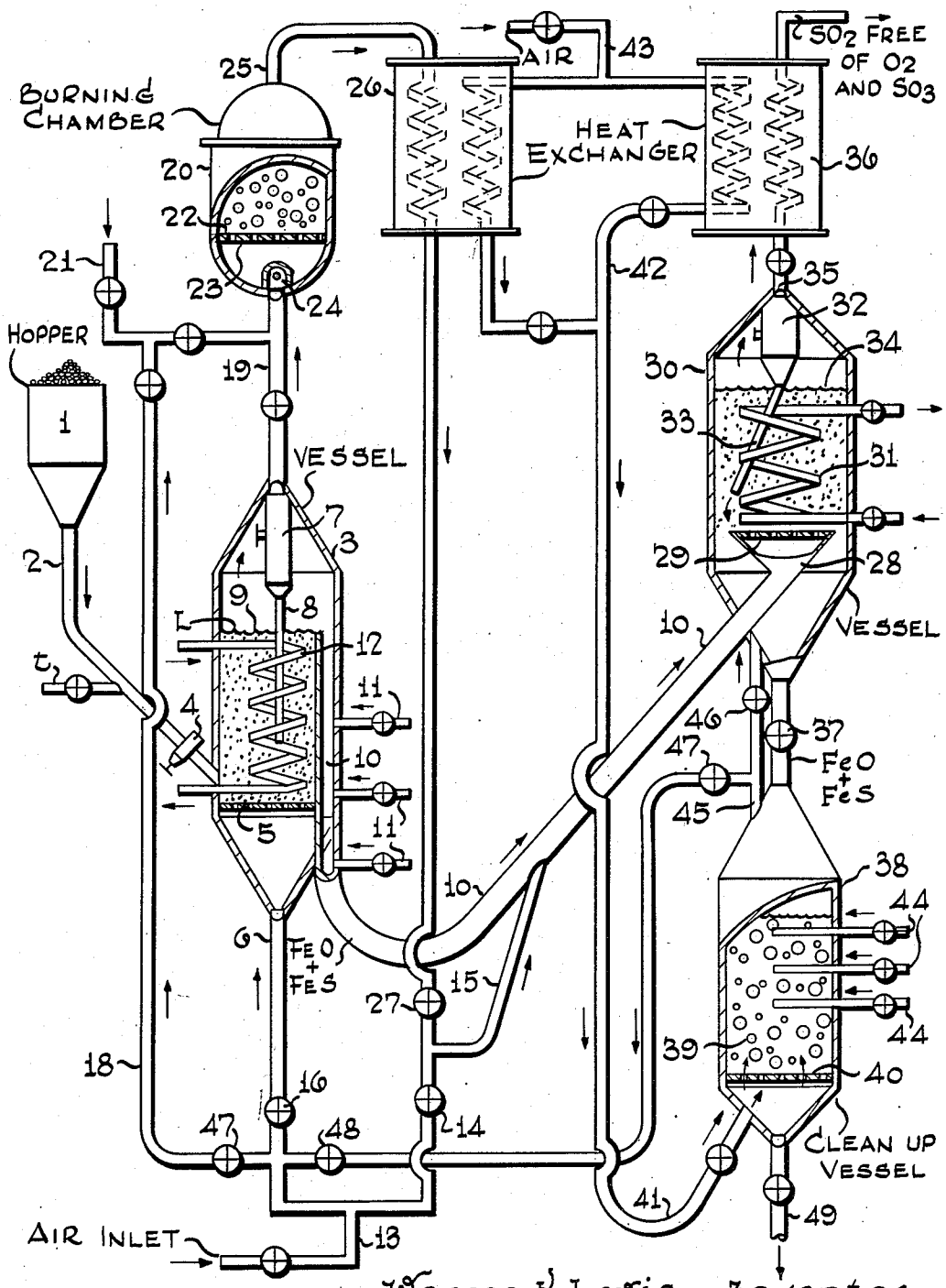
July 6, 1954 W. K. LEWIS 2,683,077

ROASTING SULFIDE ORES

Original Filed June 2, 1947



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Patented July 6, 1954 2,683,077

UNITED STATES PATENT OFFICE

2,683,077

ROASTING SULFIDE ORES

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Continuation of application Serial No. 751,780, June 2, 1947. This application June 12, 1952, Serial No. 293,051

3 Claims. (Cl. 23—177)

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This application is a continuation of Serial No. 751,780 filed June 2, 1947, now Patent No. 2,637,629 dated May 5, 1953.

