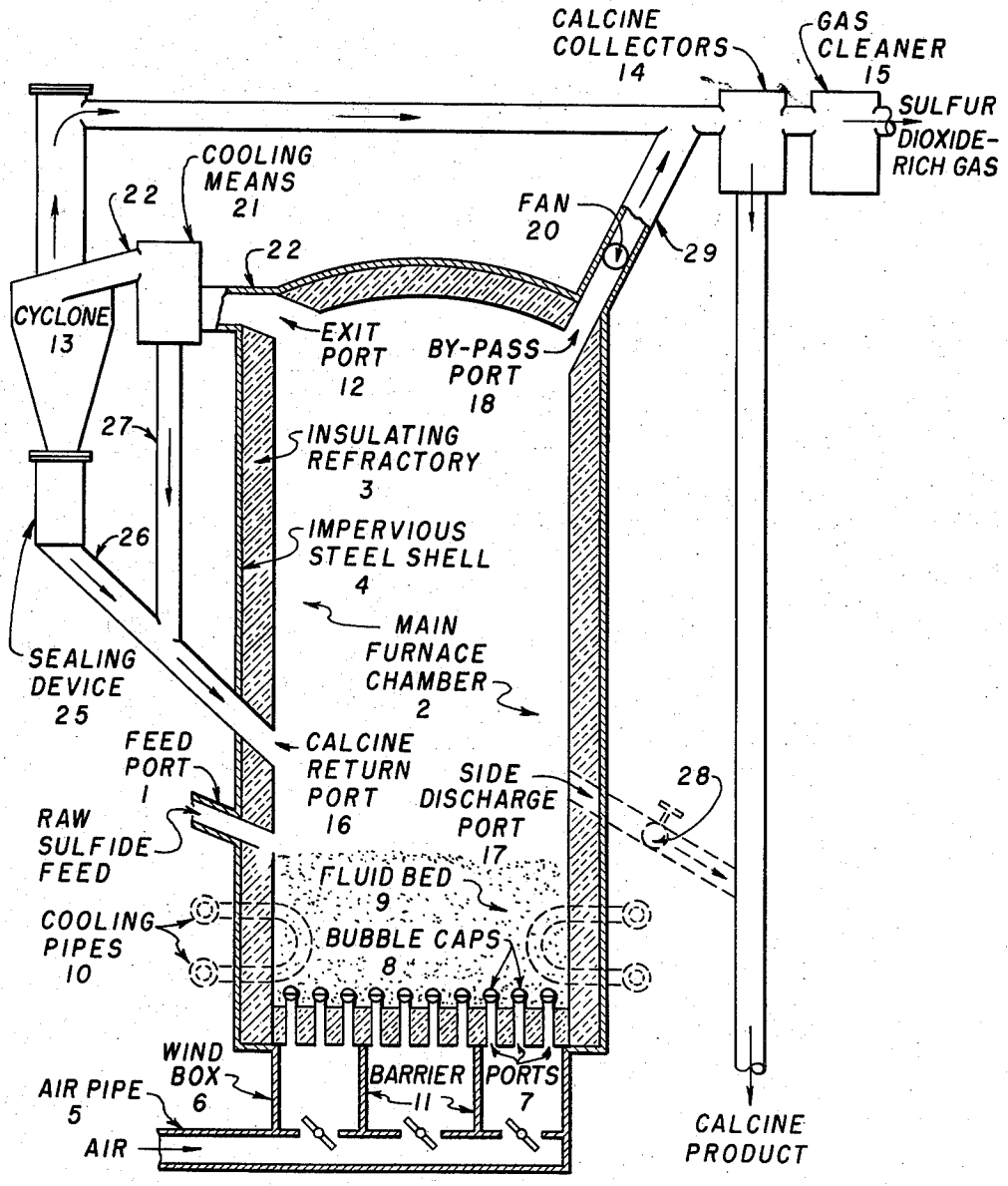
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PROCESS FOR ROASTING SULFIDES

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PROCESS FOR ROASTING SULFIDES

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The present invention relates to an improved process for roasting sulfides and, more particularly, the present invention provides an improved process for suspension roasting finely-divided iron sulfide to obtain calcine of exceptionally low sulfide-sulfur content while maintaining high treatment rates per unit of hearth area.

It is well known that conventional suspension-roasting, i.e., flash roasting or fluid-bed roasting, of sulfide materials, such as pyrite, pyrrhotite, etc., has possessed certain limitations. In order to obtain a desired low sulfur content in the calcine, the art has heretofore found it necessary to employ relatively low feed rates per unit size of roaster. Where high feed rates and correspondingly high gas velocities have been employed, the calcined products had undesirably high sulfide-sulfur contents due to the extremely short retention time of the finer fractions of calcine in the roasters, and, if any great increase in feed rate were attempted, fluidized bed roasters became inoperative as such due to loss of the bed. Sulfide concentrates having higher initial sulfur contents and having finer particle sizes have become increasingly available in recent years for roasting and, as a result, the fluid-bed and flash-roasting techniques have come into prominence in spite of the limitation discussed hereinbefore.

It has now been discovered that finely-divided sulfide materials, particularly iron sulfides, can be suspension roasted at high feed rates and at high oxidizing-gas velocities either by flash-roasting or by fluid-bed roasting techniques, to obtain a roasted sulfide product of exceptionally low sulfide-sulfur content and gases rich in sulfur dioxide.

It is a main object of the present invention to provide an improved process for the substantially complete roasting of finely-divided sulfides at very high throughput rates per unit of hearth area.

Another object of the invention is to provide a process for suspension roasting finely-divided sulfides whereby fractions thereof are recovered from the exhaust gases and recirculated through the roasting operation in an amount bearing a minimum ratio relationship to the amount of raw sulfide feed entering the process.

