United States Patent [19]

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[11] **3,773,494**

[45] **Nov. 20, 1973**

[54] **SMELTING OF COPPER SULPHIDE CONCENTRATES WITH FERROUS SULPHATE**

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[22] Filed: **Dec. 10, 1971**

[21] Appl. No.: **206,881**

[52] **U.S. Cl.** **75/23,** 75/74, 75/75, 75/101, 75/117

[51] **Int. Cl.. C22b 15/02,** C22b 15/00, C22b 15/14

[58] **Field of Search** 75/1, 2, 7, 21, 23, 75/72–76, 115, 117, 119

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[57] **ABSTRACT**

In smelting ores and concentrates of copper or nickel, matte fall is obtained by recycle of ferrous sulfate which is produced when the matte is leached with sulfuric acid. The residue from leaching then contains the copper, nickel or cobalt values in concentrated form. In this method the ferrous sulfate is reduced to ferrous sulfide at elevated temperatures. This is the basis of molten matte, wherein the metal values are collected and then separated from the iron sulfide by leaching. The iron contained in the concentrate is removed ultimately in slag.

8 Claims, No Drawings

SMELTING OF COPPER SULPHIDE CONCENTRATES WITH FERROUS SULPHATE

BACKGROUND OF THE INVENTION

In the conventional smelting of copper, nickel or cobalt sulfide, concentrates are combined with flux and reduced in a reverberatory furnace, producing slag, which is discarded, and a molten mixture of sulfides called matte. Metal bullion is obtained by oxidation of this matte with air in a converter. The sulfur is discharged from the mouth of the converter as sulfur dioxide, together with nitrogen, dust and fumes. Flux is added to the converter to collect the iron and other impurities as a silicate converter slag, which is returned to the reverberatory furnace for the recovery of its copper content. This has been the standard practice for many years for the extraction of copper and nickel. When the concentrates contain both copper and nickel the matte may be flotation concentrates, separated into copper- and nickel-rich fractions, which are converted separately into bullion.

Recently legislation has been enacted which severly limits the emissions of sulfur oxides and particulates from smelters. It is extremely expensive to remove the sulfur dioxide and particulates from conventional smelters because of the low concentrations in the large volume of reverberatory gases and the cyclic variations of gas composition and volume from the converters.

There are a number of modifications of conventional smelting which have been developed to reduce the magnitude of the problem of smelter emissions of sulfur and particulates. For example, electric smelting has been used in place of reverberatory smelting of concentrates to achieve a reduction of the gas volume from the furnace. This is at a considerable cost of electric energy for heating and melting the charge.

A second method which is practiced at several major copper smelters, and which eliminates the greater part, or all, of the combustion gases, is to smelt autogenously, i.e., using heat generated by oxidation of sulfur and iron to supplement or replace the heat of fuel combustion. The concentrates are blown into the furnace, either horizontally or vertically downward, with air, which may be preheated or oxygen enriched. A gas is obtained which is relatively high in SO_2 content, and the charge is reduced to slag and matte as in conventional reverberatory smelting. The matte is then converted to copper in a copper converter as in conventional practice, as has been described above. The quantity of matte in autogenous smelting is reduced from that of conventional reverberatory smelting because of the transfer into the slag of some of the iron of the concentrates by the oxidation reaction which generates the heat in the reduction furnace.

This, unfortunately, results in a higher copper loss in the slag, which is in equilibrium with the higher copper-containing matte. Sometimes this loss is reduced by adding iron sulfides with little or no copper, but this is at a considerable cost of added slag production when the iron sulfide is oxidized in the converter. It is an object of the present invention to achieve the benefits of improved control of sulfur dioxide emissions without sacrifice of copper recovery and without increasing the total slag volume.

The methods of electric or autogenous smelting in the prior art do not eliminate the converting of matte to blister, or crude, copper in conventional copper converters with all of the attendant costs and legal and economic problems of gaseous emissions from the converters, as has been mentioned above. Also, as in conventional smelting the converter slag, which is relatively high in copper content, must be returned to the concentrate reduction furnace.