The present invention is directed to a method for roasting sulfide ores, particularly pyrites.

In the roasting of sulfide ores, of which pyrites is the most commonly employed, for the production of SO_2 for use as such or for conversion to its salts, the principal objective is to produce a gas substantially free from SO_3, excess oxygen and sulfur vapor. Sulfur vapor, if contained in the final product, condenses on cooling surfaces when it is sought to liquefy the SO_2 and interferes with cooling. Excess oxygen oxidizes SO_2 to SO_3 when the SO_2 is dissolved in aqueous solution as such or in the form of sulfites or bysulfites. Hitherto difficulty has been encountered in achieving this objective.

The principal object of the present invention is the provision of a method for producing from sulfide ores SO_2 substantially free from SO_3, free oxygen and elemental sulfur.

Another objective in the roasting of sulfide ores is the complete recovery of the sulfur from the ore. In the case of pyrites, this is particularly important because the presence of residual sulfur in the cinder renders the latter unusable for many purposes, for example, as charge to an iron blast furnace or as a catalyst or catalyst base. It is an additional object of the present invention to insure substantially complete elimination of sulfur from the sulfide ore.

Briefly, in the method of the present invention, the sulfide ore is processed in finely divided form. It is preferred that the ore be ground to a size such that substantially all of it will pass through 100 mesh screen. For the best performance the ground ore should include a wide range of particle sizes ranging upwardly from about 20 microns to about 100 mesh with a large proportion of material between about 200 and 400 mesh.

In essence, the method of the present invention resides in the processing of the ore in stages, the initial distillation and partial oxidation occurring in a first stage with the finely ground ore in a fluidized condition, the residual partially oxidized ore being further oxidized in a second stage, again in a fluidized condition so as to bring the sulfide content down to a very low level, and the residual ore from this stage being subjected to a clean-up stage. It is a feature of the present invention that the oxidation of the vaporized sulfur from the initial ore is substantially segregated from the distillation step proper. Another feature of the present invention is that

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sintering temperatures are avoided at all points where solids are present.

Other features of the present invention will be evident from the following detailed description of the accompanying drawing in which the single figure is a front elevation in diagrammatic form of a plant suitable for the practice of the present invention.

Referring to the drawing in detail, numeral 1 designates a hopper for ground sulfide ore having a drop leg 2 which discharges into the bottom portion of a vessel 3 which may be termed a distillation zone. The drop leg is provided with a suitable feed control valve 4 and may also be provided with suitable aeration jets so as to maintain the powdered material therein in an aerated condition.

The vessel 3 is provided near its bottom, preferably below the point of entry of the drop leg 2, with a grid or grate 5 below which is an inlet line 6 for air, pure oxygen, or oxygen-enriched gas. At its upper end the vessel 3 is provided with an internal cyclone 7 having a dip leg 8 which terminates at a point in the reactor where the solid is present in the form of a dense suspension. To achieve such a suspension, the velocity of the gas introduced through line 6 through the vessel is maintained at a value between about ½ and 5 ft./second, preferably about 1 and 3 ft./second. At velocities in this range the powdered material exists in the form of a dense, fluidized suspension having a definite upper level such as indicated by 9. By dense is meant a suspension containing at least 6% by volume of solid, and, preferably, between 10 and 25% by volume of solid. The exact density of the suspension will depend on the rate of feed of the solid as well as on the velocity of the gas. With enough solid in the zone to provide a given density at a given velocity, this density can be maintained by feeding solid at the same rate at which it is withdrawn from the vessel.

Vessel 3 is also provided with a dense phase drawoff 10 which in the embodiment shown is in the form of a duct arranged along one side of the vessel having its open upper end terminating at about the level desired for the dense phase in the reactor so that solid material can overflow from the dense phase into the drawoff. Suitable aerating jets 11 are provided along the duct 10 to maintain the material therein in an aerated condition.