It is a further object of the invention to provide a new process for suspension roasting finely-divided sulfides at high throughput rates, from which a roasted calcine of exceptionally low sulfide-sulfur content is obtained.

The invention further contemplates providing a unique process for suspension-roasting finely-divided sulfides from which gas rich in sulfur dioxide is obtained.

It is likewise within the contemplation of the invention to provide a novel suspension-roasting process having unique characteristics which permit the suspension roasting at unusually high feed rates of finely-divided sulfides to produce calcines of extremely low sulfide-sulfur contents.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying drawing wherein there is shown an elevational view partly in section of an embodiment of a suspension-roasting furnace of the fluid-bed type in which the novel process provided by the present invention can be carried out as indicated in the drawing.

Generally speaking, the present invention contemplates a novel process, an embodiment of which is schematically illustrated in the drawing, for roasting finely-divided sulfide materials at elevated temperatures to oxidize said sulfides to calcines containing very little sulfide-sulfur. The autogenous suspension-roasting process provided by the present invention yields the foregoing improved results at unusually high throughput or feed rates and high oxidizing-gas velocities by virtue of passing at least a major portion of the solids-laden, sulfur dioxide-rich exhaust gases through a gas-solids separator which separates the exhaust gases from the bulk of the entrained solids. The recovered solids are returned to the suspension-roasting operation in an amount bearing a ratio relationship to the amount of raw sulfide feed being introduced into the roasting operation such that a recirculating feed of solids is built up in the roasting operation in an amount substantially greater than the amount of incoming raw sulfide feed.

The exhaust gases, now free from the bulk of the entrained solids, may be treated to recover most of the remaining entrained solids as calcine product. The now substantially solids-free exhaust gases may then be treated in dust collectors to recover therefrom the small amounts of the finest dust still remaining in the gases.

Advantageously, a further and minor portion of solids-laden exhaust gases may be removed separately from the roaster and solids separated from this minor portion of solids-containing exhaust gases may be withdrawn as calcined product of low sulfur content.

Calcine may, if desired, be removed either intermittently or continuously from a port or ports located at various levels in the side of the roaster, in order to regulate the amount of material in the roaster bed. Roasting temperature, exposure time of the material in the roaster and the free oxygen content of the oxidizing gas are the variable operational factors controlling the desired low sulfur content in the calcine product. By employing the novel process provided by the present invention, permeable calcines having satisfactory chemical reactivity in subsequent metal-extraction operations, such as selective reduction followed by ammoniacal leaching as disclosed in U.S. Patent No. 2,556,215 or selective sulfation followed by water leaching as disclosed in U.S. Patent No. 2,719,082, are obtained. The low sulfide-sulfur content of calcined iron sulfides produced by employing the present process, if initially low in contaminating constituents such as non-ferrous metals and silica, is particularly suitable as high-grade iron oxide for direct smelting to iron and steel without further desulfurization. Where the iron ore is required in agglomerated form, methods such as briquetting, etc., can be employed.

More particularly, the present process involves suspension roasting finely-divided sulfides, such as iron sulfide concentrates, having a coarseness less than about 20 mesh and containing at least 15% sulfur, with oxidizing gases containing free oxygen, such as air, at temperatures between about 1000° F. and about 1800° F., and particularly between about 1100° F. and about 1600° F. to decrease the sulfur content, and particularly the sulfide-sulfur content, of the roasted sulfides to the extent required, depending upon the particular processing and end-use requirements subsequent to roasting. Thus, in roasting iron sulfides to obtain a calcine suitable for direct processing to high-grade iron ore, calcines having very low sulfur contents are required. On the other hand, if the calcines are to be subsequently selectively-sulfated or selectively-reduced prior to leaching, as discussed hereinbefore, somewhat higher sulfur contents can be tolerated. One of the marked advantages obtained by employing the novel process provided by the present in-

vention as compared to prior art processes is that, for comparable throughput or feed rates and roasting temperatures, calcines containing very much lower sulfide-sulfur contents are obtained. This is clearly shown by the data given in Tables I, II, III, and IV presented and discussed hereinafter.

In fluid-bed roasting finely divided sulfides by the present process, the relation between feed rate and furnace cross-section is such that gas velocities are about 2 to about 6 feet per second in the upper region of the roasting chamber. Even higher gas velocities may be employed in certain cases depending upon the particular particle size of the sulfide material being roasted, upon the feed rate of the sulfide material into the furnace, and upon other factors as those skilled in the art will understand. More usually, gas velocities of more than about 2 to about 5 feet per second will be employed. The pressure of oxidizing gas introduced into the bottom of the furnace is broadly between about 1 and about 5 pounds per square inch. In any specific case, however, the actual depth of the fluid bed places a minimum limit on the gas pressure to be employed to obtain the desired quantity of gas, as those skilled in the art will readily understand.

The exhaust gases when analyzed on a dry basis normally contain more than 7% sulfur dioxide, less than 10% free oxygen, and the balance mainly nitrogen. Where a high waste heat recovery is desired or where the gases are processed for sulfur recovery, the gases when analyzed on a dry basis usually contain 10 to 13% sulfur dioxide when pyrrhotite is being rosated, corresponding to little or no free oxygen in the exhaust gas. It was found that even with roaster temperature under 1500° F., calcine containing less than 0.1% sulfide-sulfur can regularly be produced from a 37% sulfur pyrrhotite concentrate when controlling the oxygen in the roaster exhaust gas at about 1% oxygen. This oxygen content corresponds to use of only about 5% excess air over that required to produce Fe_2O_3 and SO_2. A fluidized bed roaster has also been operated on a 20-ton per day scale using oxidizing gas containing free oxygen in an amount insufficient to oxidize the iron in the sulfide completely to hematite (Fe_2O_3), thereby producing calcine containing some of the iron as magnetite, although still containing less than 0.25% sulfur, and producing a gas virtually free from oxygen.