It is also well known in the prior art that iron sulfide may be removed by acid dissolution of matte, leaving cuprous sulfide for further treatment. If aqueous sulfuric acid is used for leaching, the iron enters the aqueous solution as ferrous sulfate, while hydrogen sulfide is liberated. Recovery of copper from cuprous sulfide is also well known, for example, by utilizing sulfuric acid in combination with air or oxygen at elevated temperatures to dissolve the copper, as the sulfate, and leaving elemental sulfur for recovery. The copper may be recovered from the aqueous solution by electrowinning or by precipitation of cuprous cyanide, as taught in Roberts, U.S. Pat. No. 3,321,303, May 23, 1967.

It is also well known that prior to leaching, matte must be "activated" if it is to react with acid to remove iron sulfide. Active matte contains an excess of iron stoichiometrically over the sulfur, and such active matte is produced by the action of reducing gases or by addition of metallic iron to the molten matte from the reduction furnace.

SUMMARY OF THE INVENTION

According to the present invention ferrous sulfate is used, which by combination with the fuel and oxygen-containing gas may be converted into molten ferrous sulfide matte. The conversion can be in any suitable apparatus; one very desirable known type of apparatus is a flash smelting furnace. The conversion occurs when the finely divided ferrous sulfate is introduced into the combustion space of the furnace. The molten products fall through this space onto a hearth, where they are collected and utilized as will be described in more detail below.

In the present invention this matte-forming reaction is used in combination with the smelting of ores or concentrates of copper, cobalt and nickel for the purpose of collecting the metal values of these ores or concentrates in a matte below a slag layer. The slag contains most of the iron and gangue elements from the ore or concentrates while the matte contains the principal metal values.

It is an advantage of the present invention that the matte is processed after physical separation of the slag and/or molten iron alloy layers from the matte. The particular process of recovering metal values from the matte is not, in general, changed by the present invention, which from one standpoint might be considered as ending when the matte is produced. While any suitable method of metal values recovery from the matte is included, a typical method is leaching of the matte with aqueous sulfuric acid to produce aqueous ferrous sulfate and a gas containing hydrogen sulfide. Substantially all of the copper sulfide together with some of the nickel and cobalt sulfide, if they are present, remains undissolved in the solid residue. This is subsequently treated to recover the values, including where desired, sulfur. The processes of treating the matte are known, and it is an advantage of the present invention that the matte is of a form suitable for application of the known recovery processes. It is thus not necessary to develop a new recovery technique and the present invention

can be used in connection with any recovery process and is not limited to such typical procedures as will be described below in a more specific section of the present application.

It will be noted that in the process of the present invention ferrous sulfate is recycled and so constitutes a circulating load. The ferrous sulfate is, of course, transformed by chemical reaction in the present process and is regenerated. Excess iron present in the ores and concentrates, which is usually the case, is eliminated in the slag. In the case of an ore containing no iron sulfide, the ferrous sulfate in the circulating load can be obtained from any suitable source. Iron-free copper sulfide ores and concentrates are very rare, but the present invention also includes their treatment.

The present invention is essentially a process and is not limited to any particular apparatus. Types of apparatus referred to are simply illustrative and the invention is not limited thereto. Of course while the apparatus is old, the process, which involves the nature of the materials treated, is, of course, a new process.

If the matte contains nickel and cobalt, these are dissolved in the acid to a greater or lesser extent depending on the temperature, acid strength and the matte composition. Cobalt and nickel which are dissolved may be recovered, as by cementation by scrap iron or steel, prior to the recovery of the ferrous sulfate from the aqueous solution. The scrap iron or steel is, of course, largely transformed into ferrous sulfate and so constitutes another, though minor, source of ferrous sulfate. Of course the iron content of the ferrous sulfate produced is eventually rejected in the slag just as in the case of ores and concentrates containing substantial amounts of iron sulfides.

While the proportions of ferrous sulfate, fuel and oxygen do not require critical or difficult operating conditions, they should be controlled so that the heat which is released by combustion is sufficient for the reduction of ferrous sulfate and for the heating of the products to the smelting temperature range of smelting. Ferrous sulfide melts at about 2,180° F. and mixtures of this with other components reduces the freezing point of the matte. Most of the slags require temperatures of at least 2,300°–2,400° F. for reasonable fluidity, although with special fluxes temperatures of 1,900° F. are possible. The maximum temperature is determined by practical considerations of fuel economy and refractory life and is usually about 2,800° F. The fluxes used, as such, are known fluxes, and the present invention is not limited to nor does it require any special new flux. This is an advantage of the invention as it simplifies operations.

