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THE ROASTING of ZINC ORES in the MANUFACTURE of
SULPHURIC ACID by the CONTACT PROCESS

by

Clarence Eugene Peterson

A

T H E S I S

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

D E G R E E O F
METALLURGICAL ENGINEER

Rolla, Mo.

1919

Approved by _____

Assistant Professor of Metallurgy.

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THE ROASTING OF ZINC ORES IN THE MANUFACTURE
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INTRODUCTION

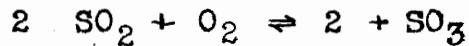
The unprecedented demand for sulphuric acid of the higher strengths (98% and higher) in the manufacture of explosives, has stimulated the zinc smelters to increased efforts in the recovery of their Roaster gases in the form of Sulphuric Acid. The Lead-chamber process is unsuitable, however, in making "strong" acid and the smelters naturally turned to the contact mass or catalytic processes.

In the roasting of zinc ores practically all of the sulphur is removed as sulphur dioxide, the disagreeable odor and unmistakable injury to surrounding localities, of which, first led to the adoption of sulphuric acid plants by most zinc smelters. This sulphur dioxide so formed has little value unless converted into sulphuric acid.

In the Lead-chamber process this conversion is brought about by certain chemical reactions with nitric acid familiar to everyone.

In the contact process the dry, cleaned Sulphur dioxide is passed through a mass containing a substance which acts as a catalyzer converting the sulphur dioxide to sulphur trioxide according to the follow-

ing reaction:



This reaction is reversible but proceeds to the right at a temperature about 425°-475°C. Above 480°C the SO₃ will be broken up into SO₂ and O₂ and below 380°C the reaction proceeds too slowly for practical purposes.

A number of substances can bring this reaction to pass, but the most widely used catalyzer is platinum. The contact-mass is usually made by sprinkling platinum-chloride on trays containing magnesium sulphate in particles of about 1/2 inch in size. The trays are arranged in the converters and gas passed through which expels the chlorine and leaves a deposit of platinum throughout the mass. Usually the contact mass will contain about 2/10 of 1% of Platinum when ready for use.

The SO₂, now converted to SO₃, leaves the converters and goes to the absorbers, where it is dissolved in dilute sulphuric acid up to the desired strength. This acid is then pumped to storage tanks where it is held for loading to tank-cars.

GENERAL CONDITIONS NECESSARY TO THE SUCCESS OF THE PROCESS.

While it is true that the process works out in practice quite as simply as just described, it is equally true that it depends, from the very nature of it, on a particularly close attention to minute details for its commercial success.

We will discuss briefly these details before taking up their application to roasting.

FIRST, the strength of the roaster gas in SO_2 . This is an important economic point. It has been found in practice that ordinarily it will not pay to treat gas leaner than 3-1/2% in SO_2 . When the gas is too rich in SO_2 , conversion does not go to completion and the upper commercial limit has been found to be about 8.5%. The usual strength which works out most economically in practice is from 4.5 to 7.5%.

SECOND, the presence of water vapor in the roaster gas. In climates which are unusually damp the sulphuric acid plants have a considerable initial loss of sulphur to face in the solution of SO_2 and SO_3 in the water-vapor of the roaster gas which is condensed and thrown away at

the "coolers." A leaky muffle in a roasting furnace means the presence of an additional amount of burnt hydrogen or water-vapor.

THIRD, the presence of deleterious substances in the roaster gas. The chief cause of annoyance and loss in the plant is "poisoning" of the contact mass by the presence in the roaster gas of deleterious substances which deposit on the platinum and "kill" its catalytic action. Under this head may be placed arsenic, bismuth, antimony and fluorine. The arsenic, bismuth and antimony are usually removed in the dust catchers and coolers but fluorine, tho never present except in minute quantities, attacks the silica in the Glover towers and is carried over to the converters as Si F_4 and deposited there as such. The only way to prevent this is by using acid of 45° strength in the Towers, this being the only strength which will decompose practically the tetrafluoride.

FOURTH, the presence of other gases in the roaster gas. Keeping in mind the reaction for the conversion of SO_2 to SO_3 it will be seen that theoretically each percent of SO_2 requires one-half percent of oxygen for the conversion. In practice it has been found that 100% excess oxygen is actually required for efficient work. SO_2 and oxygen are the only gases which enter into the reaction but

unfortunately nitrogen from the air and more often carbon dioxide and monoxide from leaky muffles are present. Nitrogen and carbon dioxide have no effect on the reaction except insofar as they cut down the concentrations of the reacting gases, and carbon monoxide has no effect other than in reacting with the oxygen it further decreases the oxygen content.