The bulk of the calcine carried out of the furnace with the exhaust gases is separated from these gases by means of a gas-solids separator, e.g., a cyclone-type separator (which, for convenience, may be called a primary or circulating solids-gas separator throughout the specification and claims) and returned, via a sealing device, to the roasting operation in amounts preferably equal to at least about five times the amount of incoming unroasted sulfide feed. In prior art processes employing conventional suspension roasters, many such processes and roasters involved returning to the roaster the dust collected from the outgoing gases. However, this dust has normally been only the dust unavoidably present in the gas and no prior art efforts were made to deliberately increase the solids content of the outgoing gas to a level very much higher than the raw feed introduced into the furnace in order to circulate to the roaster an amount of recovered solids preferably equal to at least about five times the amount of incoming raw feed.

By circulating the calcine through the roasting operation in a ratio of not less than about 2:1, preferably at least about 5:1, and advantageously not more than about 20:1, relative to the fresh incoming raw sulfides, sufficient retention time under roasting conditions is obtained to secure a high degree of desulfurization, even at high feed rates of the order of 1 to 2 tons per day per square foot of roaster hearth area. Sulfur present in the calcine product other than sulfide-sulfur is generally in the form of sulfate-sulfur and water leaching to remove this sulfur and/or to recover any sulfated metal values can be employed if desired. To promote sulfation, particularly of the non-ferrous metal constituents, the roasting temperature should be maintained between about 1100° F. and about 1300° F. and the exhaust gases when anlyzed on a dry basis should contain more than about 7% sulfur dioxide and less than about 10% free oxygen. Where sulfate-sulfur is objectionable in the product, it may be decreased by employing higher temperatures and by avoiding undue exposure of the calcine to sulfur-containing gases at intermediate temperatures during cooling.

When attempting to roast at high feed rates and high gas velocities in conventional fluid-bed roasters in which no efficient means is provided for returning to the roaster the material carried out in the gas, a fluidized bed of material being roasted cannot be maintained and the roaster empties itself. Consequently, important advantages of fluidized-bed roasting, including retention of the ore in the furnace under roasting conditions for appreciable lengths of time, ability to withstand prolonged operational interruptions without serious loss of temperature, and stability of operation, are lost. Due to the greatly decreased retention time of the material being roasted under appropriate conditions but at high oxidizing gas velocities, the sulfide-sulfur content of the calcine material will remain undesirably high. However, by operating in accordance with the novel process contemplated by the present invention for returning to the roaster most of the material carried out in exit gases, a gas-permeable dense phase or bed can be maintained in the roaster which, in combination with the aforesaid operations more completely described hereinafter for controlling the proportion of solids withdrawn from the circuit, permits feed rates and oxidizing gas velocities much higher than have been possible heretofore when roasting fine sulfide concentrate.

Previous investigators have presumably made an effort to determine the maximum capacity of their fluid-bed roasters, and in course of so doing would raise feed rate and gas velocity to the point where, depending on the fineness of the material being treated, a fluid bed could not be retained due to its being blown from the furnace. It has not previously been realized that use of an efficient gas-solid separator for circulating back into the roaster a large portion of the solids, deliberately blown out of the furnace by virtue of high gas velocity, would permit much higher feed rates while retaining the usual advantages of suspension-roasting and, at the same time, would permit at both moderate and high feed rates a much more complete desulfurization of the calcine than has heretofore been possible, especially when employing temperatures at which a reactive calcine is produced.

A bed, containing relatively coarse particles not readily blown out of the roaster, can be employed.

As an optional feature of the present invention, the desired depth of bed or dense phase in the suspension roaster can be controlled by means to by-pass the circulating solids-gas separator in such a manner that a controlled proportion of the solids-containing exhaust may be directly withdrawn from the roasting operation without passing through the circulating gas-solids separator. However, if it is desired to maintain constant the amount of dense body of material in the roaster, i.e., maintain a constant bed depth, the fraction of solids-containing exhaust gas permitted to by-pass the circulating solids-gas separator must be less than the reciprocal of the ratio of circulated or returned solids to incoming raw feed. For example, when employing a circulating load of recovered solids equal to 20 times the incoming raw feed, less than one-twentieth of the total exhaust gas can be withdrawn through the by-pass, otherwise the amount of dense material within the roaster would be depleted. The circulation rate can be controlled by employing any of the well-known means for regulating the volume of gas bypassing the circulating solids-gas separator. For example,

by means of a damper, fan, or other type of control unit in the by-pass, the solids-containing roaster exhaust gas can be split into two fractions with the major volume bearing a definite relationship to the minor volume. To obtain calcines that are highly desulfurized, and to maintain high feed rates, it is desirable that the ratio of the major volume of gas passing through the circulating solids-gas separator to the volume by-passing it, should not be less than about 2:1, preferably at least about 5:1, and advantageously not more than about 20:1. By-pass calcine can be recovered from the exhaust gas in the same operation employing the same equipment as calcine recovered from the gas leaving the circulating operation and equipment; or, the by-pass calcine can be recovered separately.

