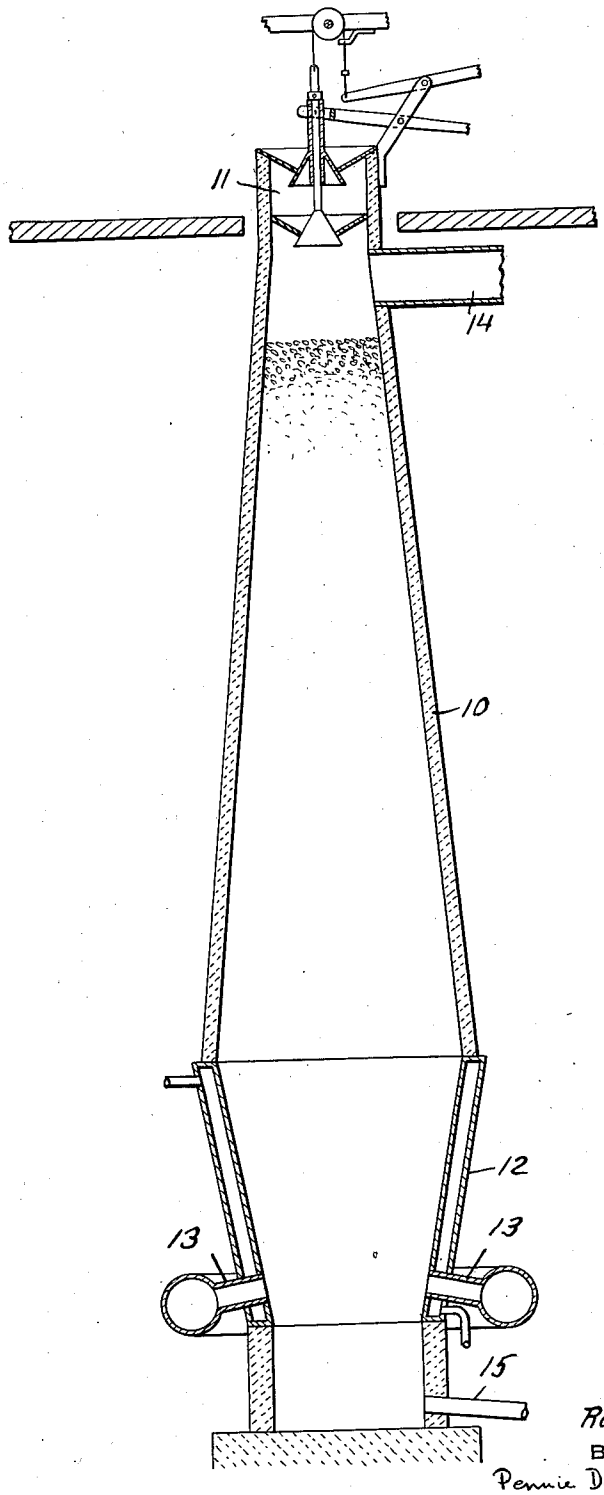
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SMELTING SULPHIDE ORES

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## SMELTING SULPHIDE ORES

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This invention relates to the blast furnace smelting of pyrites and has for its object the provision of a pyrites smelting process wherein the sulphur liberated is recovered in elemental form.

While from a theoretical standpoint, the heat developed by the oxidation of the sulphur and the iron, should be sufficient to meet the smelting requirements, it is, nevertheless, almost the universal custom to provide in addition, some 2 to 6 per cent of carbonaceous material such as coke, partly as safety factor in maintaining the heat in case of irregularity of operation and largely to keep the charge open to promote gas diffusion. The presence of this available reducing agent in the charge might seem to warrant the expectation that elemental sulphur would be present in the exit gases in much greater amount than the sulphur dioxide.

As a matter of fact, however, the exit gases from the usual pyritic smelting furnace contain elemental sulphur in a very much smaller proportion than these considerations would warrant, for the exit gases from the furnace contain the sulphur largely in the form of sulphur dioxide.

This disadvantageous reduction in the amount of elemental sulphur recoverable from the exit gases, can be mainly attributed to the oxidizing effect of the material amounts of excess air used in operating the furnace and also as a result of the more or less open top with which the usual smelting furnace is run.

In accordance with the process of my invention, the large amount of volatile sulphur originally liberated is protected against subsequent oxidation, and in addition the sulphur dioxide provided by the smelting combustion is reduced to elemental form and likewise protected against such oxidation.

The manner in which I accomplish the same consists in general, in regulating the air fed to the furnace, in slower feeding, in reducing the sulphur dioxide from the combustion zone by the action of the ferrous sulphide (FeS) in the charge, maintaining a non-oxidizing atmosphere in the upper part of the charge to prevent the oxidation of the sulphur so reduced as well as that liberated by volatilization, and operating the furnace with a closed top to prevent the ingress of air above the charge which would result in oxidation of the elemental sulphur. I also prefer to use a hot blast in my process.