GENERAL CONSIDERATIONS IN ROASTING FOR THE PROCESS.

In the roasting of ores there are a number of points which must be borne in mind.

In the first place, many zinc ores are not to be used in the manufacture of spelter but to make zinc oxides. As a rule, these ores are complex sulphides containing as low as 20% zinc. If the remaining sulphides are chiefly iron sulphides the ore will be more nearly self-roasting, and from the acid-manufacturer's stand-point more acceptable.

Unfortunately many of these complex sulphides carry manganese, lead and silica which usually cause trouble by fusing the whole ore charge into large cakes impossible to rabble or remove without breaking.

Other gangue materials such as ferric oxide act as catalytic agents and cause loss of sulphur by premature conversion of the SO_2 to SO_3 .

In pyritic ores, the temperatures attained in roasting often are so high as to cause fusion and also

conversion by the formation of Fe_2O_3 .

Zinc ores are never fully self-roasting and it will be found that after the removal of about 60% of the sulphur, continued external heat must be applied for any further reaction. To remove the smaller percentages of remaining sulphur requires fully 50% of the total heat necessary.

In the roasting of the complex sulphides of zinc and iron there is always some zinc ferrite formed. In order to break up this compound, high temperatures are necessary which means high heat consumption.

To summarize, the roaster will be expected to remove nearly all of the sulphur from ores which may have a tendency to fuse and cake, and in most cases, from ores whose calorific value is not only low, but of such a nature that there is usually the tendency to form refractory compounds (zinc ferrite) which require abnormally high temperatures for decomposition. The roaster, therefore, must have a high heat efficiency. It must be

so constructed that the caking which may take place will cause a minimum of trouble. Then, finally, from the acid-manufacturers point of view, it must accomplish the metallurgical requirements with a maximum sulphur recovery in concentrated gas volumes.

Recalling now the details of the conditions of the gases necessary to success of the process, it will be noted that the roaster should deliver a gas high in SO_2 and oxygen, low in water vapor and the carbon gases. It is obvious, therefore, that the roaster must utilize to the fullest extent whatever air is admitted for the burning of the sulphur in order to keep a high concentration of SO_2 and should be so designed that the admission of combustion gases into the system be kept at a minimum to prevent a decrease in SO_2 and oxygen concentration.

The quality of the gas determines, of course, the success of the operation of the acid process, but it must be remembered that the roasting of zinc ores is not a major step in zinc metallurgy and the recovery of acid must always be looked upon as a by-product in the industry. The original reason for the installation

of roasters applies with but slightly lessened force today, namely, the necessity for the removal of the sulphur before the manufacture of zinc products can begin. How successfully and economically the roaster can remove the sulphur determines largely, of course, the value of the roaster, its ability to do so successfully from the stand-point of the acid manufacturer being usually secondary.

From the purely roasting or sulphur removal point of view the roaster should remove the sulphur completely (within practical limits), it should do so at a small expenditure for fuel, labor and up-keep materials.

A SHORT DISCUSSION OF TYPES OF ROASTERS USED

EUROPE:- With one notable exception the Roasters used in continental Europe may be characterized as hand roasters. They are all of the muffle type, hand fired, hand fed and discharged and hand rabbled. Cheap labor has, of course, made this possible. The exception mentioned above is the Spirlet furnace, an invention by a Belgian metallurgist by that name and in whose country it had received practically national approval. It will be discussed more fully under American Roasters.

AMERICA:-The high cost of labor in America early determined that the exhausting work of operating zinc roasting furnaces should be done by mechanical means as far as possible, and the economics which applies so generally to American industries determined also that large units should be used.

The Mathiesen-Hegeler Kiln

The first mechanical roaster to come into general use was the Mathiesen-Hegeler Kiln. This roaster with very few modifications is still the most generally accepted one, in spite of its many inherent disadvantages.

It is, essentially, a large rectangular brick structure, consisting of, usually, seven superimposed hearths, the lower two or 3 of which are heated by means of muffles. Throughout the length of this kiln on each hearth are operated "plows" or "rabbles" which turn and advance the ore burden. At the end of each hearth are holes through which the ore drops to the immediately succeeding hearth on completion of its path for the length of the hearth. The lower two or three hearths are heated by means of gas, oil or coal burned in muffles below each one. Usually in the case of gas fired furnaces, the air for combustion is pre-heated by means of regenerators or "checker-boards" underneath the kiln.