Where delivery of the finished calcine at a high elevation is not required, the amount of dense phase in the roaster may be regulated by withdrawing calcine at a selected level or levels from the side of the roasting chamber above the bed level except when operating the roaster at below normal capacity. When such withdrawal of calcine from the side of the roasting chamber is employed, it is normally continuous, but it may be intermittent. The port or ports for controlled withdrawal of calcine from the roaster are situated well above the bed level, in contrast to the overflow ports employed in conventional fluid-bed roasters in which roasted material is discharged through an overflow at the upper rim of the turbulent bed. A screw discharge, level with the top of the bed, has also been found useful in maintaining a constant bed level, especially when operating the roaster at below normal feed rate.

It has also been found that by utilizing the high circulating loads characteristic of the present invention, the operating range of feed rates over which the roaster will perform satisfactorily is markedly increased.

I have no knowledge of any prior art processes for roasting of iron sulfides (even when employing high temperatures of up to 2000° F. which would tend to clinker the calcine and render it unfit for subsequent leaching) which permit as complete a sulfur elimination under commercial conditions as does the present process.

The temperature of the roaster can, if desired, be effectively controlled by various means, such as by the use of cooling coils inserted in the calcine bed, the heat extracted from said bed via the cooling coils being employed to generate steam. Another means of controlling the temperature of the roaster, particularly when the temperature is to be maintained between about 1100° F. and about 1600° F., is partially to cool the calcine circulated or returned to the roaster. In cases where the oxygen content of the exhaust gas is not critical, temperature of the roaster may be finally adjusted by variation in the ratio of air or water to sulfide feed introduced into the furnace.

An embodiment of a suspension roasting apparatus for carrying the invention into practice and including a kiln, namely a roaster of the fluid-bed type, is depicted in the drawing. Finely-divided sulfide feed is introduced into the main or roasting chamber **2** of the roaster through at least one feed port **1** which may be provided with suitable means to prevent gases flowing out through the feed port or ports. The chamber **2** may be constructed of insulating refractory lining **3** held within an impervious steel shell **4**. The furnace chamber **2** may be provided with suitable burners (not shown), well known to those skilled in the art, for the purpose of pre-heating the chamber to a selected temperature in order to initiate the exothermic roasting reaction between the finely-divided sulfides which are undergoing autogenous suspension roasting and the free oxygen of the oxidizing gas. Oxidizing gas containing free oxygen, for example, air, for roasting the finely-divided sulfides in suspension in chamber **2**, is introduced under a suitable pressure, which may be, for example, about 2 pounds per square inch, through supply pipe **5** to wind box **6**, from where it flows into the preheated furnace chamber **2** through ports **7**. The ports **7** may be fitted with devices for preventing back flow of calcine when oxidizing gas flow is stopped, such as conventional bubble caps **8**. Calcine is permitted to accumulate in the form of a fluidized bed **9**, which may have a depth, for example, of about 1 to 4 feet, and which may be prevented from rising further by means described hereinafter. There may be a rather indistinct line of division between the fluidized bed in the lower portion of the roasting chamber **2** and the solids-laden gases in the upper portion of the roasting chamber due to the high gas velocities and the heavy dust burden in the roaster gases of not less than about three times the burden based on the fresh sulfide feed rate employed in the roaster of this invention. Temperature of the fluid-bed may be controlled by means of cooling pipes **10**, located in the fluid-bed which may also serve to produce steam for useful purposes, and by means for adjustment in the ratio of oxidizing gas, such as air, or water to ore introduced into the furnace as well as by other means. Temperature of the fluid bed can also be controlled by separate regulation of the oxidizing gas entering the zone of the roaster most closely associated wtih the cooling pipes **10**. As depicted in the drawing, the control of the oxidizing gas may be obtained by dividing the wind box **6** with barriers **11** permitting regulation of the flow of oxidizing gas from the oxidizing gas supply pipe **5** to each of the portions of the wind box formed by the barriers **11**. The temperature of the roaster may also be controlled by partially cooling the calcine circulated to the roaster, as pointed out hereinbefore. Hot combustion gases, rich in SO_2 and entrained solids, rise to the exit port **12** in the upper region of the roasting chamber **2** from where they are passed via a conduit **22** to the primary or circulating solids-gas separator, e.g., cyclone **13**, which desirably is located externally of the roasting chamber **2**. From the primary solids-gas separator **13** the gases may proceed to a secondary solids-gas separator, e.g., calcine collector or collectors **14**, and then to a gas cleaner **15**. Advantageously, at least 80% of the solids leaving the furnace via port **12** may be returned via calcine return port **16** to the main furnace chamber. The solids removed from the exhaust gases in the circulating solids-gas separator **13** may be passed through a sealing device **25** at the bottom of the solids-gas separator **13** and return to the roasting chamber **2** via solids-return conduit **26** and calcine return port **16**, which advantageously may be located in the roaster wall at a level above the raw sulfide feed port or ports **1**. When the temperature of the roaster is to be controlled by partially cooling the calcine to be circulated to the roaster, a cooling means **21** is provided which advantageously may be located in the line of the conduit **22** between the exhaust port **12** and the primary or circulation solids-gas separator **13** are depicted in the drawing. Solids separating out from the exhaust gases in the cooling means **21** may be returned to the roasting chamber **2**, for example, via conduit **27** connecting the cooling means **21** with the solids-return conduit **26**. The aforementioned location of the cooling means **21** is particularly advantageous because the exhaust gases leaving port **12** as well as the solids to be circulated to the roaster are thereby cooled. However, the means for cooling solids to be circulated back to the roaster may be located anywhere in the solids circulating system from exhaust port **12** to return port **16**, comprising line or conduit **22**, primary solids-gas separator **13** and solids-return line or conduit **26**.

Depth of fluid bed present in the furnace can be controlled by providing side-discharge ports **17**, having controlled opening and closing means **28**, at various levels above the level at which it is desired to maintain the top of the fluid bed.