Vessel 3 is also provided with an internal coil 12 through which may be circulated a cooling medium suitably selected with regard to the tem-

perature to be maintained in the vessel 3. It will be understood that other forms of heat exchange devices may be employed and that a simple coil is depicted for illustrative purposes only.

Air or other oxygen-containing gas enters the system at several points. One of these points is designated by 13. Gas from this point of entry supplies the inlet 6 and, by suitable manipulation of valve 14, also helps to supply line 15 which discharges into a line which is a continuation of drawoff duct 10. By suitable manipulation of valves 16 and 17 air from this source may also be divided between inlet line 6 and line 18 which connects with a line 19 conducting gas from the upper end of vessel 3 to an upper burning chamber 20. A supplemental supply of air or other oxygen-containing gas may be introduced into the system at this point through line 21.

The chamber 20 may assume any desired form and may be, as shown, filled with packing 22 such as Raschig rings, ceramic balls, or the like, resting on a grate or grid 23. It is preferred that the gases entering chamber 20 pass through a mixing device 24 so as to insure thorough mixing of the components.

Combustion gas leaves the upper end of burning zone 20 through a line 25 which passes through a heat exchanger 26 and thereafter connects with line 15 through valve 27.

The fluidized solid leaving vessel 3 through duct 10 passes through a continuation of this duct, in which its movement is facilitated by gas entering through line 15, and discharges through a funnel-shaped member 28 covered with a suitable grid 29 into a vessel 30, which may be similar in construction to vessel 3. This vessel is also provided with internal cooling means represented by coil 31 and with an internal cyclone 32 having a dip leg 33 extending below the level 34 of the suspension of fluidized solid maintained in this vessel. Gas leaves the upper end of this vessel through a line 35 which passes through a heat exchanger 36 and thence to storage or to recovery apparatus in which it is further processed.

Solid material leaves the bottom of the vessel 30 through a star feeder 37 which discharges the solid into the upper portion of a vessel 38. This is a clean-up vessel in which residual sulfur is removed from the ore. In the embodiment shown, this vessel is filled with packing 39 in the form of Raschig rings, ceramic balls, or the like, resting on a grate or grid 40. Hot air or other oxidizing gas is fed into the bottom of this vessel through line 41 which receives this gas from a loop 42 which includes both preheaters 26 and 36 and which receives fresh gas through line 43.

Vessel 38 is also provided at various levels with cold air inlets 44. Gas leaves the upper end of vessel 38 through line 45 and may be conducted by suitable manipulation of valve 46 through vessel 30 or, by suitable manipulation of valve 47 and valve 48, to line 18. It will be understood that part of this gas may, if desired, be caused to pass through vessel 3. Residual Fe_2O_3 is removed from the bottom of vessel 38 through bottom drawoff line 49.

The first thing that happens when FeS_2 is heated is distillation of half the sulfur. The burning of this sulfur is difficult in that it must be completely mixed with air and even then oxidation to SO_2 is relatively slow unless the temperature level is very high. Modern sulfur burner design provides for these conditions, but excess air is always required for complete combustion and some SO_3 formation results. In a pyrites roaster much sulfur oxidation together with oxidation of FeS occurs at or near the point of distillation of the sulfur. The high heats of reaction cause high localized temperature, resulting in well recognized sintering difficulties. The system of the present invention segregates final sulfur vapor oxidation from the distillation zone but furnishes the heat of distillation by partial combustion of sulfur vapor and of FeS in vessel 3.

In the operation of the present invention, all distillable sulfur is removed from the solid in vessel 3. In order to insure this result enough air is fed upwardly through the vessel to burn some of the FeS to FeO, thereby providing heat for the distillation of sulfur from FeS_2. As a feature of the invention, the duct 10 together with its connecting pipe are sufficiently long so that if there is any FeS_2 left in the solid leaving vessel 3 it will react with the FeO contained in the solid to produce FeS and SO_2. Thus, it is desirable to conduct the operation in vessel 3 so that some FeO will be formed and to maintain at least in the duct 10 a sufficiently high temperature to support the reaction between FeS_2 and FeO. The completion of this reaction in the duct prevents the entry of FeS_2 into vessel 30 and the sublimation of sulfur from this vessel.

