SMELTING OF COPPER OXIDES TO PRODUCE BLISTER COPPER

Inventors: Willard L. Hunter; William A. Stickney, both of Albany, Oreg.

Assignee: The United States of America as represented by the Secretary of the Interior, Washington, D.C.

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Primary Examiner—Walter R. Satterfield
Attorney, Agent, or Firm—Roland H. Shubert; Frank A. Lukasik

ABSTRACT

Blister copper is produced from copper oxides or dead-roasted copper sulfides in a cyclic smelting process using a carbon reductant. In the first stage of the cycle, carbon reductant is added to the furnace charge in stoichiometric excess to form a copper-depleted slag and a molten black copper fraction. The slag is tapped, leaving black copper in the furnace, and a second charge containing carbon is stoichiometric deficiency is then smelted to form a copper-rich slag and blister copper. Blister copper is then tapped, leaving copper-rich slag in the furnace, and the cycle is repeated.

11 Claims, 3 Drawing Figures
FIG. 1.

FIG. 2.

Fe IN METAL, PCT. vs. Cu IN SLAG, PCT.
FIG. 3.
SMELTING OF COPPER OXIDES TO PRODUCE BLISTER COPPER

CROSS-REFERENCE TO RELATED APPLICATION

This patent application is related to patent application Ser. No. 401,004, filed of even date herewith, which is directed to a process for “Smelting of Nickel Oxide Ores to Produce Ferronickel” by Willard L. Hunter, Danton L. Pauleson and William A. Stickney. The two patent applications are commonly assigned.

BACKGROUND OF THE INVENTION

The extractive metallurgy of copper sulfide concentrates, as it is conventionally practiced today, consists of three main steps; roasting, reverberatory smelting, and converting. Roasting is usually continued to the point whereat most of the iron sulfide contained in the copper concentrate is converted to the oxide leaving a calcine composed of copper sulfide, iron oxide, some iron sulfide and the gangue which was originally present in the concentrate. Depending on the type of ore and the roasting conditions, the off-gas from roasting contains from about 1 to 12% sulfur dioxide. In the reverberatory smelting step, the calcine is smelted, usually with silica and lime additions, to produce matte and a slag. The composition of the matte is essentially a mixture of copper and iron sulfides. Gases generated from the smelting step generally range from about 0.25 to 2.5% sulfur dioxide content depending on smelting conditions and sulfur concentration of the calcine. Matte from the smelting step is treated further in a converter where it is blown with air to oxidize the iron sulfide and to reduce the copper sulfide to copper metal. Sulfur dioxide content of the off-gas may range from about 3 to 12% during the converting cycle.

Copper smelters today are faced with the problem of treating the off-gases from these three major unit operations to remove a minimum of 90% of the sulfur oxides from the gas streams before venting. The established method for sulfur oxide removal at this time is the production of sulfuric acid by the contact process. Contact acid plants require a minimum of about 3.5 to 4% sulfur dioxide content in the feed gas to economically and efficiently convert the sulfur oxides to acid.

Roaster off-gases provide an appropriate feed for a sulfuric acid plant but the amount of sulfur conventionally removed from a copper sulfide concentrate in the roasting step is only in the range of 30 to 40%. About a quarter at most of the remaining sulfur is removed in the reverberatory furnaces but the sulfur dioxide content of these off-gases is too low to constitute an appropriate acid plant feed. Nearly half of the total sulfur contained in a typical copper sulfide concentrate remains to be removed in the converters. Concentration of sulfur dioxide in these off-gases varies during the converting cycle and gas processing is further complicated by the fact that the converter operation is a batch process. However, if multiple converters are used, their operation can be phased to smooth out major variations in gas flow and sulfur dioxide content.

Because of the problems and limitations imposed by current smelting practice, it is difficult for the copper industry to economically meet the imposed 90% collection standards for sulfur dioxide using presently available technology.

SUMMARY OF INVENTION

Smelting of copper oxides may be accomplished in a two-stage cyclic smelting process using a carbon reductant to produce blister copper having a purity comparable to that produced by traditional methods and, at the same time, holding copper levels in the slag to about 1%. The first stage of the cycle is accomplished under carbon-rich conditions to yield a copper-depleted slag while the second stage is accomplished under carbon-poor conditions to yield a high quality, blister copper.