As disclosed hereinbefore, the depth of the fluid bed

can be maintained constant or varied by controlling the amount of solids-laden exhaust gas by-passing the circulating solids-gas separator **13** in various ways. In the embodiment depicted in the drawing, a by-pass port **18** is provided in the upper region of the roasting chamber **2**. The by-pass port **18** advantageously may be of a smaller size than the exit port **12** leading to the primary or circulating solids-gas separator **13**, such that the bulk or major portion of the solids-containing exhaust gases pass to the circulating solids-gas separator **13** and a further and minor portion of the solids-containing exhaust gases is separately withdrawn from the roaster through by-pass port **18**. The exhaust gases withdrawn through by-pass port **18** are passed through exhaust gas line or conduit **29** to the secondary calcine collectors **14** where the entrained solids are withdrawn as a calcine product of low sulfur content. If desired, the line or conduit **29** may conduct the minor portion of solids-laden exhaust gases to a calcine collector or collectors (not shown) other than the collectors **14** for separate removal and withdrawal of the entrained solids from this minor portion of the exhaust gases. A fan or damper or some other type of control unit **20** may be provided in the exhaust gas line or conduit **29** and serves as means for regulating the relative flow of solids-laden exhaust gases out of the two exhaust ports **12** and **18**. The gases passing upwards through the roaster may be maintained at such high rates and velocities as will entrain and carry out of the roaster the entire roasted feed particles which may then be separated from the exhaust gases and withdrawn from the apparatus as calcine product of low sulfur content. The recovery of the entire product as finely-divided solids separated from the exhaust gases is exemplified in the data presented in the third test run of Table I hereinafter presented and discussed. Accordingly, the suspension roaster advantageously may be operated so that regulation of the circulating load of solids may be obtained by proportioning of the two portions of solids-laden exhaust gases to each other. Thus, a controlled proportion of the solids-laden exhaust gases may be withdrawn directly from the roaster through by-pass port **18** without passing through the circulation solids-gas separator **13** so that the volume of exhaust gases withdrawn from the roasting operation via the circulation solids-gas separator **13** may be not less than about twice the volume of exhaust gas directly withdrawn from the roaster through by-pass **18** without passing through the circulation solids-gas separator.

Equilibrium between the amounts of incoming raw sulfide and outgoing calcine may be controlled by the aforementioned means for withdrawing calcines from the roaster.

The sulfur-dioxide-rich gases are substantially cleaned of entrained solids by use of dust-recovery equipment or gas cleaner **15** prior to treatment of the gases for the recovery of sulfur dioxide therefrom. Solid residue, including oversize particles which are not entrained in and removed by exhaust gases leaving the furnace chamber, may be removed from the hearth of the furnace chamber by any suitable means, such as a clean-out port located at or near the hearth level of the furnace chamber.

In carrying the invention into practice on ore which is to be subsequently leached, it is preferred to roast the finely-divided iron sulfide concentrates, e.g., pyrrhotite, at a coarseness of not more than approximately 10% plus 200 mesh in a roaster of the fluid-bed type such as described hereinbefore and illustrated in the drawing. In cases where the calcine is not to be subsequently leached, sulfide feeds of much coarser particle size can be successfully treated by the present process.

For the purpose of giving those skilled in the art a better understanding of the present invention and the marked advantages accruing therefrom, the following illustrative examples are given:

Finely-divided pyrrhotite concentrates containing 36% sulfur and about 5% silicate gangue were fed into a vertical fluid-bed roaster, preheated to a temperature above about 1000° F., having an inside diameter of about 2 feet, and substantially of the structure shown in the drawing. The calcine was allowed to build up to bed depths between about 1 foot and about 3 feet. Air in an amount slightly in excess of that theoretically required to burn the pyrrhotite to Fe_2O_3 and SO_2 was introduced through a perforated hearth having conventional provision for prevention of calcine flow in the opposite direction when the air was shut off. The results obtained in roasting the aforementioned concentrates at various feed rates and at various temperatures within the temperature range provided by the present invention are given in the following table:

Table I

Sulfide Feed Rate, lb./hr.	Roasting Temp., ° F.	Exhaust Gas		Calcine		Percent Calcine Removed via—		Bed Depth in Roaster, in.	Recirculation rate, lb./hr.	Ratio Recirculation v. Feed
		Percent SO_2	Percent O_2	Percent Sulfide Sulfur	Percent Total Sulfur	Side Discharge Port 17	Calcine Collector 14			
150	1400	10.6		.09	.75	51	49	26	900	6
150	1600	12.4		.03	.34	74	26	31	1,100	7
230	1550	13.0	1.6	.10	.25	Nil	100	10	5,000	22
330	1510	13.0		.17	.38	34	66	10	20,000	60

The tests from which were obtained the data given in the foregoing Table I were repeated, with the exception that recirculation of calcine was omitted. The data obtained in this second series of tests are given in the following table:

Table II

Sulfide Feed Rate, lb./hr.	Roasting Temp., ° F.	Exhaust Gas		Calcine		Percent Calcine Removed via—		Bed Depth in Roaster, in.	Recirculation, lb./hr.
		Percent SO_2	Percent O_2	Percent Sulfide Sulfur	Percent Total Sulfur	Side Discharge Port 17	Calcine Collector 14		
150	1490	12.1	2.5	.54	1.55	86	14	16	Nil
150	1600	11.0	3.5	.44	.80	81	19	16	Nil
333 [1]									Nil

[1] Inoperable in the fluid-bed roaster in this series of tests where recirculation of calcine is omitted.

