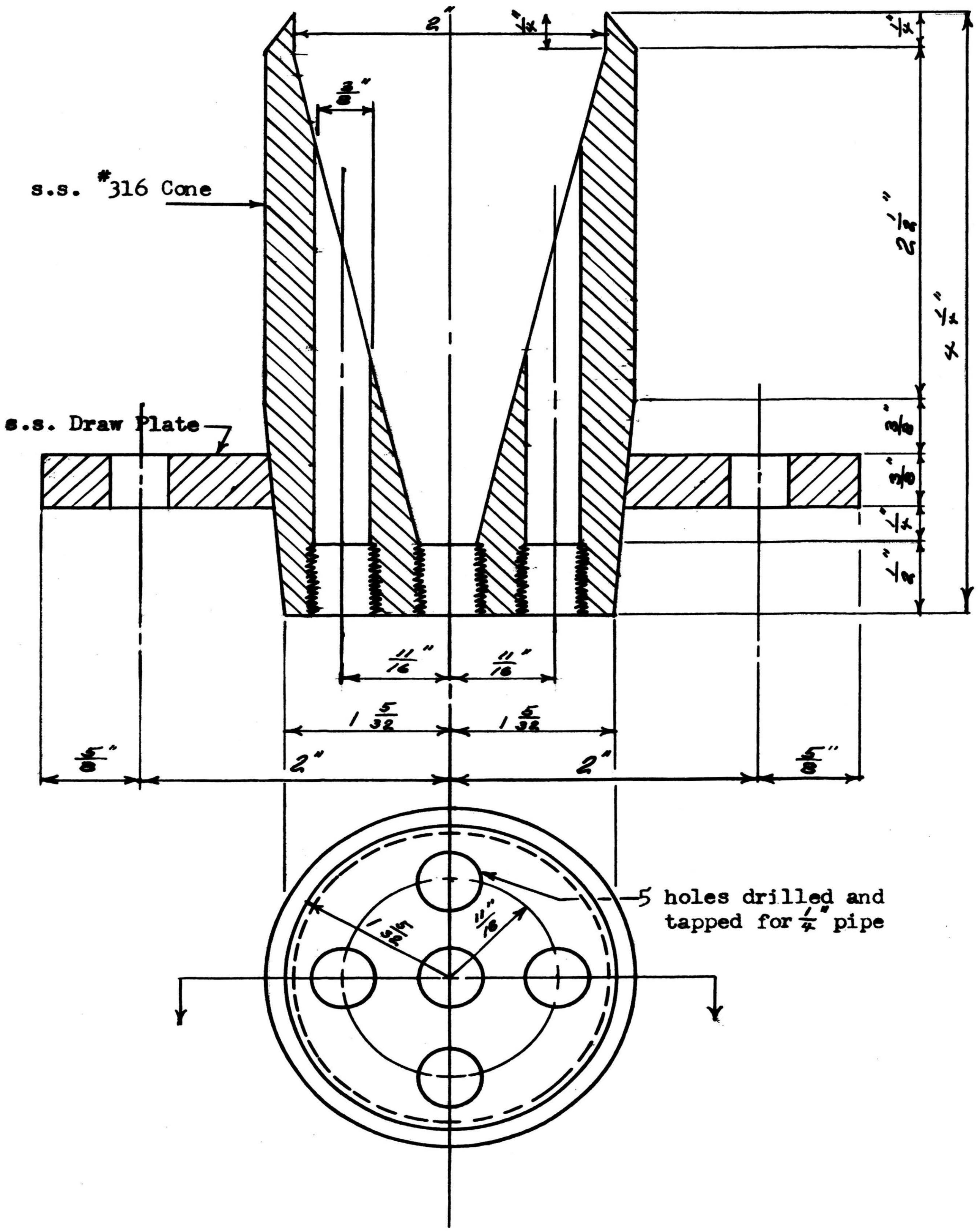
CONE DESIGN AND ACCESSIBILITY

Some method of introducing and distributing the fluidizing gas, in the base of a fluidizer, was required. A stainless steel cone shape was selected, designed, and machined from bar stock. Use of a cone eliminated the need of a grid for gas distribution, and permitted emptying the bed out through the cone at the completion of a test. Five holes were drilled and tapped for 1/4 inch pipe in the base of the cone. The center hole was used for gas introduction. The surrounding four holes were used for thermocouple wells. These wells were made from 5/16 inch stainless steel tubing brazed at one end in 1/4 inch by 1/8 inch pipe bushings. These wells were inserted into the holes and threaded into position by the bushings. Lengths of the wells were variable for the purposes of measuring temperatures at various positions.

Figure 5 is a detailed drawing of the cone. Figures 6, 7, and 8 are photographs of the top, side, and bottom views of the cone.

Accessibility of the fluidizer proper at both the top and bottom was desired to cope with any unforeseen incidents such as bed fusion. High temperatures resulting in excessive oxidation, eliminated the use of a threaded fitting for the cone, and suggested a flange fitting. This flange fitting was designed so that it extended beneath the hot furnace area and thus permitted access to the cone from outside the furnace. Cooling of the base of the cone by being outside the furnace was the only objection to such a design.

Figure 5. Cone



Scale: 1" = 1"

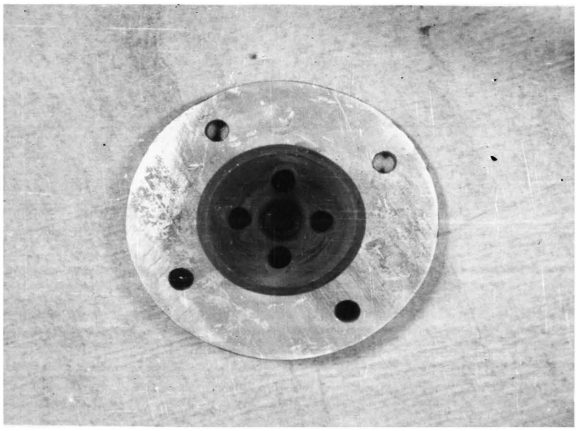


Figure 6
Top view Cone

Figure 7
Side view Cone

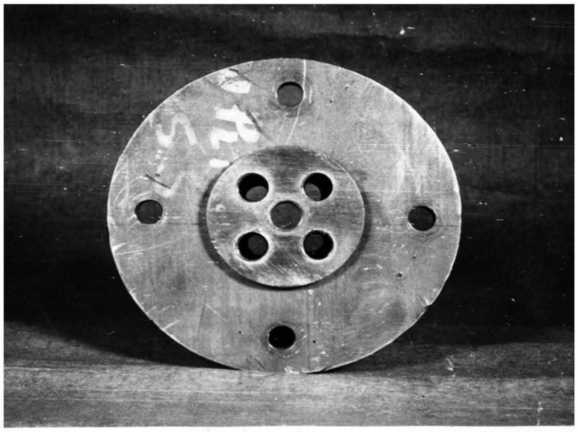


Figure 8
Bottom view Cone

Figure 9 is a detailed drawing of the base of the fluidizer proper and shows the flange arrangement. Figure 4 is a photograph of the base.

CONTINUOUS OPERATING POSSIBILITIES

Premixing of the fluidizing gas and concentrate, resulting in the gas carrying the concentrate into the fluidizer, provided a method of continual feeding. For such a small fluidizer, a very accurate, small, weight feeder was required.

A 3/4" stainless steel discharge pipe was welded to the fluidizer proper at a height of ten inches above the base and at the smallest angle possible to permit gravity overflow with minimum opposition into a discharge trap. This discharge pipe regulated the height of the bed to ten inches during continuous tests. Also this pipe was kept straight to permit easy cleaning in case of clogging. A 1 1/2 inch carbon steel pipe was welded around the overflow pipe to act as a heat shield and permit air cooling if needed. Both the discharge pipe and shield pipe extend beneath the furnace for the purpose of accessibility.

Figures 2 and 3 show side views of the discharging arrangement.