If the ore or concentrates contain sulfides, it is generally advantageous to combine the smelting with the reduction to matte of the ferrous sulfate. This is for the reason that the autogenous release of heat in flash smelting of sulfides releases a considerable amount of heat when there is sufficient oxygen availability for conversion of the sulfides to oxides and/or silicates together with SO_2. It is advantageous also to provide the necessary flux at the same time to obtain a slag which has the property of fluidity to obtain a clean separation from the underlying matte.

The fuel requirements of the process are dependent on the composition of the ore or concentrates, the amount of ferrous sulfate to be recycled, the composition of the fuel, the oxygen concentration of the oxygen-containing gas and on the amount of preheat of this gas and the preheat and moisture of the solid charge. While the invention requires a proper choice and amount of fuel and oxygen, the invention is not limited to any particular exact figures as these will vary with the particular ores or concentrates. Also, extreme exactness of fuel and oxygen amounts are not needed so that the process has sufficient flexibility to permit satisfactory operation without excessively critical control.

The matte produced as described above contains magnetite. It is necessary for leaching the matte that some of this should be reduced to iron, or that metallic iron, nickel or cobalt be added or produced by reduction. Accordingly, the matte, containing the collected metal values, is subjected to reduction while molten. This may be done by various methods well known in the prior art, for example, by treatment with reducing gas or with carbon. Treated in this manner the matte contains an iron bearing metallic phase when solidified, and it is said to be "active," i.e., leachable with sulfuric acid.

As has been stated above, the flash smelting furnaces, which are preferred in the present invention, are in general similar to those of the prior art. It is an advantage of the present invention that it does not require a specially designed furnace and is not limited to any particular type. Of course the furnace must be suitable for the process being carried out therein. It is usually desirable to oxidize all of the iron of the ore or concentrate so that it enters the slag as a silicate. This is done by controlling the ratio of oxygen to the fuel, sulfide ore or concentrate and ferrous sulfate. Nevertheless, the scope of this invention is not limited to processes in which substantially all of the iron of the ore or concentrate is brought into the slag, although in many cases this is desirable.

When the percentage of iron sulfides contained in the ore or concentrates is high, ferrous sulfate may be employed as a slag-forming component of the charge to the smelting furnace. It contributes not only its own content of iron to the slag but it also supplements the slag-forming tendency of oxygen by the reaction

$$3FeSO_4 + FeS = 4FeO(slag) + 4SO_2.$$

The equation is a generalized one and does not specify the exact chemical nature of the ferrous oxide compound in the slag.

The proportion of the iron which goes to slag and that to matte fall is determined by the proportions of oxygen, fuel, concentrates or ores, and ferrous sulfate. Thus the addition of ferrous sulfate to the charge without the addition of a corresponding amount of reducing material increases the proportion of the iron which goes from the sulfide concentrate to the slag. With the addition of carbonaceous fuel beyond that which is equivalent to the oxygen in the gas, the matte fall may be increased beyond that which is obtained from the concentrate alone without the addition of ferrous sulfate. Thus by control of the ratio of the components of the furnace charge it is possible to control the matte fall and the recycle of ferrous sulfate.

It is apparent from the foregoing that the ratio of matte to slag is controlled in accordance with this invention and also it is apparent that a greater matte fall results in improved metal collection, as a penalty, however, of increased consumption of fuel or oxygen and

with greater requirement of acid for leaching the matte. From the standpoint of facilitating the recovery of sulfur from the smelter gases, it is advantageous to convert about two-thirds of the SO_2 of the smelter gases to acid and utilize this for generating the equivalent of H_2S and hydrogen which react with the remaining one-third of the sulfur dioxide in a Claus catalytic system for producing elemental sulfur. The invention is not limited to the exact ratio of utilization of SO_2, but in some cases it is advantageous and may, therefore, perhaps be considered as a preferred embodiment.

A further preferred embodiment of this invention is one in which the ferrous sulfate and ore or concentrate are premixed with suitable flux and predried. This mixture, with natural gas fuel and preheated air, is fired into the flash smelting furnace. Matte and slag flow from the furnace hearth to a forehearth which contains a bottom layer of molten iron alloy with about 0.2 percent carbon. Supplemental heat may be furnished by means of electrical energy supplied using graphite electrodes.