A comparison of the data in Table I with those in Table II clearly discloses at once the marked advantages obtained by employing the high circulation ratios which are an essential feature of the present invention. Not

only does the process provided by the present invention obtain much more complete elimination of sulfur at moderate furnace feed rates, but it also permits the advantages of fluid-bed roasting to be realized at much higher feed rates in a furnace of given size than is possible when employing conventional fluid-bed roasting practice.

As another example of the unusually low sulfide-sulfur contents obtainable in calcines treated in accordance with the present invention, tests were conducted at moderate feed rate on roasting finely-divided pyrrhotite concentrate having the same composition disclosed in the previous example in a fluid-bed roaster having an internal diameter of 7½ feet. The test results are given in the following table:

Table III

Sulfide Feed Rate, Tons/Day	Roasting Temp., ° F.	Exhaust Gas, Percent SO_2	Calcine		Approximate Percent Calcine Removed via—		Ratio Recirculation v. Feed
			Percent Sulfide Sulphur	Percent Total Sulphur	Side Discharge Port 17	Calcine Collector 14	
21	1,600	12–13	.04	.10	80	20	10
31	1,630	12–13	.07	.18	70	30	20
25	1,665	11–12	<.05	<.10	75	25	12

As an example of the effectiveness of the present invention on producing calcines with a high degree of desulfurization when operating at very high feed rates in large scale practice, tests were conducted on finely-divided pyrrhotite. The roaster employed in these tests comprised a refractory-lined cylindrical steel shell 43 feet in height from hearth to roof brick. The inside diameter for 6 feet above the hearth was 22 feet, then increased to 26 feet through a vertical rise of 12 feet and remained at 26 feet up to the top of the roaster. A six foot diameter off-take or exhaust port in the roof led to the circulation or solids-return system which included a cooler, solids-gas separators and means for returning the separated solids back to the roasting operation. A second off-take, or by-pass port, 2½ feet in diameter led to the production system which included solids-gas separators that removed over 75% of total calcine production. The remainder of the calcine production was removed by secondary solids-gas separators treating the gas leaving both the circulation or solids-return system and the production system. Slurry feed of the sulfide material to be roasted was introduced into the roaster through four feed ports which discharged into the roaster 8.5 feet above the grate or hearth. Some water, additional to that in the slurry feed, was added at the feed ports in one of the tests for temperature control. The test results are given in the following table:

Table IV

	Test A	Test B
Feed rate in tons/day of pyrrhotite	550	550
Percent solids in pyrrhotite slurry feed	75	75
Percent sulfur in pyrrhotite	34	34
Percent plus 200 mesh	11	11
Roaster control temperature, ° F.	1400	1380
Volume of solids-containing gas in cubic feet per minute, to circulation system (at 1,320° F.)	96,100	83,300
Volume of solids-containing gas, in cubic feet per minute, to the production system (at 1,320° F.)	13,800	18,000
Ratio of major volume of solids-containing gas to circulation system/minor volume of solids-containing gas to production system	7:1	4.6:1
Additional water added to roaster	Nil	About 5 g.p.m.[1]
Calcines from production system:		
Percent total sulfur	0.15	0.2
Percent magnetite	10	10
Percent hematite	90	90
Gas from roaster:		
Percent SO_2 (dry basis)	13	13
Percent O_2	<0.2	<0.2

[1] G.p.m.=gallons per minute.

It is seen that in the tests reported in Table III and Table IV remarkably high elimination of sulfur was obtained, together with a satisfactorily high recoverable sulfur dioxide content in the exhaust gas, in spite of moderate roasting temperatures of the order of about 1600° F. and of the order of about 1400° F. having been employed.

While the preferred roaster contemplated by the present invention is of the fluidized-bed type, it is also within the purview and scope of the invention to employ a roaster of the flash type in carrying out the present process. As in the case of the fluid-bed roaster illustrated in the drawing, the controlled circulation of the bulk of the solids carried out of the roaster by the exhaust gas is obtained in the same manner.

This application is a continuation-in-part of my co-pending U.S. application Serial No. 356,756, filed May 22, 1953, now abandoned.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Thus, sulfides other than iron sulfide, e.g., nickel sulfide, cobalt sulfide, copper sulfide, etc., can be successfully calcined by employing the novel process and apparatus provided by the present invention. Furthermore, although air per se has been disclosed as the preferred oxidizing gas, nevertheless, in certain cases, it may be desirable to employ oxidizing gases containing free oxygen in concentrations higher than the oxygen content of air, e.g., oxygen-enriched air. Likewise, certain cases may require that the free oxygen content of the oxidizing gas be less than that of air, e.g., air diluted with combustion gases or exhaust gases containing sulfur dioxide. Also, the finely-divided solids may be introduced to the roaster in the form of a slurry, or water may be introduced separately for temperature control. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim :

1. A process for suspension roasting finely-divided iron sulfide to obtain calcines of low sulfur contents which comprises feeding the finely-divided iron sulfide having a particle size of less than about 20 mesh and containing at least 15% sulfur into a fluid-bed roasting operation to establish a gas-permeable bed of solids; controlling the temperature of said bed between about 1000° F. and about 1800° F. while passing upwardly therethrough an oxidizing gas containing free oxygen at a volume sufficient to roast said sulfide and to fluidize said bed; separating from the solids-containing exhaust gases the bulk of the solids entrained therein; returning the separated solids to the fluid bed in an amount equal to at least about 5 times the amount of unroasted sulfide being fed to said fluid-bed roasting operation; and withdrawing a calcine product of low sulfur content.

2. The process set forth in claim 1 in which the temperature of the fluid bed of iron sulfide being roasted is controlled by cooling with a fluid medium via a heat-exchange wall.

3. The process set forth in claim 1 in which the temperatures of the fluid bed of iron sulfide being roasted

is controlled by lateral distribution of the amount of oxidizing gas passing upwardly through the fluid bed.