DUST CONTROL

Excessive dusting of the fine particles in the concentrate presented the greatest single deterrent to the use of a fluidizer for this deleading test. Several possibilities existed for handling the dust problem. These were:

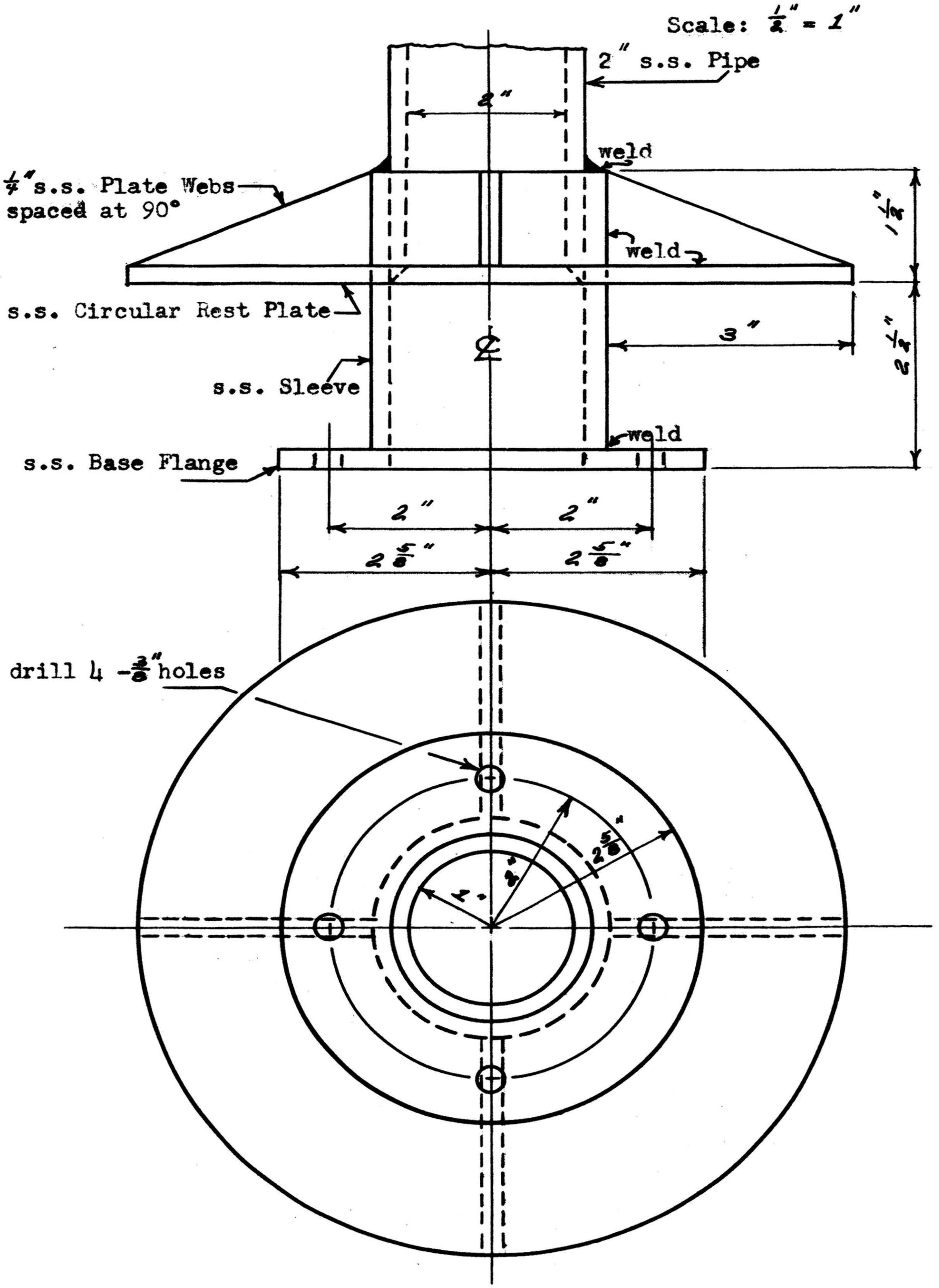
1.) Collect the dust after it leaves the fluidizer

2.) Use only sized ranges of the concentrate particles

3.) Devise some means of minimizing dusting

4.) Ignore dust losses and concentrate only on the remaining bed

Figure 9. Base of the Fluidizer Proper



Number 3 provided the most desirable but not the simplest solution. Minimizing dusting requires a decrease in gas flow below that required for fluidization. This decrease in gas flow requires an increase in cross sectional area of the fluidizer.

An enclosed funnel shape was designed and constructed from stainless steel plate. This funnel was fastened with a simple flange to a matching flange on the top of the fluidizer proper. A two inch stainless steel pipe extension, welded to the top of the funnel, permitted access from outside the furnace.

The funnel was included within the furnace for the purpose of retaining all vaporized lead sulfide as a gas until the exhaust carrier gas left the dust system.

Figure 10 is a detailed drawing of the funnel. Figure 11 is a photograph of the same.

A one inch cyclone was designed and constructed out of stainless steel pipe. This cyclone was fastened by a small flange fitting to the carrier gas discharge of the funnel. The cyclone exhaust extended out of the furnace through the furnace top and completed the dust system.

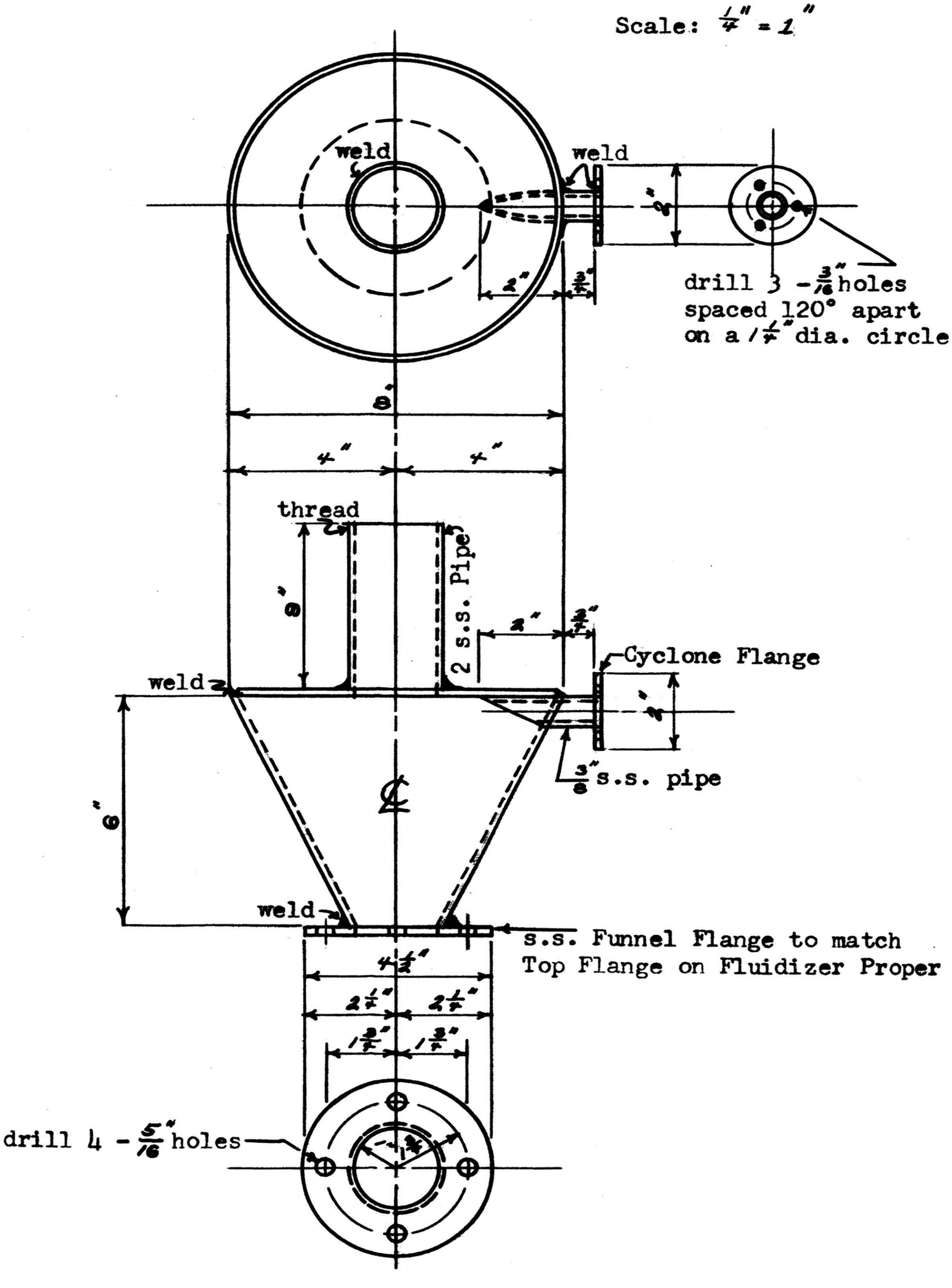
Figure 12 is a detailed drawing of the cyclone. Figure 13 is a photograph of the same.

Figure 14 is a photograph of the entire assembled fluidizer.