The reaction of the carbon in the iron with the magnetite of the matte releases metallic iron, which is appreciably soluble in the matte. The carbon which is consumed in this reaction may be replaced by immersion of electrode carbon in the molten iron alloy. Carbon monoxide, which is generated by reaction of the matte with the carbon of the molten iron alloy, may be admitted to the flash smelting section to be consumed as fuel.

The slag is discharged from the forehearth and discarded, whereas the matte, containing the principal metal values, is retained after tapping the furnace and after cooling, as by quenching in a stream of water or aqueous solution. This cooled matte is then leached using sulfuric acid to convert the iron sulfide and metallic iron to iron sulfate and hydrogen sulfide gas containing a small percentage of hydrogen. The iron sulfate dissolves in the solution or crystallizes if the solution is saturated. Cuprous sulfide remains for further treatment.

Ferrous sulfate is recovered from the solution after separation of cuprous sulfide and other insoluble substances. Preferably the recovery of ferrous sulfate is by methods well known in the prior art, as by evaporation followed by centrifugal separation. It may be desirable to assist in the separation of ferrous sulfate monohydrate by adding to the solution some, or all, of the sulfuric acid required in the process. After utilizing the acid in this way to reduce the solubility of ferrous sulfate, the mother liquor, containing the acid, may be recycled for leaching the matte.

Another example which illustrates the utility of this invention is that of the electric furnace smelting of a secondary copper-bearing material known as "irony brass." When this material is charged into a smelting furnace together with flux, ferrous sulfate and solid reducing material, such as coal, the charge may be reduced at a temperature of about 2,100° F. to produce a matte and slag layer. Some of the ferrous sulfate is reduced by the coal to produce ferrous sulfide and carbon oxides, while the remainder of the ferrous sulfate produces iron and copper sulfides together with iron oxide which enters the slag. The generalized equations are as follows:

$$3Fe + FeSO_4 + 2Cu = Cu_2S + 4FeO$$

$$4Fe + FeSO_4 = FeS + 4FeO$$

Other elements, such as zinc, lead, tin and nickel, become converted into sulfides in the matte or to oxides in the slag. The matte is discharged from the smelting furnace and then it is leached with aqueous sulfuric acid to dissolve iron and nickel as sulfates while leaving copper, lead and zinc sulfides for subsequent treatment. Ferrous sulfate is recovered from the solution by crystallization with copper sulfide, dehydrated and returned to the smelting furnace. The mother, liquor containing nickel sulfate, is treated by methods of the prior art to recover the nickel salt.

The proportions of ferrous sulfate, coal, flux and irony brass are controlled in combination with air or oxygen to the furnace so that the slag and matte compositions are suitable for satisfactory metal recovery and for producing a matte which contains sufficient metallic iron for reactivity with aqueous acid.

The residue from leaching the matte contains substantially all of the copper, nonferrous metals and tin, while nickel, cobalt, zinc and lead are dissolved in varying degrees, depending on the matte composition and conditions of leaching. As indicated above in the example of nickel and cobalt concentrates, the nickel and cobalt may be precipitated by cementation with iron. Other metal values are recovered by methods known in the prior art. If there is incomplete separation of the metal values and impurities contained in the aqueous solution, these may be precipitated with the ferrous sulfate and recycled to the smelting furnace. Ultimately they find their way into the slag or into a fume which is carried with the furnace gases.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following example is a typical illustration of the invention.

Copper flotation concentrates at the rate of 1,000 tons per day (dry weight), containing 25 percent Cu, 30 percent Fe, 34.5 percent S, are dewatered on a filter and blended with 250 tons per day of silicious flux and with 1,050 tpd of monohydrated ferrous sulfate produced in a later stage of the process to be described below. The mixture is dried in a rotary dryer which is direct fired at the feed end of the kiln.

The dried kiln product is air-conveyed to the feed hopper of the smelting furnace. From this hopper it is transferred with constant weight feeders through a rotary seal and check valve into a stream of 34,000 scfm of air, preheated to 800° F., in a pipeline which leads to the burner. Natural gas, at the same temperature, enters at a rate of 3,570 scfm into the stream at the burner.

In the subsequent reactions within the combustion space of the furnace heat is produced, while the concentrates, flux and ferrous sulfate react to produce a melt and a gas phase containing sulfur dioxide. This leaves the furnace through a flue leading to a waste heat boiler and recuperator and then to a gas cleaning and absorption system to clean and concentrate the SO_2 for utilization as described below. The concentration of SO_2 in the gas from the smelting furnace is 14 percent (dry basis).