4. A process for suspension roasting finely-divided metallic sulfide to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; subjecting said finely-divided sulfide to suspension roasting at elevated temperatures in the presence of oxidizing gas containing free oxygen; separating from the solids-containing exhaust gases the bulk of the solids entrained therein; returning the separated solids to the suspension-roasting operation in an amount equal to at least about 5 times the amount of unroasted sulfide being fed to said suspension-roasting operation; and withdrawing a calcined product low in sulfur content.

5. The process set forth in claim 4 in which the particle size of the sulfide is less than about 20 mesh, the suspension-roasting temperature is between about 1000° F. and about 1800° F., and the weight ratio of solids recovered from the exhaust gases and returned to the roasting operation to the unroasted sulfide being fed to said roasting operation is between about 5:1 and about 100:1.

6. The process set forth in claim 4 in which the sulfide is fluid-bed roasted and in which the fluid-bed level is controlled by regulated withdrawal of calcine at a level above the fluid-bed level.

7. The process set forth in claim 4 in which the temperature of the sulfide material being suspension-roasted is controlled by cooling with a fluid medium via a heat-exchange wall.

8. The process set forth in claim 4 in which the finely-divided sulfide is fluid-bed roasted by passing upwardly therethrough an oxidizing gas containing free oxygen at volumes sufficient to roast said sulfide and to obtain gas velocities above the bed of the order of about 2 to about 5 feet per second.

9. A process for the fluid-bed roasting of finely-divided metallic sulfides to obtain calcines of low sulfur contents which comprises feeding the finely-divided metallic sulfides into a fluid bed roaster to establish a gas-permeable bed of solids; passing an oxidizing gas containing a substantial proportion of free oxygen upwardly through the bed of finely-divided solids at a volume sufficient to roast said sulfides at an elevated temperature and to fluidize said bed; withdrawing solids-containing exhaust gases from the roaster; separating the bulk of the solids from said solids-containing exhaust gases; returning the separated solids to the fluid bed in an amount equal to at least about 5 times the amount of unroasted sulfides being fed into the roaster; controlling the depth of fluidized bed in the fluid bed roaster by regulated withdrawal of a further portion of solids-containing exhaust gases from the fluid bed roaster; mixing the exhaust gases from which the bulk of the solids has been removed with said further portion of solids-containing exhaust gases; and separating and recovering from said mixed exhaust gases substantially all the solids entrained therein to obtain calcine product of low sulfur content.

10. A process for suspension roasting finely-divided metallic sulfide to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; subjecting said finely-divided sulfide to suspension roasting at elevated temperatures in the presence of oxidizing gas containing free oxygen; withdrawing solids-containing exhaust gases from the roasting operation; cooling and separating from the solids-containing exhaust gases the bulk of the solids entrained therein; returning the separated solids to the suspension-roasting operation in an amount equal to at least about 5 times the amount of unroasted sulfide being fed to said suspension-roasting operation; and withdrawing a calcined product low in sulfur content.

11. A process for suspension roasting finely-divided metallic sulfide to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; subjecting said finely-divided sulfide to suspension roasting at elevated temperatures in the presence of oxidizing gas containing free oxygen; separating from the solids-containing exhaust gases the bulk of the solids entrained therein; returning the separated solids to the suspension-roasting operation in an amount equal to not less than about two times the amount of unroasted sulfide being fed to said suspension-roasting operation; and removing a further and minor portion of solids from the exhaust gases, in an amount substantially equal to the unroasted sulfide feed, as calcine product of low sulfur content.

12. A process for suspension roasting finely-divided metallic sulfide to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; passing through the roasting operation an oxidizing gas containing free oxygen to roast said sulfide; maintaining the gases passing upwards through the roasting operation at such high velocities as will entrain substantially all the roasted feed particles in the exhaust gases carried out of the roasting operation; separating from the exhaust gases carried out of the roasting operation a major portion of the solids entrained therein; returning the separated solids to the roasting operation in an amount greater than the amount of unroasted sulfide being fed to said suspension-roasting operation; and removing a further and minor portion of solids from the exhaust gases, in an amount substantially equal to the unroasted sulfide feed, as calcine product of low sulfur content.

13. A process for suspension roasting finely-divided metallic sulfides to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; passing through the roasting operation an oxidizing gas containing free oxygen to roast said sulfide; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all the roasted finely-divided feed particles will be entrained in the exhaust gases carried out of the roasting operation; withdrawing the solids-containing exhaust gases from the roasting operation in two portions of different volume, in which the volume of the major portion of exhaust gases is not less than about two times the volume of the minor portion of exhaust gases; separating from the major portion of exhaust gases the bulk of the solids entrained therein; returning the separated solids to the roasting operation in an amount equal to at least about two times the amount of fresh sulfide feed; and separating from the minor portion of exhaust gases solids entrained therein, in an amount substantially equal to the unroasted sulfide feed, as calcine product of low sulfur content.

14. A process for suspension roasting finely-divided metallic sulfides to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; passing through the roasting operation an oxidizing gas containing free oxygen to roast said sulfide; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all the roasted feed particles will be entrained in the exhaust gases carried out of the roasting operation; withdrawing the solids-containing exhaust gases from the roasting operation in two portions of different volume, in which the volume of the major portion of exhaust gases is at least about five times the volume of the minor portion of exhaust gases and the major portion of exhaust gases contains entrained solids equal in amount to at least about five times the amount of unroasted sulfide being fed to the suspension-roasting opera-

tion; separating from the major portion of exhaust gases the bulk of the solids entrained therein; returning the separated solids to the roasting operation; and removing a further and minor portion of solids from the exhaust gases in an amount substantially equal to the unroasted sulfide feed, as calcine product of low sulfur content.