FURNACE CONSTRUCTION

A table supported the fluidizer proper and furnace. One interesting feature of this table was the thin water cooled table top which permitted projection of the cone-flange arrangement and the discharge pipe

Figure 10. Funnel



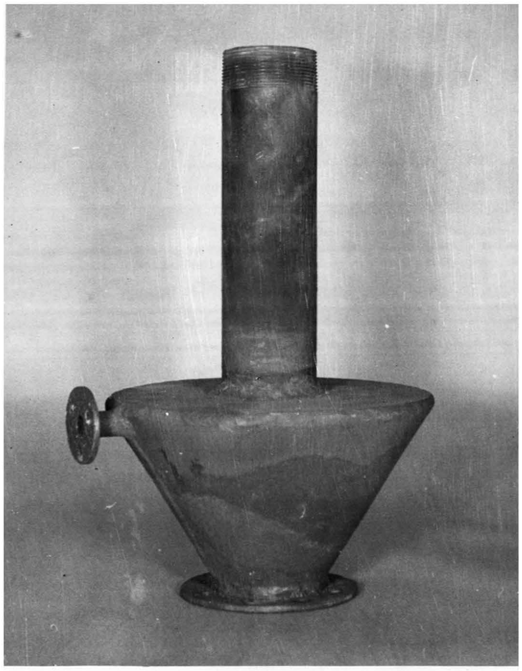
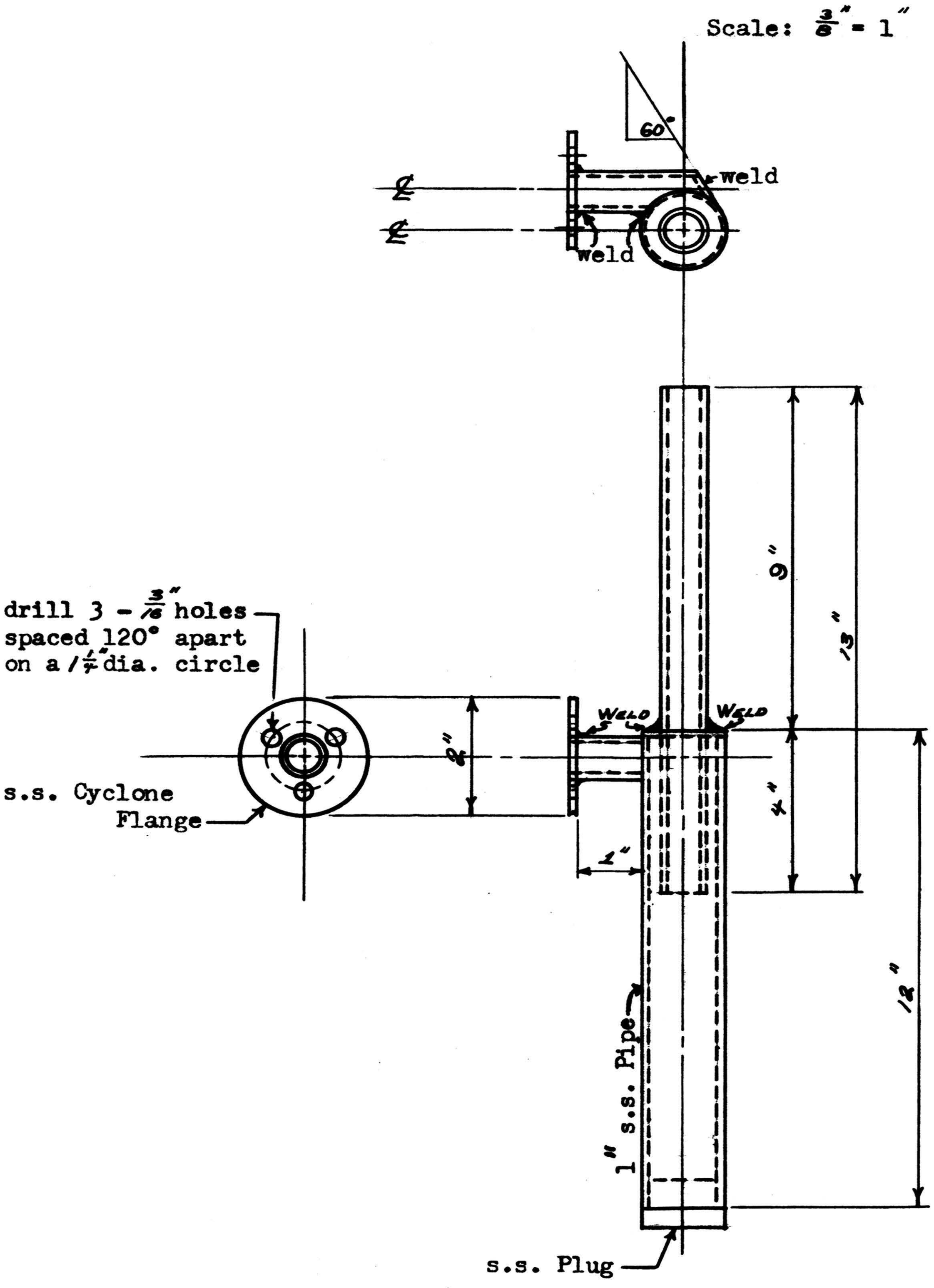


Figure 11. Funnel

Figure 13. Cyclone

Figure 12. Cyclone



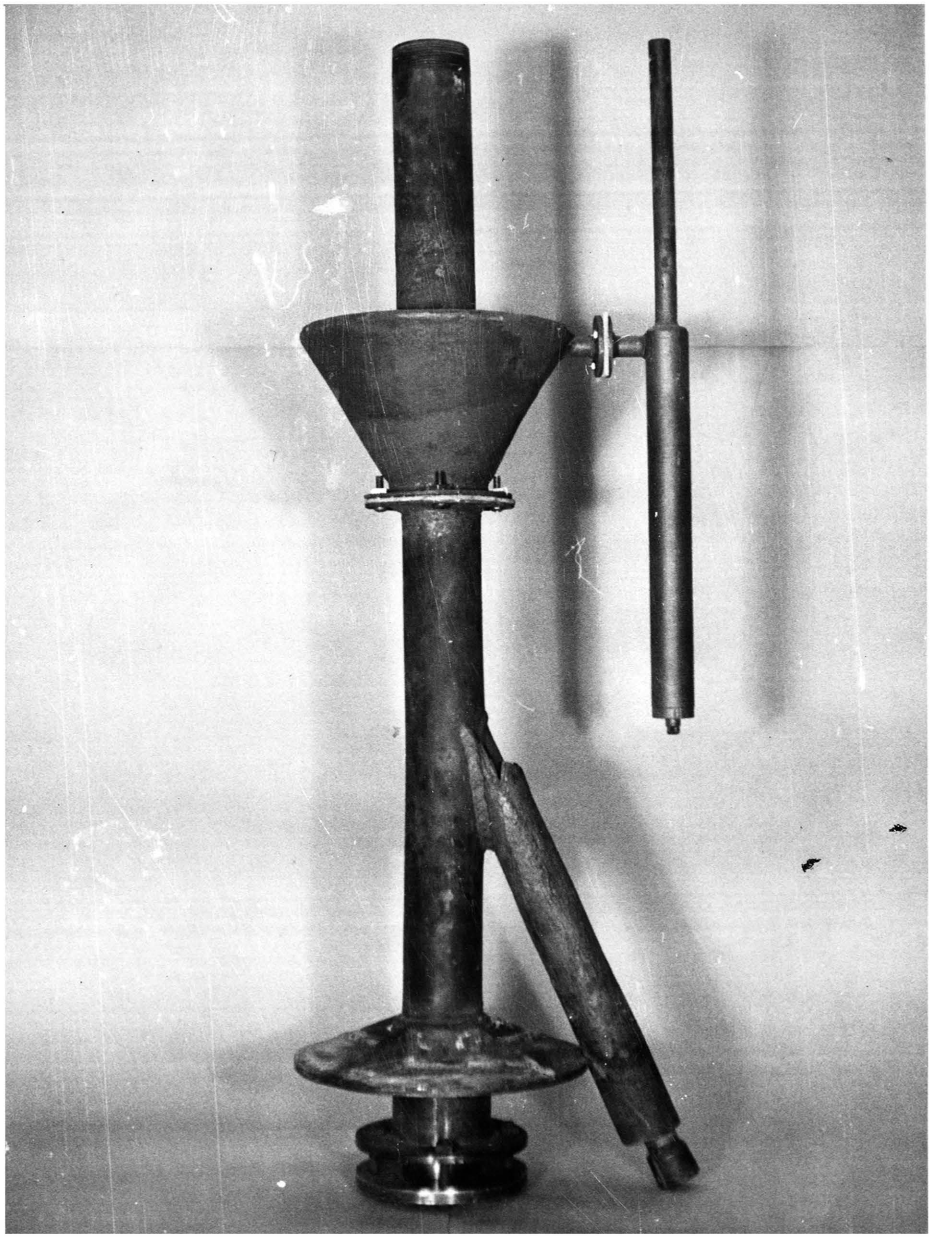


Figure 14. Assembled Fluidizer

beneath the furnace. This water jacket was constructed from 1/4 inch carbon steel plates separated by a 1/2 inch space for water. Four legs made from pipe were welded to the table top. Grog scattered on top of the water jacket inside the furnace minimized heat losses. Figure 15 is a detailed drawing of the table.