The Mathieson-Hegeler kiln because of its low arch construction and long ore-path lends itself admirably to a sparing use of air for the roasting and this fact together with its comparatively high heat efficiency has contributed largely to its popularity. The cost of upkeep and repairs of the kiln is small and the life is usually estimated at 4 years. The arrangement of the

muffles is such that very little carbon gas enters into the system, over a long period at no time could more than .8% CO₂ be found, the average being considerably below this. Then, too, from the stand-point of sulphur removal the kiln has few equals. But it is doubtful whether accurate analyses of the situation would not show that the disadvantages of this type would not outweigh the advantages. In the first place, the enormous first cost of the kiln means an unusual overhead charge. The number of mechanical accessories means the cost and maintenance of a machine shop and intelligent, hence expensive labor, to operate. The intermittent rabbling of the charge means that on the peak the gases often reach 12.5% in SO₂ content, with the attendant sulphur losses through poor conversion, and then drops down to 2 to 3%, with the consequent drop in production and increase in overhead.

Data On M & H Kiln

| | | |
|------------------------|---|----------------------|
| Capacity | - | 55-60 Tons per day. |
| Fuel ratio- | | 30% |
| Sulphur Removal | - | 2% "false" sulphur |
| Men required per shift | | (-8-hrs..) = 5 |
| Gas made | - | 2.5- 12.5% variable. |

Spirlet Furnace

The Spirlet Furnace, which originated in Europe, consists essentially of circular superimposed hearths, the alternate ones of which revolve. The ore is rabbled by wedge-shaped bricks set in the arch of the hearth above. One or two muffles furnish the heat necessary for the roasting. The Spirlet Furnace utilizes to a remarkable extent the air necessary for the roasting and delivers a gas uniformly high in SO_2 . The heat efficiency of the furnace is high and because of the muffle construction combustion gases are absent in the SO_2 gases. The Spirlet Furnace is without question the best roasting furnace developed in the zinc-acid industry. Its chief drawback from the American point of view is the smallness of the units, none of them so far, constructed having a capacity of over five tons of ore per day. Replacements are simple and maintenance costs low.

Data On Spirlet Furnace

| | | | | | |
|-------------------------|---|------|---|------|---------------|
| Capacity | - | 2 | - | 5 | Tons per day. |
| Fuel Ratio | - | 21 | - | 25% | |
| Sulphur Removal | - | 1.2% | | | False sulphur |
| Men required per shift- | | 1/2 | | | man |
| Gas made- | | 4.5- | | 6.5% | |

Wedge Furnace

The Wedge Furnace had been used so successfully in roasting various ores, that it seemed to the builders and others that with but slight modifications it should be used in the roasting of zinc ores in the manufacture of sulphuric acid. A Furnace installed for experimental purposes is described in the Appendix of this paper. Operations covered a period of some months and the conclusions drawn from this operation are described fully in the appendix.

In general, however, the Wedge Furnace as originally designed for this work was not entirely successful for the following reasons: Replacements were frequent particularly of the rakes and rake-holders; the high arch prevented good air distribution; the amount of surface exposed to radiation as compared to actual capacity was high and the heat

efficiency of the furnace correspondingly low; the sulphur removal of the ore was not complete enough above the sixth hearth to avoid throwing too much sulphur on the two lower hearths; the dust losses were rather high. The furnace had, however, a number of advantages, namely, low labor costs, low power costs, ease of operation, low supervision costs and compared to the M & H Kiln, low original cost.

The following will give some data on the operation:

| | | |
|------------------------|---|--------------------------------|
| Capacity | - | 25 Tons per day. |
| Fuel Ratio | - | 32% |
| Sulphur Removal | - | 5th Hearth - 7.9 False Sulphur |
| | | Total - 1.3 " " |
| Men required per Shift | | - 1-1/2 |
| Gas Made | | - 4.3% SO ₂ |

The Merton- Ridge Furnace

In addition to the three furnaces mentioned above, there is the Merton-Ridge Furnace which has attained some degree of popularity in England, and has been tried in this country. It consists primarily of a rectangular structure similar to the M & H Kiln, but instead of advancing the ore

by means of straight-line rakes, it is done by means of revolving arms whose paths intersect as shown by the following sketch.