It is to be noted, moreover that this is accomplished and the smelting operation carried out as well, with the employment of only the normal amount of coke or other carbonaceous materials used in pyritic smelting; viz. 2 to 6 per cent. If reliance were to be placed upon coke as the reducing agent for the sulphur dioxide it would be necessary to use it in an amount of about 10 per cent for the usual pyrites charge.

A specific procedure illustrating the process of my invention is as follows:

A blast furnace smelter of any well known type, for example the common water-jacketed pyritic smelter, will serve for the purpose of my process, but specific provision should be made therein for running the furnace with a closed top to prevent the ingress of air during feeding. For this purpose any suitable and well known type of air-sealing construction for the feeding device, of which there are many, may be utilized. Furthermore I prefer a furnace whose height is greater than the ordinary pyritic smelter.

With the use of a closed top, the only air which will have access to the charge will be that blown in, in regulated amount through the tuyères.

A suitable furnace for use in carrying out the process of my invention is shown in the accompanying drawing. The furnace shown in the drawing is generally in the form of a blast furnace, but its height is preferably substantially greater than the height of any ordinary blast furnace. Ore is charged into the chamber 10 of the furnace through a double gate 11, so arranged that the top of the furnace may be maintained closed even during the charging operation. The bottom of the furnace is advantageously provided with water-jackets 12, and tuyères 13 extending through the water-jackets provide for the introduction of an air blast into contact with the charge. Gases are withdrawn through an offtake conduit 14 adjacent the top of the furnace, and a suitable tap-hole or spout 15 is provided for the removal of molten products of the furnace.

The pyritic charge for the furnace may be of any common type, for example a pyrites-chalcopyrites charge, to which is added a suitable amount of silica and calcium earths to provide an iron calcium silicate slag.

To this charge is added a small amount of coke or other suitable carbonaceous material, primarily to impart suitable porosity to the ore to promote diffusion, and to an extent, to provide a safety factor in maintaining the heat in case of irregularity of operation. This function can likewise be served by any material other than coke which will accomplish the same result with-

out interfering with the smelting or recovering operations.

The amount of coke used will depend upon the physical nature of the ore and the requirements of the particular operation. In general it will vary between approximately 2 and 6 per cent as in ordinary pyritic smelting, in so far as it is not relied upon to any material extent for fuel value or as a reducing agent for the sulphur dioxide.

The differentiation of my invention from the ordinary pyrites smelting operation, is not concerned particularly with the amount of coke used provided the use of such coke is limited by the dictates of porosity maintenance and the necessity of providing a fuel safety factor.

This charge is introduced into the furnace without the ingress of air during such operation, and the desired depth of bed is controlled by periodic additions to the charge as the operation proceeds.

Air is blown in through the tuyères in the well known manner, and in accordance with my invention the air blast is introduced at such a controlled rate that the oxygen will be substantially entirely consumed in the smelting zone, in order to assure the maintenance of a substantially non-oxidizing atmosphere in the upper part of the furnace.

In addition the air blast is introduced at such a rate that an elongated hot zone is produced and the temperature of the furnace is higher in the zone above the tuyère zone than is usual in pyritic smelting, this for the purpose of accelerating the reduction of the sulphur dioxide by the FeS. To further amplify the thermal resources of the process and to assure virtually complete consumption of the oxygen in the combustion zone, it is also desirable that a very hot blast be used. If desired the blast may also be dry, to promote uniformity of operation and to facilitate the attainment of the elongated focus.

As a result of this production of an elongated focus, it is desirable to increase the normal height of the charge, and where necessary a suitably higher furnace should be provided for this purpose. By so doing, sufficiently prolonged contact of the sulphur dioxide with the iron sulphide will be provided, and an unduly high temperature in the gases escaping from the top of the charge will be avoided. The temperature at the top of the furnace is desirably held at 350° to 450° C.

The most suitable height of charge for the particular ore and operating conditions can be readily ascertained in each instance by the effect of its variance upon the operation. The effect, for example, upon the nature of the slag, the concentration of the matte, and the composition of the exit gases from the furnace, particularly as regards their relative sulphur dioxide and free sulphur contents will serve to indicate the changes which should be made.

In any case, however, the charge should not be extended to such a height that the sulphur would tend to deposit in the furnace as a result of an unduly low top temperature.

By careful observance of the conditions heretofore noted, a very high percentage of elemental sulphur will be present in the exit gases from the furnace and the smelting operation will proceed in a markedly effective manner.