A furnace wall, constructed from 4 1/2 inch thick 2600°F insulating brick, was laid at the periphery of the table to a height of twenty six inches. A removable furnace top was constructed by bolting 2 1/2 inch thick insulating brick to a transite board. This top simply rested on the furnace wall.

The furnace was heated by six globars spaced symmetrically around and parallel to the fluidizer proper. The latter required transmission of the globars through both the water cooled table top and the furnace top for the purpose of making electrical connections. These globars were supported beneath the table top by a doughnut shaped transite board which was fastened to the table legs. The table top was electrically insulated from the globars by ceramic tubing placed over the globars as sleeves. Figure 16 is a photograph of the bottom of the table top showing globar support, and protrusion of the cone-flange arrangement and discharge pipe.

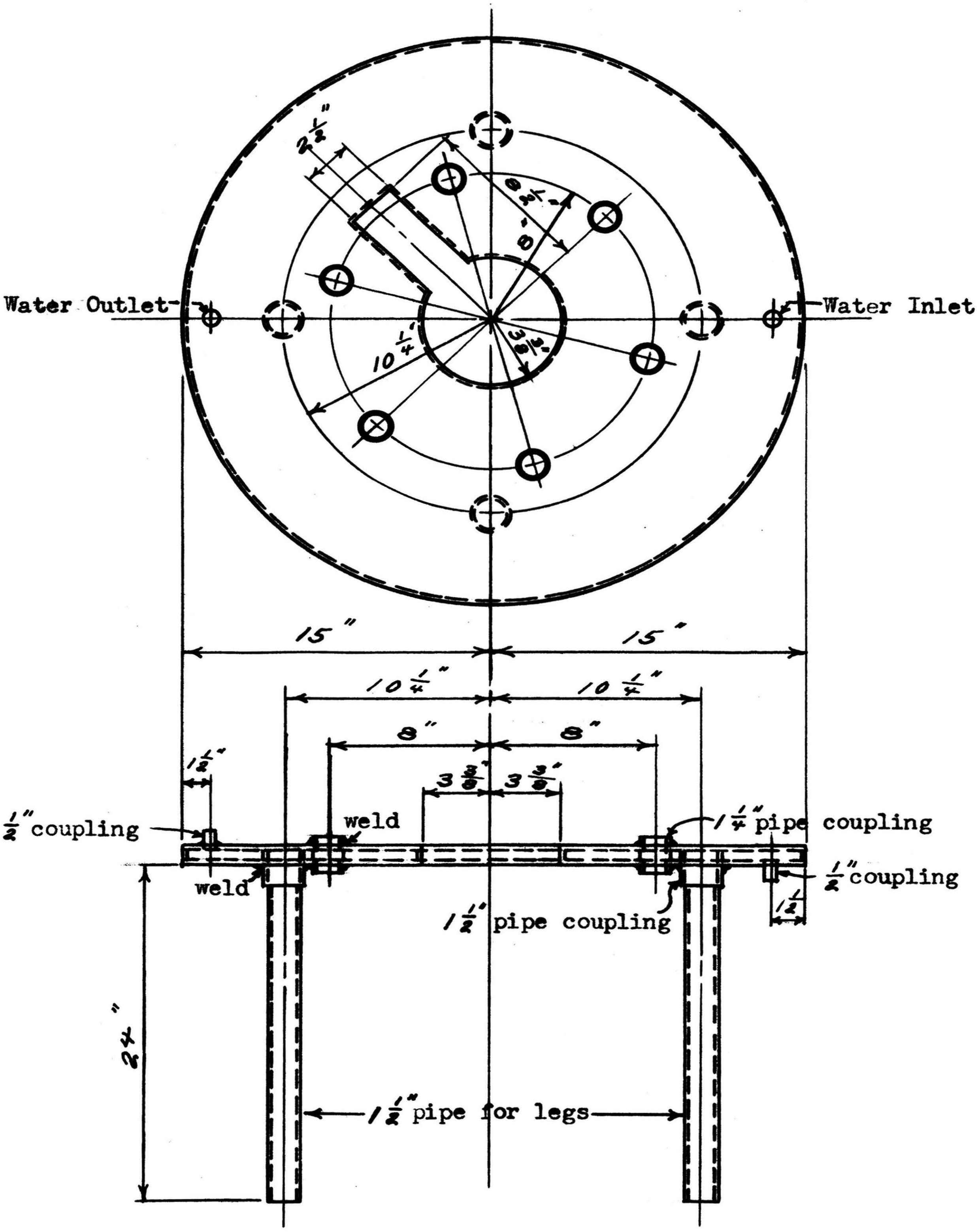
All globars were connected in parallel by aluminum straps. Lead wires were connected to these straps above and below the furnace.

An asbestos board placed over the top of the globars and connecting straps prevented accidental contact when working around the furnace. Placement of this insulating board completed the furnace construction.

Figure 17 is a photograph of the assembled furnace and surroundings.

Figure 15. Table

Scale: 1/2" = 1'-0"



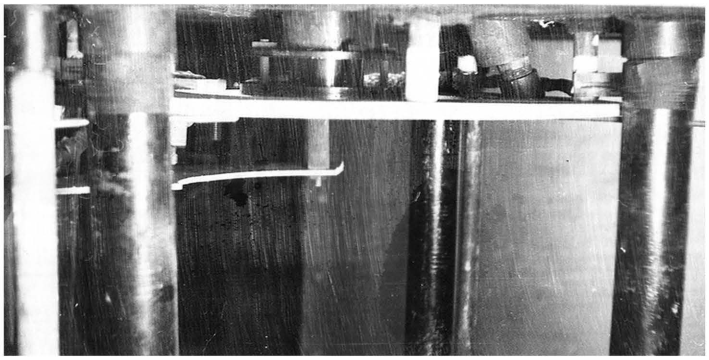


Figure 16. Bottom of Table

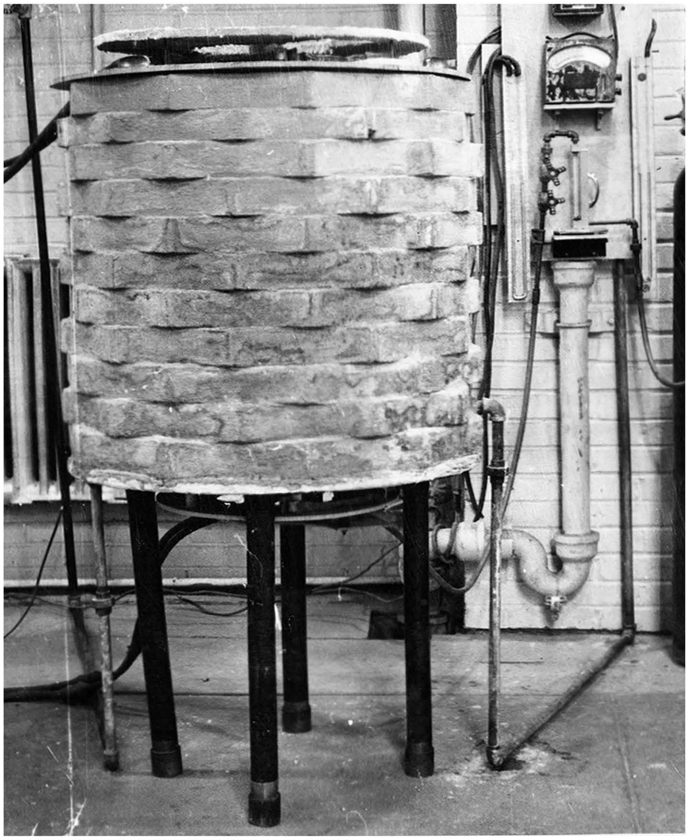


Figure 17. Assembled Furnace

Globar specifications are listed below.