In a preferred embodiment, a copper sulfide concentrate is dead-roasted to yield a copper oxide calcine and a sulfur oxide-rich off-gas. The roaster off-gas is then treated in a contact process acid plant to recover more than 90% of the sulfur originally present in the sulfide concentrate as sulfuric acid. Calcine is then smelted with coke in an electric furnace to yield blister copper and a lean slag.

Hence, it is an object of our invention to produce blister copper from a copper sulfide concentrate while recovering more than 90% of the contained sulfur.

Another object of our invention is to produce blister copper and a lean slag from copper oxide by carbon reduction.

Yet another object of our invention is to smelt dead-roasted copper calcine in an electric furnace without significant copper loss to the slag.

DETAILED DESCRIPTION OF THE INVENTION

The invention will be described with reference to the accompanying drawings in which:

FIG. 1 is a diagrammatic flow sheet representing a preferred embodiment of our process.

FIG. 2 is a plot representing the relationship of copper content in the slag to iron content in the metallic copper.

FIG. 3 graphically represents the relationship of copper contained in the slag to iron contained in the copper as a function of the amount of carbon in the furnace charge. These figures will be discussed in more detail later.

The sulfide ores of copper constitute the most important source of copper metal. Iron is almost invariably present in significant amount in copper sulfide concentrates either in the form of mixed copper-iron sulfides such as chalcopyrite and bornite or in the form of iron sulfides such as pyrite and marcasite which are associated with copper sulfides in the ore body.

In conventional practice, only a portion of the sulfur contained in a copper sulfide concentrate is removed in the roasting step since the presence of sulfur is required to form a matte during reverberatory smelting. It is well known that roasting can be continued to the point where all of the concentrate is in the oxide form. This is commonly referred to as dead-roasting and may be accomplished in a fluidized bed reactor provided that care is taken to avoid fusion within the reaction zone. It is also known that such dead-roasted calcines may be reduced with carbon to produce a metal product known as black copper which is essentially an alloy of copper with iron and small amounts of various other metals. Principally because of its high iron content, black copper is unsuitable for electrolytic refining. If a selective reduction is attempted to avoid the reduction of iron oxides to the elemental form and thus obtain a more highly pure copper metal product, then copper
losses to the slag become so high as to be unacceptable.

Yet from the standpoint of controlling sulfur oxide emissions, dead-roasting is attractive since essentially all of the sulfur is removed in the roaster off-gas at a concentration of about 10 to 15%. Gases of such composition can be easily and economically treated by the contact process to recover the sulfur oxides as sulfuric acid. Another advantage accruing from this approach is that the composition and volume of gases to be treated can be maintained at a relatively constant level.

We have found that dead-roasted copper calcines may be reduced in a cyclic process to recover copper metal of comparable purity to the blister copper produced in conventional processes and to produce a lean slag containing no more, and in some cases considerably less, copper than is discarded in the converter and reverberatory slags of the traditional process.

Referring now to FIG. 1, there is shown a stylized flow sheet of our process. A copper sulfide concentrate 10 is introduced into a roaster 11 where it is contacted at elevated temperatures with an oxygen-containing gas such as air 12. Roaster 11 may comprise a kiln of multiple hearth type roasting furnace but is preferably a multitage, fluidized bed reactor. The ignition temperature for copper sulfide concentrates is on the order of 350° to 400°C but the dead roasting operation must be carried out at temperatures high enough to decompose intermediate sulfates and oxy-sulfates formed at lower temperatures. In practice, temperatures of about 750° to 900°C are employed. Care must be taken to avoid fusion within the reaction zone which occurs at temperatures as low as about 900°C depending upon the gangue constituents present. Air is conveniently used to provide oxygen for the reaction but oxygen or oxygen-enriched air may also be employed to increase the sulfur dioxide content of the roaster off-gases.

Roaster off-gases 13, containing from about 10 to 15% sulfur dioxide when air is used as the oxidizing medium, are employed as a feed stream to an acid plant 14 to produce a sulfuric acid by-product 15 and a sulfur oxide-depleted gas stream 16 suitable for venting through a stack. It is generally necessary to cool the roaster off-gases prior to introduction into the acid plant and this may be accomplished using a waste heat boiler (not shown). Well over 90% of the sulfur contained in sulfide concentrate 10 may be recovered in the by-product sulfuric acid stream 15.