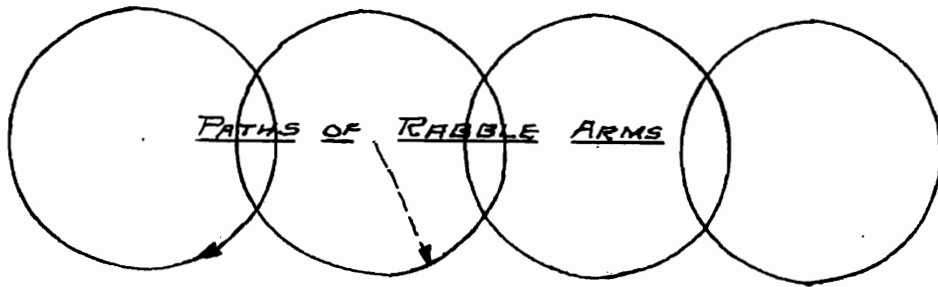


Fig.1.

CONCLUSION

In general, for all requirements, the Spirlet Furnace is the best of the Furnaces in use in America for the roasting of zinc ores in the manufacture of sulphuric acid. It is probable that a modification of this furnace of larger capacity will be ultimately adopted. The Mathieson-Hegeler kiln, in spite of its disadvantages, is used successfully and is the most popular furnace. The Wedge Furnace can, no doubt, be improved upon to such an extent that it can, at least, successfully compete with the M & H kiln. The Merton-Ridge Furnace should offer no great advantages over the M. & H. kiln.

APPENDIX

SUMMARIZED REPORT ON EXPERIMENTAL OPERATION OF WEDGE FURNACE

Description of Furnace.

The Furnace consisted of seven superimposed roasting hearths and one drying hearth. Directly under the fifth hearth was a semi-muffle, the combustion gases from which were removed thru holes in the muffle opening into the sixth hearth. Producer gas was burned in this muffle and also on the sixth and seventh hearths. The combustion gases so formed, together with the sulphur gases produced on the sixth and seventh hearths, were removed from the seventh hearth and turned into a steel stack which emptied directly into the air.

The System or Roaster gases formed above the sixth hearth were removed just below the drying hearth and by means of suction-blowers drawn into the acid system.

The accompanying sketch will show the general construction of the furnace. It will be noted that the rabbling arms on the sixth and seventh hearths were water-cooled and on all of the others air-cooled. The experimental work developed no reason for using water-cooling on the two bottom hearths in preference to air cooling. The cooling-water and-air entered and returned thru pipes in the large central shaft.