26"	effective heating length
25"	furnace chamber width
3/4"	diameter
61.36"^{2}	nominal radiating surface
3"	furnace wall thickness
34"	overall length
2.288 ohms	nominal resistance

AUXILIARY EQUIPMENT

Bottled nitrogen was used as an inert fluidizing gas. Analysis of this gas was given as 99.7% nitrogen with the balance consisting of a combination of hydrogen, argon, oxygen, and hydrocarbons.

For accurate metering of the nitrogen flow, a direct reading Fischer and Porter nitrogen flow meter was installed in the nitrogen gas line.

Pressure taps, connected to manometers on a control panel, were taken from above and below the bed. These pressure taps gave the pressure drop across the bed, and the pressure above the bed.

All thermocouples were connected to a multi point switch on the control board. The multi point switch was connected to a direct reading voltmeter and a potentiometer. The voltmeter was used for indicative readings only, while the potentiometer was used for accurate temperature determinations.

Figure 18 is a photograph of the control board showing the flow meter, manometers, multi point switch, and voltmeter. To the right of the control board is a nitrogen cylinder with a two stage pressure regulator connected by a pressure hose to the flow meter.

The instrumentation was simple yet gave accurate control during the tests.

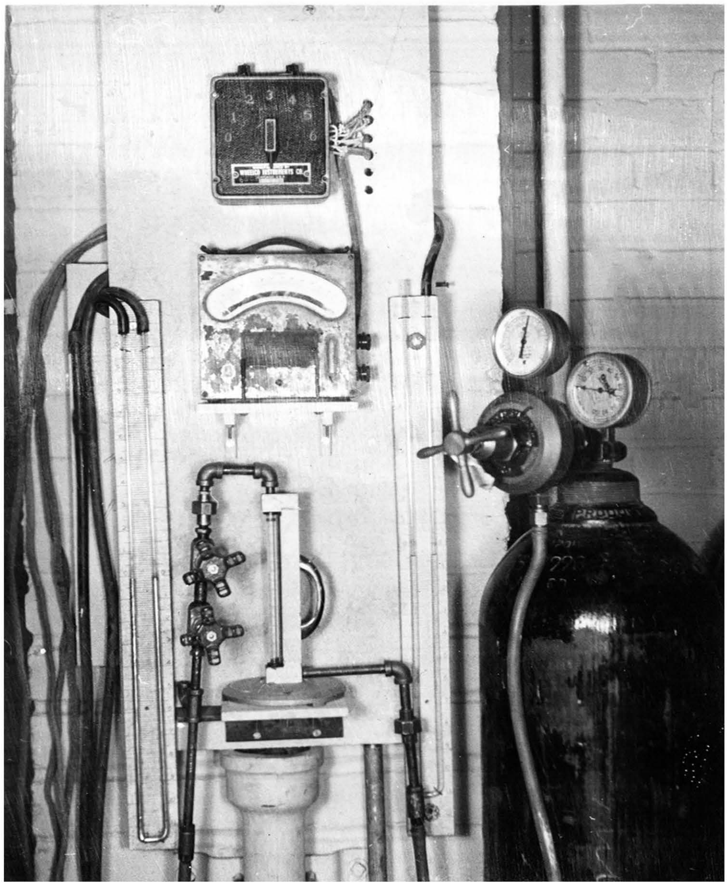


Figure 18. Control Board

PRELIMINARY TESTING OF THE APPARATUS

ASSEMBLY OF THE APPARATUS

Permanently fixed parts of the apparatus were: the brick furnace wall on the water cooled table, and the control panel. All other parts were removable.

To begin assembly of the apparatus, the fluidizer proper was inserted into the furnace where it was supported on the table by the circular rest plate. Grog was then scattered on all exposed parts of the table top to minimize heat losses.

Next the funnel was fastened, by means of a flange arrangement, with 1/4 inch carbon steel bolts to the top of the fluidizer proper. Later removal of the funnel after hot tests required cutting the bolts with a chisel. A ceramic cement was used as a seal for the flange fitting. The cyclone was fastened, by means of another flange, with 1/8 inch carbon steel screws to the exhaust of the funnel.

Attachment of the cyclone completed all internal furnace assembly, so the furnace top was placed in position. The six globars were inserted through the holes provided in the furnace top, and were extended through the holes in the table top (insulated by ceramic tubing) until they rested on a transite board as was described previously. The globars were connected in parallel with aluminum straps. Lead wires were connected to these straps both above and below the furnace. An asbestos board, serving as an electrical insulator, was placed over the top of the globars to prevent possible accidental contact while working around the furnace.

The cone was inserted from beneath the table into the bottom of the fluidizer proper, and was bolted in place by means of the flange arrangement. Next the fluidizing gas line, coming from the nitrogen cylinder through the flowmeter, was threaded into the center 1/4 inch pipe hole in the base of the cone. A pressure tap was taken from this line and connected to a manometer for measuring the pressure at the bottom of the bed. Thermocouple wells and thermocouples were inserted into the cone for the purpose of measuring temperatures in the bed at various elevations. These thermocouples were connected through a multipoint switch on the control panel to a potentiometer.

Next a stainless steel ball bearing was dropped into the reactor and fell to the interior base of the cone. This ball served as a stop valve by preventing bed material from falling into the fluidizing gas line, but permitted entrance of the fluidizing gas. Discharging of the bed past this stop valve was simply accomplished by inserting a probe through a pipe tee in the gas line, and raising the ball with this probe, enough so that the concentrate dropped past the ball out of the fluidizer proper.

A two inch pipe cap, threaded on the extension pipe above the funnel, closed the system. A thermocouple well and thermocouple were inserted through this cap into the funnel which provided a means for checking funnel temperature. Finally a pressure tap was taken from the two inch pipe cap and lead to a manometer. This tap served as a check on pressures above the bed.

COLD TESTS WITH CONCENTRATE

Initially it was decided to conduct only batch tests, so the discharge pipe which extended beneath the table was capped to prevent discharging.

Before conducting cold tests, the quantity of concentrate required for a 10 inch fluidized bed was determined. Knowing the approximate specific gravity of the concentrate, calculating the volume of a fluidized bed 10 inches in height, and assuming 40% expansion of the settled bed into a fluidized bed resulted in a calculated value of about 735 grams.

With the quantity of concentrate determined, the cold tests were performed to determine the following: nitrogen flow required for good fluidization, efficiency of the dust collecting system, and to check the apparatus in general.

A nitrogen flow of 0.5 cfm was calculated from commercial practice (22.5 cfm/sq. ft.) as the flow required for good fluidization. To check this, 735 grams of a concentrate were dropped into the reactor, forming a settled bed above the ball stop valve. The two inch cap was threaded in position, and the top pressure tap was connected to a water manometer. The fluidizing gas was turned on slightly, and the flow was gradually increased until the differential bed pressure reached a constant value signifying fluidization. The flow required was 0.5 cfm which checked with the calculated value. This flow was then selected for use with all future tests, except where gas flows above 0.5 cfm would be tested as a variable.

In commercial practice, difficulties, especially dusting, are encountered with Volcan concentrate. So it was selected for the dust collecting efficiency test. A bed, consisting of 735 grams of this concentrate, was fluidized for two hours. At the end of this time, only 5% of the original concentrate was lost as dust, 95% was still in the system. Of this 95%, 5% had collected in the cyclone as a very fine dust. So 90% was actually retained in the fluidizer proper-funnel area as a fluidized concentrate. This quantity was considered quite acceptable. The top pressure above the bed never exceeded 0.2 inches of H_2O, a negligible amount, so the top pressure tap was eliminated.

In general, the apparatus as observed during the above cold tests, functioned very well. Only one other check of significance was the possibility of fluidizing gas leaks around the cone-fluidizer proper joint. Application of a soap solution during a test showed that small leaks were present, but were significantly small so as to be ignored.

FURNACE HEATING AND CONTROL

The maximum allowable current for the globars at 2300°F was calculated from the manufacturers' specifications to be 260 amps. Eventually it was determined that a maximum current of 180 amps was sufficient to reach the highest temperatures required.

Initial heating was started with a low current of about 50 amps and was gradually increased to the value required to maintain the desired temperature.

Temperatures of above 1150°C were obtainable, but care was taken to avoid going higher for fear of seriously damaging the steel apparatus.

Normal operating temperatures were in the neighborhood of 900°C which required a current of about 140 amps. Time to reach this temperature was about 4 hours.

During the first slow heating of the furnace, expansion cracks developed in the insulating brick. These cracks were noticeable, but did not cause any trouble. Patching didn't eliminate the expansion, so the cracks had to be tolerated throughout the study. The furnace top consisted of only 2 1/2 inches of insulating brick resulting in a noticeable heat transfer. The transite board supporting these brick withstood the heat, so the furnace top served its purpose. The immediate area around the furnace was warm due to cracks and heat transfer, but working conditions were satisfactory.