If it is desired to concentrate the SO_2 further, this can be done by absorbing the SO_2 in a water solution and

then stripping with air at sub-atmospheric pressures. The stripping is described in two applications of Gunther, U.S. Pat. Ser. Nos. 132,752, filed Apr. 9, 1971, and 285,109, filed Aug. 30, 1972. The second application describes a preferred method in which absorption and stripping are in multiple stages, with stages paired, using stripped solution from the stripping stage in the paired absorption stage. The present invention is not limited to SO_2 concentration as described in the Gunther applications, and for some purposes the concentration of SO_2 is sufficiently high to be used without further concentration. It is, however, an advantage of the invention that the SO_2 produced can be further concentrated by absorption and stripping where higher SO_2 concentrations are desired.

The SO_2 containing gas is generated at a rate of 46,100 scfm. Of this amount, 60 percent, or 27,660 scfm, is utilized for conversion to sulfuric acid required for leaching of matte as described below. The remainder, 18,440 scfm, is available for producing elemental sulfur by reaction with hydrogen sulfide from the leaching of matte, to be described below, or for any purpose whatever. The conversion to acid or to elemental sulfur is in accordance with methods which are known in the prior art, and the present invention is not limited to any particular known processes for utilizing the SO_2.

The molten layers which collect on the hearth of the smelting furnace at 2,400° F. consist of matte containing 30.3 percent Cu, 33.4 percent Fe and 9.35 percent magnetite and slag containing 0.3 percent Cu. In the forehearth of this furnace these layers separate and collect over a bath of a molten alloy of iron which contains 0.2 percent carbon. In this section of the furnace the carbon reacts with the magnetite in the matte, causing a reduction to metallic iron which remains dissolved in the matte and carbon monoxide which is liberated, joining the gases of the smelting section while passing to the flue and waste heat boiler.

The slag is tapped and discarded as waste while the matte, after reduction, is collected and granulated for leaching with acid at a rate of 820 tpd. Sulfuric acid which is required for leaching amounts to 580 tpd, and the reaction produces all of the ferrous sulfate which is required in the charge to the smelting furnace, as well as 3,510 scfm of H_2S and 520 scfm of hydrogen. When this gas stream is combined with the SO_2 other than that for the acid requirements, the combined stream is suitable for conversion to elementary sulfur in a Claus plant according to a method which is well known.

In the leaching of the reactive matte which has been granulated, acid is combined with matte to produce a nearly neutral solution substantially saturated with ferrous sulfate. This solution is separated from the cuprous sulfide and other acid insolubles, and these are treated for copper recovery. The filtrate, which is saturated in ferrous sulfate, is then treated by adding acid to reduce the solubility of the monohydrate, which is recovered by filtration. The filtrate contains the acid which is returned to the matte leaching operation.

The recovery of copper from the cuprous sulfide residue of the matte leaching is effected by any of the well known pyrometallurgical or hydrometallurgical methods which have been used hitherto for this purpose.

Although reference is here made to the recovery of copper, it will be understood that other metals, such as lead, nickel, cobalt and precious metals are similarly recovered. It will be understood also that reference herein to ferrous sulfate is intended to refer to an intermediate product which may include substantial amounts of impurities and substances which are included or mechanically entrapped.

I claim:

1. A method for producing copper matte from an ore or concentrate containing copper sulfide which comprises heating the ore or concentrate with ferrous sulfate and a flux to a temperature at which a molten copper sulfide matte and slag is produced and separating the molten matte from the slag.

2. A method according to claim **1** in which the ore or concentrate also contains substantial values of at least one metal selected from the group consisting of nickel and cobalt.

3. A method according to claim **2** in which the heating is effected with fuel and oxygen-containing gas.

4. A method according to claim **1** in which the heating is effected with fuel and oxygen-containing gas.

5. A method according to claim **1** in which the ferrous sulfate is obtained by leaching the matte with sulfuric acid.

6. A method according to claim **2** in which the ferrous sulfate is obtained by leaching the matte with sulfuric acid.

7. A method according to claim **5** in which the matte is activated by subjecting it to reduction while in the molten state prior to leaching.

8. A method according to claim **6** in which the matte is activated by subjecting it to reduction while in the molten state prior to leaching.

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