15. A process for suspension roasting finely-divided metallic sulfides to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; passing through the roasting operation an oxidizing gas containing free oxygen to roast said sulfide; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all the roasted feed particles will be entrained in the exhaust gases carried out of the roasting operation; withdrawing the solids-containing exhaust gases from the roasting operation in two portions of different volume, in which the volume of the major portion of exhaust gases is at least about five times and not more than about twenty times the volume of the minor portion of exhaust gases; separating from the major portion of exhaust gases the bulk of the solids entrained therein; returning the separated solids to the roasting operation in an amount more than about five times and less than about twenty times the amount of unroasted sulfide being fed to said suspension-roasting operation; and removing a further and minor portion of solids from the exhaust gases, in an amount substantially equal to the unroasted sulfide feed, as calcine product of low sulfur content.

16. A process for roasting metallic sulfides to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; passing upwardly through the roasting operation an oxidizing gas containing free oxygen in an amount insufficient to oxidize the iron in the sulfide completely to Fe_2O_3 thereby leaving some of the iron as magnetite; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all of the roasted feed particles will be entrained in the exhaust gases carried out of the roasting operation; withdrawing the solids-containing exhaust gases from the roasting operation in two portions of different volume, in which the volume of the major portion of exhaust gases is not less than about two times the volume of the minor portion of exhaust gases; separating from the major portion of exhaust gases the bulk of the solids entrained therein; returning the separated solids to the roasting operation in an amount not less than about two times the amount of unroasted sulfide being fed to said suspension-roasting operation; and separating from the minor portion of exhaust gases solids entrained therein in an amount substantially equal to the unroasted sulfide feed as calcine product of low sulfur content, the exhaust gases thus substantially freed from entrained solids providing a gas containing sulfur dioxide substantially devoid of free oxygen.

17. A process for roasting metallic sulfides to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; passing upwardly through the roasting operation an oxidizing gas containing free oxygen at a volume sufficient to roast said sulfide; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all of the roasted feed particles will be entrained in the exhaust gases carried out of the roasting operation; withdrawing the solids-containing exhaust gases from the roasting operation in two portions of different volume, in which the volume of the major portion of exhaust gases is not less than about two times the volume of the minor portion of exhaust gases; separating from the major portion of exhaust gases the bulk of the solids entrained therein; returning the separated solids to the roasting operation in an amount not less than about two times the amount of unroasted sulfide being fed to said suspension-roasting operation; regulating the temperature of the roasting operation by cooling the solids to be returned to the roasting operation between their withdrawal from the roasting operation in the major portion of solids-containing exhaust gases and their return to the roasting operation; and separating from the minor portion of exhaust gases solids entrained therein in an amount substantially equal to the unroasted sulfide feed as calcine product of low sulfur content.

18. A process for roasting metallic sulfides to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; passing upwardly through the roasting operation an oxidizing gas containing free oxygen at a volume sufficient to roast said sulfide; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F.; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all of the roasted feed particles will be entrained in the exhaust gases carried out of the roasting operation; withdrawing the solids-containing exhaust gases from the roasting operation in two portions of different volume, in which the volume of the major portion of exhaust gases is not less than about two times the volume of the minor portion of exhaust gases; separating from the major portion of exhaust gases the bulk of the solids entrained therein; returning the separated solids to the roasting operation in an amount not less than about two times the amount of unroasted sulfide being fed to said suspension-roasting operation; regulating the temperature of the roasting operation by cooling the major portion of solids-containing exhaust gases withdrawn from the roasting operation before the bulk of the entrained solids are removed therefrom for return to the roasting operation; and separating from the minor portion of exhaust gases solids entrained therein in an amount substantially equal to the unroasted sulfide feed as calcine product of low sulfur content.

19. A process for suspension roasting finely-divided metallic sulfide to obtain calcines low in sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; controlling the temperature of the roasting operation between about 1000° F. and about 1800° F. by regulated introduction of water into the roasting operation; passing upwardly through the roasting operation an oxidizing gas containing free oxygen at a volume sufficient to roast said sulfide; maintaining the feed rate of metallic sulfide and the velocity of the oxidizing gas such that substantially all the roasted feed particles will be entrained in the exhaust gases carried out of the roasting operation; separating from the exhaust gases carried out of the roasting operation a major portion of the solids entrained therein; returning the separated solids to the roasting operation in an amount greater than the amount of unroasted sulfide being fed to said suspension-roasting operation; and removing a further and minor portion of solids from the exhaust gases, in an amount substantially equal to the unroasted sulfide feed, as calcine product of low sulfur content.

20. A process for suspension roasting finely-divided metallic sulfide to obtain calcines low in sulfide sulfur content which comprises feeding the finely-divided metallic sulfide into a suspension-roasting operation; regulating the temperature of the roasting operation at a level between about 1100° F. and about 1300° F. to obtain a desired degree of sulfation of the feed particles; passing upwardly through the roasting operation an oxidizing gas containing free oxygen at a volume sufficient to roast said

metallic sulfide and produce gases containing more than about 7% sulfur dioxide and less than about 10% free oxygen and at such velocities as will entrain substantially all the roasted feed particles in the gases carried out of the roasting operation; separating from the exhaust gases carried out of the roasting operation a major portion of the solids entrained therein; returning the separated solids to the roasting operation in an amount greater than the amount of unroasted sulfide being fed to said suspension-roasting operation; and removing a further and minor portion of solids from the exhaust gases, in an amount substantially equal to the unroasted sulfide feed, as calcine product with the desired degree of sulfation; and leaching the product to recover sulfated metal values.

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