The bed area temperature was adjusted to about 900°C. Temperature measurements were taken at various positions in the system. Temperatures obtained were:

Thermocouple Position	Temperature	With N_2 Flow
in cone 1/2" below 2" diameter	540°C	
at 2" diameter	562	
5" above cone	900	868
funnel	961	943

As was mentioned previously, the cone temperature was expected to be below that of the bed area. With a fluidized bed present, a decrease in this temperature deficiency was anticipated. The bed area-funnel temperature difference was not expected. Evidently an appreciable temperature gradient existed from the bottom to the top of the furnace. This gradient caused some concern, but until a hot test with a fluidized bed was conducted, no definite conclusions could be reached.

Temperature control was good with maximum variations of ± 15°C.

The stainless steel withstood oxidation quite well, but the carbon steel bolts and the 1 1/2 inch carbon steel shield pipe for the discharge pipe oxidized badly. Very little stress was present on the 1/4 inch bolts, so oxidation of these, which was expected, was not detrimental. The 1/8 inch carbon steel screws used to fasten the cyclone to the funnel did have a shearing stress on them. Oxidation of these resulted in the cyclone falling down, so #316 stainless steel screws were substituted for the carbon steel screws. After continued use for some time, the shield pipe oxidized so badly that it fell off. The design of this shield should have originally specified stainless steel.

The above concluded initial observations of hot tests conducted with the apparatus alone, without the presence of concentrate.

HOT TESTS WITH CONCENTRATE

The temperature difference between the bed area and funnel was of primary concern. As was mentioned previously, this difference was found to be 60°C during the heating up period, and 75°C with a flow of 0.5 cfm nitrogen passing through the reactor.

Next, a bed of 735 grams of concentrate was placed in the reactor which was preheated to 900°C. The bed was fluidized and temperature equilibrium with a fixed current setting was obtained. The temperature distribution was as follows:

	Thermocouple Position	Temperature
in cone	1/2" below 2" diameter	684°C
	at 2" diameter	693
	5" above cone	762
	funnel	950

The bed area-funnel temperature difference had increased from about 75°C without a bed to 190°C with a bed. Also the cone temperature failed to increase as much as was desired. Further temperature measurements throughout the bottom of the bed indicated only a 15°C drop from the center of the bed to one inch above the cone. Evidently only the exposed cone was unduly cool, while temperature differences in the bed were small.

A method was required for eliminating or minimizing the bed-funnel temperature difference. Shielding the funnel from direct radiation of the globars, compressed air cooling of the funnel, and exposure of the funnel to the cooling atmosphere failed. Some other temperatures equilization method besides cooling of the funnel was needed.

Previously, with a 10 inch fluidized bed, anexcess height, consisting of an 8 inch free board height for splashing and a 6 inch funnel height, existed above the bed. With better contact between the bed and this excess area, an important property of fluidized beds, that is, uniform temperature, might be utilized to eliminate the temperature gradient. More contact required a larger bed. With cold tests, a 1500 gram sample of concentrate, when fluidized, completely filled the total 18 inches of the fluidizer proper and splashed into the funnel. A hot test was then conducted with 1500 grams. This larger bed did eliminate the temperature gradient between bed and the funnel. The problem was apparently solved.

With the temperature gradient problem apparently solved, a two hour hot test was conducted with 1500 grams of concentrate. As the test progressed, the bed-funnel temperature gradually separated with the latter becoming hotter. Examination of the bed revealed that the 18 inch height of the fluidizer proper was no longer filled with a bed. The lost bed material had collected in the funnel. Knocking down this material again resulted in temperature equilization. After a period of time, collection and resultant temperature difference again occurred. Cleaning out the funnel, which again filled the 18 inch fluidizer proper with a fluidized bed, eliminated the temperature difference. Evidently the fine particles in the concentrate, which the funnel collected, fell back into the bed when cold, but when hot were sufficiently sticky to be retained. With this observation, it was concluded that an unwanted but necessary periodic cleaning of the funnel was required during each test.

Further hot tests with periodic cleaning of the funnel minimized the temperature gradient problem. During these tests, the next fallacy noted was the apparent loss of efficiency of the dust collecting system with high temperature operation (from 95% cold to 60% hot). Two possible explanations existed: overloading of the dust collecting system due to a much larger quantity of concentrate tested; increasing fluidizing gas velocity with increasing temperature had a much greater affect than the decreasing density of the gas. The former was found responsible for a small part of the increased dust loss, so the quantity of concentrate used was decreased to 1000 grams. The latter accounted for the remainder of the increased dust loss and will be discussed in detail.

Hot tests were conducted with each of four concentrates to determine what minimum nitrogen flow was required for fluidization at 900°C as compared with 0.5 cfm at room temperature. The analyses of the concentrate tested are given below.

Concentrate	% Pb(total)	%Pb(oxidized)	% Cu
Copperhill	0.28	0.10	0.61
Ticlio	1.11	0.47	0.36
Ozark Mahoning	0.87	0.15	0.13
Leadwood	1.24	0.032	0.02

The reason for inclusion of the percent copper will be given later.

Each concentrate was separately fluidized, and by water manometer readings, the following gas flows were found to give approximately equivalent fluidization.

Concentrate	N_2 Gas Flow
Copperhill	no fluidization
Ticlio	0.4 cfm
Ozark Mahoning	0.3
Leadwood	0.2

The flow required for a particular concentrate at 900°C seemed to be a function of stickiness of the concentrate. The greater the stickiness, the greater was the gas flow required for good fluidization up to the extreme Copperhill concentrate which was very sticky and couldn't be fluidized. For the first time, the very great differences in fluidizing characteristics of the concentrates from various sources become quite apparent. The percent lead seemed to have no connection with the stickiness, but the greater the percent copper, the greater was the stickiness.

Further two hour hot tests demonstrated that by decreasing the gas flow from 0.5 cfm to that minimum required for fluidization resulted in a parallel decrease in dust losses. The magnitude of this permissible gas flow decrease determined the magnitude of the decrease in dust losses. Also, by decreasing temperature a corresponding increase in gas flow was required, but dust losses were unaffected. The conclusion drawn was that a balance between dust losses and minimum gas flow had to be obtained, with the latter, a function of the particular concentrate tested (stickiness), being the regulating variable.

The difficulty confronting this writer was how to correlate the many variables, which seemed to be inherent in the apparatus and the concentrate, so as to have relative deleading results. When this seemingly impossible task became apparent, my advisor suggested taking the concentrate most easily fluidized, removing from this concentrate all small particles which may be lost as dust, and testing only the coarser particles. Leadwood concentrate was selected, the dust was removed, and all tests recorded in this paper were conducted with the remaining concentrate.

DELEADING TESTS

PRELIMINARY CONCENTRATE PREPARATION

Leadwood concentrate had excellent fluidizing characteristics as compared with other available concentrates. For this reason, the Leadwood concentrate was selected for all deleading tests.

Approximately 50% of the concentrate was removed as dust by using the fluidizer as a cold separator. This dust was composed of practically all -200 mesh particles. The remaining beds, from a series of dusting operations, were combined, split on a Jones splitter into 1000 gram batches, and bagged for future tests. One of these batches was carefully sampled by splitting, the remainder was screened, and each particle size was sampled for a lead analysis. Particle and lead distributions were as follows.

Table 1.

Leadwood Concentrate Particle Size and Lead Distribution

Screen Size	Wt. % Dist.	% Pb	% Pb Dist.	(Oxidized) Pb
+ 100	8.8	1.19	10.2	
- 100 + 150	21.3	1.12	24.0	
- 150 + 200	37.5	1.12	40.8	
- 200	32.4	0.80	25.0	
Head Sample	100.0	1.03	100.0	0.23

The lead content of the head sample was calculated from the lead contents of the various particle sizes. The head sample submitted for analysis was reported to contain 1.47% lead, an excessive amount. All head samples submitted during the many tests contained approximately 1.1% lead.

TEST PROCEDURE

The following procedure gradually developed during the many preliminary hot tests as the one best suited for the deleading tests.