The reactions which take place in the furnace are probably constituted as follows:

In the intense combustion zone or focus, the iron and a large proportion of the sulphur in the iron sulphide mixture remaining after the volatile sulphur has been driven off, will be oxidized by the hot air blast with the formation of sulphur dioxide, an iron calcium silicate slag, and a matte containing the copper or nickel and other values. This matte and slag will descend to the bottom of the furnace, and may be tapped off in the usual manner.

The hot sulphur dioxide will ascend into the charge, and upon contacting with the hot iron sulphide will be reduced to elemental sulphur with the accompanying production of an iron oxide. This reaction probably proceeds more or less in accordance with one or both of the equations—

$$SO_2+{}_2FeS={}_3S+{}_2FeO$$

$${}_3SO_2+{}_4FeS={}_2Fe_2O_3+{}_7S$$

In the lower part of the furnace the first reaction is more likely to take place than the latter, in view of the silica present which will tend to avidly take up ferrous oxide at the prevailing high temperature to form a slag.

Furthermore, the higher temperature provided in the elongated focus, will materially accelerate these reactions, which proceed more rapidly at higher temperatures. The removal by the silica of the FeO formed, reduces the possibility of the action reversing, and the same is true of the velocity of the gas current which will carry the elemental sulphur produced to the regions where reversing is less likely to occur.

Proceeding upwardly through the charge, the reactions will tend to progress to substantial completion, for a temperature as low as 800° C. is ordinarily satisfactory for rapid reaction, a requirement amply satisfied by the attendant smelting conditions.

To further assure the substantial completion of this reducing reaction and particularly as regards the cooler portion of the charge, I have found an intimate admixture of magnesia with the charge to be peculiarly effective in catalyzing this reaction, a material reduction in the necessary temperature being thereby made possible. In the case where magnesia is added to the charge as for instance a dolomitic lime, it passes into the slag, whose composition will be modified in accordance with rules well known in the art. Lime and iron oxide also act as catalysts for this reaction, but not as effectively as magnesia.

In the upper portions of the charge the heat ascending from the focus through the medium of the gases will volatilize the feeble sulphur atom of the pyrites present in the charge.

Due to the regulation of the air blast to assure consumption of practically all of the oxygen in the combustion zone, the atmosphere in the upper part of the charge will be non-oxidizing, and the volatilized sulphur and that produced by reduction of the sulphur dioxide will not be subject to oxidation therein.

Furthermore, upon their escape at the top of the charge, the provision of the closed top under which the furnace is operating, will assure the substantial absence of air at the top of the furnace and the exit gases will retain their high content of elemental sulphur substantially unaffected.

Upon discharge from the furnace, the gases may be conducted to a suitable dust collector, for example a mechanical dust separator such as a baffle chamber, or an electrostatic precipitator such as the well known Cottrell, and the dust-free gases subsequently conducted thru a cata-

lyzer to form sulphur from gaseous sulphur compounds and then to an apparatus for recovering the sulphur. For this purpose a waste heat boiler or similar cooling means may be utilized to condense the sulphur and its partial separation may be accomplished therein, or subsequently by the use of an electrostatic precipitator.

The gases from the dust separation usually contain appreciable amounts of sulphur compounds which warrant further treatment, to recover the sulphur values or remove noxious constituents.

The sulphur compounds which may be present in these gases would ordinarily consist of $SO_2$ and/or $H_2S$, and where carbon was provided in the charge for gas diffusion, a slight amount of COS.

These particular compounds are capable of interaction with the production of elemental sulphur according to the equations—

$$SO_2+2H_2S=3S+2H_2O$$
$$SO_2+2COS=2CO_2+3S$$

These reactions are carried out in a catalytic chamber containing a catalyzer such as porous alumina or bauxite, where they will readily react to yield the additional sulphur in elemental form.

Where insufficient amounts of sulphur dioxide are present in the gases, supplemental amounts may be added if desired, to carry out the aforenoted reactions, or by slightly increasing the blast the amount of $SO_2$ may be increased.

The gases remaining after the final sulphur separation may then be discharged into the atmosphere, practically entirely freed of the constituents which ordinarily constitute a very objectionable nuisance in the usual smelting operation.

By proceeding in accordance with the process herein described, many advantages are provided over the processes heretofore available.

An economical and very effective recovery of elemental sulphur as an incident to pyrites smelting, is made possible, thereby opening up a substantial and inexpensive source of this element.

The amount of air necessary calculated on the pyrite is less than half that required in the usual pyritic smelting process; and the noxious gas nuisance ordinarily encountered in the operation is entirely eliminated.

The amount of air used in my process is also much less, calculated on the pyrites charge, than in any process in which coke or coal or other carbonaceous fuel is used in the furnace in relatively substantial quantity, say 9 to 10 per cent or more. Due to this fact the sulphur content of the exit gases is much higher in percentage than in such processes which is a marked advantage of my process, as completely condensing the sulphur vapor from very dilute hot gases adds cost to a process.