VERTICAL SECTION- WEDGE FURNACE

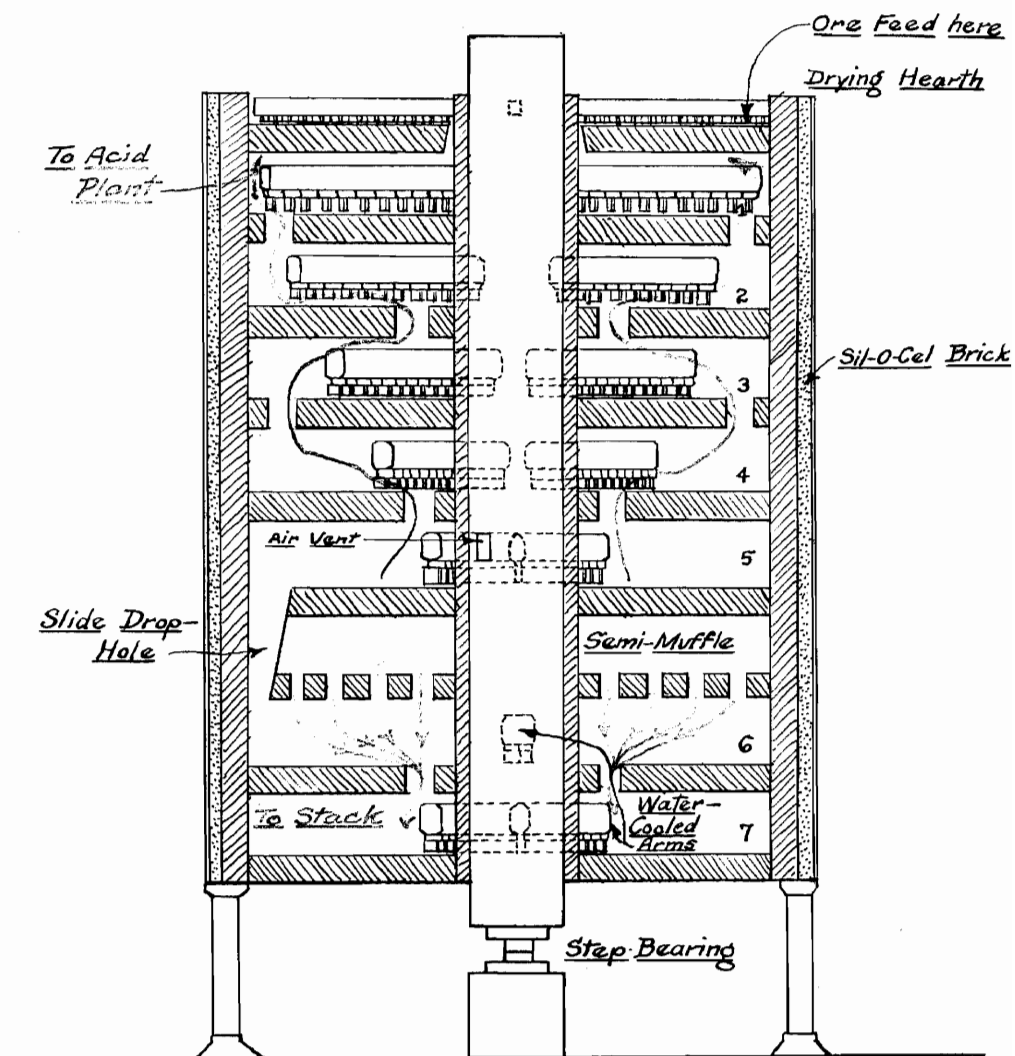


Fig. 2

III

Ore was raised to the drying hearth by means of a belt and bucket elevator and dumped on the outside of the hearth and gradually rabbled towards the centre where it fell to the hearth below thru an "ore-seal." The ore was worked alternately on the various hearths from the centre to the outside until it reached the fifth hearth. It fell at the centre and was rabbled to the outside, but instead of falling directly it was discharged at three drop-holes which avoided the muffle below as shown on the sketch.

The Producer gas Burners consisted simply of six inch sheet steel pipes placed into the furnace at two points on each hearth and the muffle and the gas flow was regulated by gate valves.

Operating Results

It was found in operating this furnace that a certain definite amount of sulphur had to be burned per square foot of hearth area per unit of time in order to maintain the temperature necessary for the roasting to continue.

With ores of a fixed amount of sulphur, the heat input by the ore was limited, therefore, by the actual amount of ore which could be charged, on the one hand, and

IV

by the chilling effect of the ore charged and the ability of the furnace to remove the required amount of sulphur, on the other. Pyritic ores for that reason gave the best heat results, hence roasting results.

Upon the amount of air admitted and its distribution depended very largely the success of the roasting. The natural tendency of the furnace as designed was for a large excess of air to be required in order to properly remove the sulphur. Besides the cooling effect of the additional air, this excess cut down the concentration of SO_2 in the Roaster gases. The original provision for air intake was thru two holes about 9 inches square placed in the central shaft on the fifth hearth. The air was blown in by the blower used to furnish air to the cooling arms at a pressure of about 1-1/2" water-pressure. The air when in amount great enough to roast on the upper hearths, chilled this hearth unduly. The openings were, therefore, closed and air was admitted only thru openings in the "peep-doors" in the furnace, the natural draft causing enough suction for the purpose. This step was an improvement, but it was still seen that the air was not properly utilized and a further change was made. To cause an

actual "swirling" motion of the gases, it was decided to instal on the fourth and fifth hearths nozzles bent in the direction of revolution of the rabbles, thru which air at about sixty pounds pressure could be blown. This gave a marked improvement in the roasting, particularly on the upper hearths which originally did very little sulphur removing. As an operating expense item, the using of compressed-air is, of course, too great to apply in practice, but the experiments showed in a convincing way the necessity for proper air-distribution.

The lute-rings at the centre of the furnace used to prevent the contamination of the system gas with combustion gases broke and had to be removed. It was found that this caused a leakage of the combustion gases into the acid system and it became necessary to increase the stack draft considerably in order to cut down the stack-effect of the furnace itself. In this way, however, the amount of sulphur gases thrown into the air was excessive and the test had to be discontinued.

VI

TEMPERATURE and SULPHUR REMOVAL CURVES-WEDGE FURNACE

Curves showing relations between temperature conditions on the various hearths of the Wedge Furnace and the removal of sulphur.