A copper calcine 17, essentially depleted in sulfur and containing copper oxides, iron oxides, gangue constituents and minor amounts of other metal oxides, is recovered from roaster 11. Calcine 17 is then introduced as a component of the charge to furnace 18 which is preferably an electric furnace of the submerged arc type. Added to the furnace charge is a carbon-containing reductant such as coke 19 and a fluxing agent 20. Composition and amount of flux 20 added as a component of a furnace charge is determined by the gangue composition of calcine 17 and by the concentration of impurity metal oxides, especially iron oxides, contained in the copper calcine.

Fluxing agents useful in our process include silica, lime and combinations thereof.

As has been stated before, ours is a cyclic process; one complete cycle consisting of two stages. In the first stage, carbon is added in stoichiometric excess and, upon heating to a molten state, there is produced a cop slag fraction essentially depleted of copper and a lower black copper fraction containing substantial amounts of iron dissolved in molten copper. At this point, the slag 21 is tapped while the black copper is retained in the furnace. A second charge is then added to the furnace. The second charge consists of copper calcine, fluxing agents and carbon in an amount substantially less than stoichiometric. This carbon deficiency produces in the second stage of the cycle a slag which is quite rich in copper and molten copper fraction which is low in iron and of purity comparable to blister copper. At this point, the molten blister copper 22 is tapped from the furnace but the molten copper-rich slag is retained. This sequence of operations completes one cycle which then may be repeated indefinitely.

During the reduction, there is produced a relatively small amount of furnace off-gas 23 which contains those fixed gases present in the furnace charge and the gaseous produces of reduction which are primarily carbon dioxide, carbon monoxide and small amounts of sulfur oxides. These furnace off-gases are desirably treated before being vented. This may conveniently be accomplished by recycling the furnace off-gas to the roaster wherein carbon monoxide will burn to the dioxide. Any sulfur oxides present in the furnace off-gas will be removed in the acid plant 14. Since the volume of furnace off-gas is very small compared to the volume of roaster off-gas, recycle of the furnace off-gas in the manner described does not materially affect operation of the roaster.

Slag fraction 21 will typically contain about 15% copper. Residual copper contained in the slag is mostly in the form of small metallic prills physically suspended in the slag. Copper content of the slag is dependent to a large extent upon smelting conditions and upon slag characteristics, especially upon slag fluidity. A substantial part of the residual copper contained in the slag may be recovered by comminuting the slag to a size range where there is substantial physical liberation of the copper prills and thereafter subjecting the ground slag to a flotation treatment. The flotation is of conventional type and may readily be accomplished using xanthates as promoters and flotation conditions typical of those used in the flotation concentration of copper sulfide ores. A rougher flotation concentrate consisting mostly of metallic copper and copper sulfides, may be recycled to the smelting furnace for recovery of the contained copper.

It is preferred that the furnace charge be added in a premixed state; that is as a mixture of calcine, flux and carbon reductants. In this mode, it is necessary to prepare furnace charges of two compositions; one a high carbon charge fed to the first stage of the cycle and the other a low carbon charge fed to the second stage of the cycle. The carbon reductant may be in the form of shell carbon, petroleum coke and like materials.

In the first stage of the cycle, carbon is present in stoichiometric excess while in the second stage of the cycle it is present in stoichiometric deficiency. Stoichiometry is based upon the reduction of copper compounds present in the calcine to elemental copper with carbon being converted to carbon monoxide. In the first stage, copper content of the slag is low and iron content of the copper is high. The reverse situation occurs in the second stage. This relationship between concentration of copper in the slag and iron concentration in the liquid copper metal is plotted as FIG. 2. As may be seen from that figure, an appreciable concen-
tation of copper oxide in the slag resulted in a low iron content, usually less than 0.05%, in the metal product. At copper concentrations of about 4% and lower in the slag amounts of iron in the metal increases rapidly.

FIG. 3 represents similar data to that of FIG. 2 but is plotted as a function of the amount of carbon included in the furnace charge. On the basis of operating data such as is presented in FIG. 3, we prefer that the furnace charge to the first stage of the cycle contain more than 120% of the stoichiometric carbon requirements and the furnace charge to the second stage of the cycle contain less than 80% of that stoichiometrically required. In our most preferred mode of operation, carbon in the first stage furnace charge is more than about 160% of stoichiometric while carbon in the second stage furnace charge is less than about 40% of stoichiometric.