The temperature in vessel 3 should be maintained below 2000° F. and preferably below 1800° F by suitable removal of heat by the indirect heat exchanger. The maximum temperature permissible in this vessel is just below that at which the ore will sinter.

Sufficient air or other oxygen-containing gas is fed to burner 20 to assure complete oxidation of all distilled sulfur. This requires some excess oxygen and introduces some SO_3 into the off-gas from burner 20. High combustion temperatures can be used in burner 20 because there is no solid present in this vessel to sinter other than whatever packing which may be employed which will be suitably selected to withstand whatever temperature is maintained. The gas leaving the burner 20 contains oxygen, SO_2, SO_3 and nitrogen, if air has been employed. This gas should contain at least 2% by volume of oxygen and preferably more than 5%. The oxygen content of this gas can be regulated by controlling the feed of oxygen-containing gas to burner 20.

The solid passing from vessel 3 to vessel 30 is primarily a mixture of FeS and FeO. Vessel 30 is also maintained at a temperature below 2000° F. and preferably below 1800° F., the top temperature again being regulated by the sintering temperature of the ore. The composition of the solid mixture passing from vessel 3 to vessel 30 is controlled by regulating the supply of oxygen-containing gas to vessel 3. The gas recovered from vessel 30 is primarily sulfur dioxide, mixed with nitrogen, if air has been employed.

The solids passing from vessel 30 to vessel 38 will consist primarily of FeO with a small but definite amount of FeS. This content of FeS is deliberately preserved in vessel 30 so as to preclude the formation of SO_3 in this vessel. Its presence also insures that the off-gas from vessel 30 will be free from oxygen.

In vessel 38 the last traces of sulfur are removed from the solids. To achieve this, strong oxidizing conditions must be maintained, that is, oxygen in excess of that required to carry the FeO to Fe_2O_3. Therefore, some SO_3 will be

formed in addition to SO_2. The temperature in this vessel must be high, limited only by the sintering temperature of the solid. The oxidizing gas and the solids in vessel **38** should pass countercurrent to each other and this may be assured by providing packing in this vessel. In order to prevent run-away of temperature in this vessel, cold air may be introduced through the inlets **44** at spaced points. In fact, most of the air will be introduced at these spaced points. The quantity of air entering at the bottom is relatively small in amount but should be hot in order to strip all sulfur compounds from the Fe_2O_3 cinder. The temperature of this air entering the bottom should be at least 1500° F. and preferably above 1800° F., the maximum being the fusion point of the cinder.

It will be apparent that the present invention is susceptible to considerable change without suffering any essential change in character. Wherever packing has been recommended in the processing of solids, it will be apparent that trays and bubble caps with downcomers can be used as an alternative. Considerable control of the process has been made possible by the various connections from vessel to vessel permitting adjustment of the composition of the gas passing through any particular vessel. It will be understood that the vessels do not have to have the exact relationships shown so long as the sequence of operations is substantially observed. While vessels **3** and **30** have been illustrated as the bottom drawoff type with internal cyclones, it will be apparent that the operations in these vessels can be so conducted that the solids pass off overhead to external cyclones or other suitable separators for solids and gases.

The nature and objects of the present invention having thus been set forth and a specific illustrative embodiment of the same given, what is claimed and desired to be secured by Letters Patent is:

1. In a process for roasting iron sulfides with a free oxygen-containing gas the improvement which comprises, continuously introducing into a reaction zone a suspension of finely divided iron sulfide in a free oxygen-containing gas into a bottom portion of a dense turbulent fluidized bed consisting predominantly of hot finely divided iron oxide whereby the sulfide is oxidized and SO_2 produced, indirectly cooling the contents of the fluidized bed by circulating a cooling fluid through a cooling coil immersed in said bed, removing overhead from the reaction zone a gas containing SO_2, and continuously separately removing solids consisting substantially of iron oxide with small amounts of iron sulfide from a bottom portion of said reaction zone below the point of introduction of the suspension.

2. A process according to claim 1 in which the free oxygen containing gas is air and in which the temperature in the reaction zone is maintained below 2000° F.

3. A process according to claim 1 in which the suspension introduced into the reaction zone also contains small amounts of FeO.

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