The cooling water for the table top was turned on to a flow sufficient for preventing warping and excessive oxidation of the carbon steel plates. Then the switch connecting the furnace to the main power line was closed, and the current was turned on to about 50 amp. Gradually the current was increased over a four hour period until the operating temperature plus about 75°C was obtained. The fluidizer was flushed with the fluidizing gas, and then the gas flow was set at the value wanted for fluidization. The concentrate, a 1000 gram batch, was introduced through the two inch extension pipe above the funnel into the fluidizer proper. The two inch pipe cap was immediately threaded into position, and the time for the concentrate to reach temperature was observed and recorded. At the initial current setting, of operating temperature plus 75°C, approximately 9 minutes were required. Fine adjustments in the current setting gave the desired temperature with very good control. A sample was taken immediately after reaching operating temperature followed by samples taken, at 30 minute intervals till the end of the test. These samples were obtained by dipping a small crucible, fastened to the end of a rod, down into the bed.

At the end of the test, the bed was discharged and weighed, also the samples were weighed. In general, the two weights accounted for 90% of the original charge.

The cyclone contributed little to the dust collection, and it also prevented running a series of tests at one heating of the furnace. For these reasons, the cyclone was excluded from the fluidizer assembly during all of these deleading tests.

TEST CONDITIONS

Following is Table 2 which gives the conditions for all tests conducted on the dedusted Leadwood concentrate. A brief explanation of the table will be helpful.

The fluidizing gas listed as an atmosphere was the principal gas used during the test. With three tests, air was used as an initial gas, but nitrogen was the principal gas. The time in minutes is listed for each gas individually under the general heading of time. Gas flows, given in cubic feet per minute at standard conditions, were constant during each test for both the initial and principal gases. Temperatures are given in °C. All additions of PbS and PbO were in terms of weight percent.

Table 2.

Test Conditions

Test No.		1	2	3	4	5	6	7	8	9	10
Atmosphere		N_2	N_2	N_2	N_2	N_2	N_2	N_2	N_2	Air	N_2
Time	N_2	120	120	120	120	240	120	120	120		120
	Air						10	20	30	240	
	SO_2										
Gas Flow		0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Temperature		800	800	900	900	900	900	900	900	900	900
Additions	PbS										0.5
	PbO										

Test No.		11	12	13	14	15	16	17	18	19
Atmosphere		N_2	N_2	N_2	N_2	N_2	N_2	SO_2	N_2	N_2
Time	N_2	120	120	--*	120	120	120		120	--*
	Air									
	SO_2							120		
Gas Flow		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Temperature		900	900	900	900	900	900	900	1000	1050
Additions	PbS	1.0	1.5	2.3						
	PbO				0.5	1.0	1.5			

* A dash mark under time signifies that the test was incomplete.

RESULTS

ANALYSES

All analyses were made by the analytical laboratory of the St. Joseph Lead Company, Zinc Smelting Division. Their standard polarograph method was used for the lead determination. Accuracies of ± 5% in the 1% lead ranges, and ± 10% in lower ranges were expected. All of the sulfur analyses were made with a short cut method which gave indications rather than definite, reliable values.

Following are Tables 3 and 4 which summarize the analyses for all of the tests. Table 3 contains the analyses for all tests which required lead content only. Table 4 contains both lead and sulfur contents for tests in which oxidation occurred. Note the footnote at the bottom of Table 4 which explains the sample code.

Table 3.**

Lead Content Wariation with Time During Tests in Which there was no Oxidation

Sample	% Lead for Tests												
	1	2	3	4	5	10	11	12	14	15	16	17	18
H	1.14	1.12	1.11	1.15	1.14	1.59	1.91	2.08	1.41	2.08	2.03	1.16	1.03
0	1.11	1.09	0.47	0.36	0.79	0.79	0.885	1.49	0.81	1.13	1.65	1.02	0.38
30	0.51	0.59	0.082	0.080	0.10	0.11	0.36	0.475	0.11	0.24	0.52	0.10	0.049
60	0.25	0.29	0.058	0.059	0.086	0.0825	0.057	0.24	0.075	0.072	0.086	0.091	0.033
90	0.15	0.15	0.049	0.043	0.062	0.061	0.044	0.073	0.061	0.054	0.062	0.0765	0.026
120	0.15	0.11	0.038	0.043	0.057	0.057	0.34	0.0555	0.046	0.048	0.046	0.069	0.016
150					0.057								
180					0.047								
210					0.046								
240					0.0435								
S								3.1		0.32	0.41		

Table 4. **

Lead Content Variation with Time During Deleading Tests in which there was Oxidation.

%Pb and %S for Tests

Sample	6		7		8		9	
	%Pb	%S	%Pb	%S	%Pb	%S	%Pb	%S
H	1.10	28.6	1.10	24.9	1.11	30.5	1.16	31.6
2H	0.27		0.515		0.67			
0	0.14	28.4	0.26	29.4	0.16	27.2	0.95	
30	0.040		0.0865		0.0835		0.19	
60	0.097		0.054		0.082		0.12	25.6
90	0.036		0.040		0.0328		0.088	
120	0.033		0.037		0.034		0.082	20.1
150							0.063	
180							0.050	12.0
210							0.053	
240							0.056	4.0

** H - head sample split from the initial concentrate.

2H - occurs in Table 4 only, sample taken after reaching operating temperature with nitrogen but before oxidizing with air.

0 - sample taken at the beginning of the time listed for the principal fluidizing gas under Conditions.

30, 60 etc. - samples taken 30, 60, etc. minutes after the 0 sample.

S - special sample, discussed later under Discussion.

EXPERIMENTAL DISCREPANCIES

Previously, under Procedure, it was stated that approximately 9 minutes were required for the fluidized concentrate to reach operating temperature. This time was variable, and with the rapid initial lead elimination, a variation of one minute did make an appreciable difference in the 0 or 2H samples for concentrates having the same original lead content and being tested at the same temperature. After a short time at temperature, this discrepancy disappeared.

Discrepancies in analysis due to occasional poor sampling and/or errors in the analytical work were expected, and in nearly all cases were quite apparent when observed in the presence of neighboring samples.

The total lead content of the head samples, for the concentrates to which lead additions in the form of sulfides or oxides were made, did not agree with expected values, especially when the additions were large. In all tests, the 0 samples did seem to agree with expected lead contents. Evidently, insufficient mixing of the addition and concentrate resulted in an uneven lead distribution throughout the concentrate, and a non-representative head sample. Consistency of the 0 samples with known lead additions indicated uniform composition of the fluidized bed and representative sampling.

DISCUSSION

This discussion is divided into the various sub-headings listed below. With the exception of Reproducibility, all other sub-headings represent the variable tested.

1.) Reproducibility
2.) Temperature
3.) Time
4.) Gas flow
5.) Gas composition
6.) Oxidation
7.) Lead sulfide additions
8.) Lead oxide additions

Reproducibility

Tests 1 and 2 were conducted under identical conditions. These were: 800°C, 0.3 cfm N_2 flow, 2 hours. Following are the analyses.

SAMPLE	%Pb TESTS	
	1	2
H	1.14	1.12
0	1.11	1.09
30	0.51	0.59
60	0.25	0.29
90	0.15	0.15
120	0.15	0.11

Agreement between equivalent samples was excellent, indicating that reproducibility for the equipment and procedure used was good.

Temperature

Tests 2, 3, 18 and 19 were conducted for two hours with a 0.2 cfm N_2 flow at temperature of 800°C, 900°C, 1000°C, and 1050°C respectively.

Stickiness of the concentrate was initially encountered at 1000°C, and prevented operation at the higher temperature attempted in Test 19. The temperature for this last test never exceeded 1020°C, the transition temperature of cubic sphalerite to the hexagonal modification wurtzite, which indicated an endothermic reaction. Microscopic examination of the discharged bed revealed ZnS particles very loosely bonded together by what appeared to be slight surface fusion.

Following are the analyses.

SAMPLE	%Pb TESTS			
	2	3	18	19
H	1.12	1.11	1.03	none
0	1.09	0.47	0.38	
30	0.59	0.082	0.049	
60	0.29	0.058	0.033	
90	0.15	0.049	0.026	
120	0.11	0.038	0.016	

These tests show the very definite influence of temperature on lead removal. Assuming a lead head of 1.1%, at the end of two hours of temperature, lead elimination increased from 90% at 800°C to 98.5% at 1000°C. With increased time, greater elimination would be obtained at all temperatures. At 1000°C, this increased time may result in nearly 100% lead removal.

Time

Tests 4 and 5 were conducted under identical conditions of 900°C and 0.2 cfm N_2 flow, but the time of Test 5 was four hours instead of the normal two hours. The purpose was to more thoroughly study the leveling off of lead content for a possible minimum lead content at a fixed temperature regardless of time. Following are the analyses.