As may now be appreciated, our process has a number of substantial advantages compared to those of the prior art. First, essentially all of the sulfur contained in the concentrate is removed during one unit operation at steady rates. Second, the concentration of sulfur dioxide in waste gases may be maintained at substantially constant levels thus allowing more efficient and trouble free operation of the acid plant. Third, the total volume of waste gases produced by our process is less than half produced by the typical roaster-reverberatory furnace converter process now commonly employed. Finally, our process requires but one slagging step instead of two as is conventional thus decreasing the amount of slag produced as a waste product and in some instances decreasing total copper loss to the slag.

The following example serves to more fully illustrate our invention.

EXEMPLARY

A series of cyclic tests were conducted in an 800 Kva electric arc furnace at feed rates of approximately 2,000 pounds per hour. Either slag or metal was tapped hourly. The copper calcine fed to the process had the following composition in weight percent: Cu, 38.0; Fe, 29.0; SiO₂, 3.1; MgO, 0.03; Al₂O₃, 0.9; CaO, 0.3; Pb, 0.09 and Zn, 2.1. In addition, the calcine contained 0.04 oz Au and 37.6 oz Ag per ton.

Carbon addition to the first stage of the cycle was 170% of stoichiometric while carbon addition to the second stage was 30% of stoichiometric, sufficient silica and dead-burned lime were added as fluxes to produce a slag-to-metal ratio of 0.7. Slag tapped from the first stage of the cycle contained 1.1 to 1.5% copper. Iron content of the molten copper tapped from the second stage of the cycle was consistently below 0.05%.

Slag tapped from the smelting process was crushed and ground to a nominal size range of −200 mesh. The ground slag was slurried in water to form a pulp and was then subjected to a conventional froth flotation separation using a xanthate promoter. Flotation conditions were typical of those used to concentrate copper sulfide ores.

A rougher flotation concentrate, comprising tiny prills of metallic copper and copper sulfides was recy-

cled to the smelting furnace. The flotation step reduced the copper content of the slag from a level of 1.1 - 1.5% as tapped to a level of 0.4 to 0.7% as cleaned. Thus, total copper losses to the slag amounted to 0.3 to 0.5% of the copper in the calcine fed to the smelting furnace.

We claim:

1. A process for reducing copper oxides to form blister copper which comprises:

   heating in a furnace a first charge comprising copper oxides and a carbon reductant in an amount sufficient to provide at least 120% of the carbon stoichiometrically required to reduce the copper oxides contained in said first charge to copper metal to form a liquid slag depleted in copper and a liquid black copper phase;

   tapping from the furnace a substantial portion of the copper depleted slag;

   adding to the furnace, still containing the liquid black copper phase, a second charge comprising copper oxides and a carbon reductant in an amount less than 80% of the carbon stoichiometrically required to reduce the copper oxide contained in said second charge to copper metal and heating the charge to form a liquid slag rich in copper and a blister copper phase, and

   tapping from the furnace a substantial portion of the blister copper.

2. The process of claim 1 wherein a slag-forming flux is added to both the first and second furnace charges.

3. The process of claim 2 wherein said copper oxides are a calcine produced by the dead roasting of a copper sulfide concentrate.

4. The process of claim 3 wherein said roasting is carried out at temperatures above about 750°C but below the fusion point of the concentrate.

5. The process of claim 4 wherein off-gases from the roasting step are treated in a contact process sulfuric acid plant to produce a sulfuric acid product and a residual gas depleted in sulfur oxides.

6. The process of claim 5 wherein the concentration of sulfur oxides in off-gases from the roasting step is maintained at a level about 10%.

7. The process of claim 6 wherein said carbon reductant is coke.

8. The process of claim 6 wherein off-gases from the furnace are recycled to the roasting step.

9. The process of claim 7 wherein the first charge contains more than about 160% of the carbon stoichiometrically required to reduce the copper oxides to copper metal and wherein the second charge contains less than about 40% of the carbon stoichiometrically required to reduce the copper oxides to copper metal.

10. The process of claim 2 wherein the copper-depleted slag is comminuted and thereafter subjected to a flotation separation to recover a concentrate comprising metallic copper.

11. The process of claim 10 wherein the concentrate is recycled as a feed to the smelting furnace.