The term "pyrites" as used herein is not intended to be limited to true pyrites, $FeS_2$, but also includes other forms of iron sulphide containing less sulphur than $FeS_2$, for example, pyrrhotite, also iron sulphides containing nickel and/or copper, and likewise manufactlured products, such as mattes, which consist principally of iron sulphides. When a material of the type of pyrrhotite is smelted, there is little or no feeble atom of sulphur to be removed by volatilization, hence the zone of sulphur volatilization is absent; otherwise the operation is much the same as in the smelting of true pyrites by my process with only such usual changes in the smelting operation as will be apparent to one skilled in the art.

I claim:

1. In a process of recovering sulphur from pyrites wherein the pyrites is smelted in a smelting furnace, the steps which comprise, contacting the sulphur dioxide from the combustion zone with the ferrous sulphide from the partially desulphurized pyrites in the presence of a magnesia catalyst to accelerate the reduction of the sulphur dioxide to elemental sulphur by said sulphide.

2. In a process of recovering sulphur from pyrites wherein the pyrites is smelted in a smelting furnace, the steps which comprise, contacting the sulphur dioxide from the combustion zone with the ferrous sulphide from the partially desulphurized pyrites in the presence of dolomitic lime to accelerate the reduction of the sulphur dioxide to elemental sulphur by said sulphide.

3. In a process of recovering sulphur from pyrites wherein the pyrites is smelted in a smelting furnace, the steps which comprise, intimately admixing magnesia throughout the pyritic charge to catalyze a reaction of ferrous sulphide upon sulphur dioxide to reduce the latter to elemental sulphur, contacting the sulphur dioxide gases from the combustion zone first with the hot molten ferrous sulphide of the partially desulphurized magnesia-containing pyritic charge, and then contacting said gases with the unmelted ferrous sulphide of said magnesia-containing pyritic charge.

4. The process of recovering elemental sulphur from pyrites which comprises, subjecting a charge containing the pyrites to the action of an air blast in a smelting furnace with the blast introduced at such a rate that a smelting temperature is attained in the lower portion of the furnace and the oxygen of the blast is substantially consumed in said portion, passing the sulphur dioxide produced in such combustion zone in contact with the hot iron sulphide in the charge above the combustion zone for a suitable period of time and with the sulphide provided in such amount that substantially all of the sulphur dioxide is reduced to elemental sulphur by reaction therewith, excluding oxidizing atmosphere from above the charge in the furnace, withdrawing from the furnace the gases issuing from the top of the charge, and separating the elemental sulphur from said gases.

5. The process of recovering sulphur from pyrites which comprises, subjecting a charge containing the pyrites to the action of a hot air blast in a smelting furnace with the blast introduced at such a rate that a smelting temperature is attained in the lower portion of the furnace and the oxygen of the blast is substantially consumed in said portion, passing the sulphur dioxide produced in such combustion zone in contact with the hot iron sulphide in the charge above the combustion zone for a suitable period of time and with the sulphide provided in such amount that substantially all of the sulphur dioxide is reduced to elemental sulphur by reaction therewith, excluding air from above the charge during feeding to prevent oxidation of the elemental sulphur, withdrawing from the furnace the gases issuing from the top of the charge, and separating the elemental sulphur from said gases.

6. In a process of recovering elemental sulphur from pyrites wherein the pyrites is smelted in a smelting furnace, the steps which comprise, subjecting the lower portion of a charge within the furnace to the action of a blast of oxidizing gas

to oxidize the charge and produce sulphur dioxide and to melt the resulting oxidized charge, contacting the sulphur dioxide from the combustion zone in the furnace with the hot iron sulphide in the upper portion of the charge in said furnace in the absence of air, and maintaining a suitable amount of iron sulphide in the furnace and suitably prolonging the period of contact of the sulphur dioxide with said sulphide to substantially completely by reaction therewith reduce the sulphur dioxide to elemental sulphur within the furnace, the oxidized charge being withdrawn from the furnace in a molten condition.

7. In a process of recovering elemental sulphur from pyrites wherein the pyrites is smelted in a smelting furnace, the steps which comprise, contacting the sulphur dioxide from the combustion zone and in the absence of air first with the hot molten iron sulphide of the partially desulphurized pyritic charge, and then contacting the gases with the unmelted iron sulphide in the upper portion of the furnace, the contact of the sulphur dioxide with said sulphide being maintained for a suitably prolonged period of time and with the sulphide provided in sufficient amount to substantially completely reduce the sulphur dioxide by reaction therewith to elemental sulphur within the furnace.

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