SAMPLES	%Pb TESTS 4	%Pb TESTS 5
H	1.15	1.14
0	0.36	0.79
30	0.080	0.10
60	0.059	0.086
90	0.043	0.062
120	0.043	0.057
150		0.057
180		0.049
210		0.046
240		0.0435

Immediately, the disagreement in the rate of lead removal between the two tests is apparent. No explanation is available, but the validity of Test 4 was checked by other tests.

Ignoring Test 4, Test 5 adequately demonstrates the leveling off in lead content with time at a fixed temperature. No minimum was definitely obtained, but for more extensive lead removal, excessive time at temperature would be required.

Gas Flow

Identical conditions for Tests 3 and 4 were the temperature of 900°C and the time of two hours, while the nitrogen flows were 0.3 cfm and 0.2 cfm respectively. Following are the analyses.

SAMPLES	%Pb TESTS 3	 4
H	1.11	1.15
0	0.47	0.36
30	0.082	0.080
60	0.058	0.059
90	0.049	0.043
120	0.038	0.043

Note the difference between the 0 samples of each test, which was discussed previously under Experimental Discrepancies, and elimination of this difference within 30 minutes.

A simple calculation, assuming saturation of the carrier gas by lead sulfide at 900°C, indicated that the total volume of fluidizing gas used (0.2 cfm for 2 hours) greatly exceeded the minimum carrier gas volume required for complete lead volatilization. From the above analyses, the two different gas flows had no noticeable effect on rate or extent of lead elimination. Experimentally the gas flows required for fluidization significantly exceeded the maximum gas flow which would still noticeably affect the rate of lead elimination.

Gas Composition

Identical conditions for Tests 3, 9 (first two hours) and 17 were the temperature of 900°C, the gas flow of 0.2 cfm, and the time of two hours, while the gases used were nitrogen, air, and sulfur dioxide respectively. Following are the analyses.

SAMPLES	TESTS			
	3	9		17
	%Pb	%Pb	%S	%Pb
H	1.11	1.16	31.6	1.16
0	0.47	0.95		1.02
30	0.082	0.19		0.10
60	0.058	0.12	25.6	0.091
90	0.049	0.088		0.0765
120	0.038	0.082		0.069

Placing the fluidizing gases in sequence with respect to increased rate of lead removal results in air, sulfur dioxide, and nitrogen. The oxidizing atmosphere, due to the presence of oxygen in air, was expected to decrease the rate and extent of lead removal. A comparison between PbS and PbO vapor pressure curves supports this expectation. Failure of the reducing gas, sulfur dioxide, to match the neutral gas, nitrogen, in lead removal was unexpected. No satisfactory answer can be postulated from this one test with sulfur dioxide, and the time was insufficient to permit further tests.

Oxidation

Identical conditions for Tests 6, 7, and 8 were the temperature of 900°C, the gas flow of 0.2 cfm, and the time of two hours with nitrogen, preceeded by 10, 20, and 30 minute oxidation periods respectively with air. Test 9 was conducted entirely with air for four hours. Table 4 on page 40 under Analyses contains all of the analyses obtained with the oxidation tests.

Checking the extent of oxidation, note the rather erratic sulfur analyses. A rough estimation of sulfur elimination is 1% per 10 minutes of oxidation with air at 900°C.

For Tests 6, 7, and 8, no definite statement about rate of lead elimination can be made due to the rather erratic analyses. Lead elimination after two hours at temperature with nitrogen was equivalent even though the sulfur content was decreased from 30% to 27%.

Using air alone, after two hours, the lead content of the concentrate studied in Test 9 was 0.082% as compared with a normal lead content of about 0.035% when using nitrogen. The sulfur content was decreased from about 30% to 20%. Continuation of this test under oxidizing conditions for another two hours resulted in a lead content of about 0.053%, and a sulfur content of 4%. This lead value was first reached at 12% sulfur and was maintained for the remaining 90 minutes of the test. Evidently 12% sulfur is the minimum amount required for continued lead elimination in an oxidizing atmosphere at 900°C.

Lead Oxide Additions

Identical conditions for Tests 14, 15, and 16 were the temperature of 900°C, the nitrogen flow of 0.2 cfm, and the time of two hours. Lead oxide additions of 0.5%, 1.0%, and 1.5% respectively were made to the concentrates. The lead oxide additions consisted of -48 +100 mesh particles which were obtained by melting chemically pure litharge powder and regrinding the fused solid. The feathery or lamellar like structure of the particles, which presented possible dusting losses, resulted in a larger particle size being used as compared with the lead sulfide additions.

No physical difficulty was encountered with any of the tests even though the operating temperature exceeded the melting point of lead oxide. Also the lumps obtained with a 1.5% PbS addition were not obtained with a 1.5% PbO addition.

The possibility of segregation during fluidization of the large lead oxide particles was considered The discharged beds of Tests 15 and 16 were split and sampled (special samples S) to serve as a check on the 120 minute samples. Following are the analyses.

SAMPLE	%Pb TESTS		
	14	15	16
H	1.41	2.08	2.03
0	0.81	1.13	1.65
30	0.11	0.24	0.52
60	0.075	0.072	0.086
90	0.061	0.054	0.062
120	0.046	0.048	0.046
S		0.32	0.041

Again the head samples were not in agreement with additions while the 0 samples were more representative. All analyses are consistent and indicate that this series of tests was good. Note that the special sample of Test 15 indicates segregation, while the special sample of Test 16 indicates the opposite. The good agreement of the latter with the 120 minute sample results in the assumption that no segregation occurred.

In all three tests, without regard to initial lead additions, similar lead contents were obtained at the end of two hours at temperature. This final lead content was almost as good as that obtained with the normal concentrate in Tests 3 and 4. Evidently, initial oxidation of the lead, doesn't adversely affect the rate of lead elimination.

Lead Sulfide Additions

Identical conditions for Tests 10, 11, 12 and 13 were the temperature of 900°C, the nitrogen flow of 0.2 cfm, and the time of two hours. Lead sulfide additions of 0.5%, 1.0%, 1.5%, and 2.3% respectively were made to the concentrate. The lead sulfide additions consisted of -100 +150 mesh particles which were obtained from a commercial galena table concentrate. These particles were cleaned free of oxides by washing in an ammonium acetate solution.

Tests 10 and 11 were conducted without any physical difficulty. Fused lumps were detected in the bed and samples of Test 12. Examination of these under a microscope revealed a fused bluish mass, resembling fused PbS, containing entrapped ZnS particles. A sample, listed as a special sample (S), of these lumps was submitted for lead analysis. Excessive sticking, apparently due to the 2.3% PbS addition in Test 13, resulted in this test being discontinued. Following are the analyses.

SAMPLE	%Pb TESTS			
	10	11	12	13
H	1.59	1.91	2.08	none
0	0.79	0.885	1.49	
30	0.11	0.36	0.475	
60	0.0825	0.057	0.24	
90	0.061	0.044	0.073	
120	0.057	0.34	0.0555	
S			3.1	

As was mentioned previously under Experimental Discrepancies, the head sample analyses are not in agreement with lead additions, while the 0 samples are more consistent. Also note that the 120 minute sample of Test 11 is definitely incorrect, and that the 60 and 90 minute samples do not follow the trend of Tests 10 and 12. The lack of time prevented repeating Test 11.

Considering only Tests 10 and 12, the extent of lead elimination was equivalent in two hours at temperature, but it was not as complete as that obtained with the ordinary concentrate, or with the lead oxide additions. A previous comparison between the vapor pressure curves of PbS and PbO indicated that greater or at least equivalent elimination should have been obtained with the lead sulfide additions.

The special sample contained only 3.1% lead. From the large quantity of the fused mass as estimated by eye, a much larger lead content was expected. Evidently, some other mineral must compose a majority of the mass. A more extensive analysis of this sample is needed.

CONCLUSIONS

Reproducibility, as indicated by Tests 1 and 2, was good.

Temperature has a very great affect on lead elimination. At 800°C, 90% elimination was obtained in two hours as compared with 98.5% elimination at 1000°C. No indication of leveling off of lead content was observed at the latter temperature, which in turn indicates that 99%+ elimination might possibly be obtained with increased time.

No definite limit in the extent of lead elimination at a given temperature was observed for any of the tests, with the exception of the four hour oxidation test. However, the rate of lead elimination does definitely decrease with time.

The gas flows required for fluidization significantly exceed the maximum gas flow which noticeably affects the rate of lead elimination.

Oxidizing conditions decrease the rate of lead elimination, and limit the extent of lead elimination to that content which is present when the sulfur content is reduced to approximately 12%.

The extent of lead elimination in the original concentrate was not affected by additions of free lead oxide.

The assays for the lead sulfide addition tests were erratic and prevent drawing definite conclusions.

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VITA

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