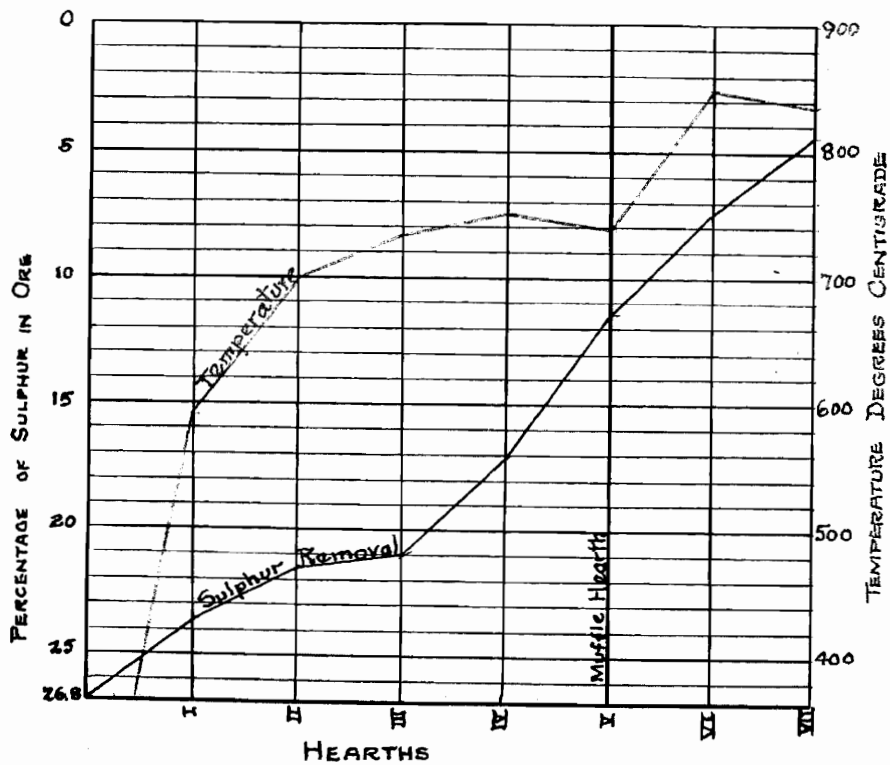


Fig. 3.

VII

CONCLUSIONS

The Wedge Furnace on the ore treated did not remove sufficient sulphur before leaving the fifth hearth. The air distribution because of the high arch construction was poor. Better roasting results could undoubtedly have been secured by additional rabbling on the upper hearths. Two complete muffles instead of one semi-muffle would have aided considerably.

VIII

SUMMARY- WEDGE FURNACE OPERATING DATA

Av. Analysis green ore.....(26.8% S
(20.0% Fe
(25.0% Zn

Av. Burden.....(27 Tons

Av. Volume of System Gas.....1175 cu.ft. per min.
at 0°C and 760 mm.

Av. Temp. of System Gas leaving Furnace....490°C

Av. Analysis of System Gas.....(SO₂ - 4.28
(SO₃ - 0.30
(O₂ - 10.76
(CO₂ - 1.45
(N₂ - 83.21

Av. Percent Sulphur in Ore leaving 3d Hearth-- 11.5%

Av. Recovery of Sulphur as SO₂..... 48.4%

.....

Av. Volume of Stack gas.....2310 cu.ft. per min.
at 0°C & 760mm

Av. Temp. of Stack gas leaving Furnace.....610°C

Av. Analysis of Stack Gas.....(SO₂ - 0.83
(SO₃ - 0.40
(CO₂ - 6.49
(O₂ - 8.76 Wet.
(N₂ - 80.45
(H₂O - 3.07

Av. Percent Sulphur in Ore leaving Furnace -- 4.2%

Av. Elimination of Sulphur of Ore -- 86.1%

Av. Temp. of cinder leaving Furnace -- 770°C.

IX

SUMMARY- WEDGE FURNACE OPERATING DATA(Cont.)

Av. Volume of Producer Gas used- 530 cu.ft. per min.
at 0°C & 760mm.

Av. Analysis of Producer Gas used-(CO- 25.8
(H₂- 12.4
(CH₄- 0.6
(CO₂- 5.1
(N₂-52.6
(H₂O- 3.5

Av. Temperature Producer Gas used.....91°C.

Equivalent to

Av. Coal Consumed.....8.6 Tons per day

Av. Fuel ratio.....31.8%

Av. Volume cooling water.....8.89# per sec.

Av. Temperature Cooling Water Inlet..... 14°C

Av. " " " Outlet.....23.46 °C

Av. Speed of revolving arms.....15 R.P. Hr.

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