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3,533,779

METHOD FOR SMELTING LOW-SULFUR COPPER ORES

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7 Claims

ABSTRACT OF THE DISCLOSURE

An improved method for smelting copper ores such as chalcocite (Cu_2S) is presented. The improvement involves the use of calcium sulfate and iron as smelting additives. The use of these materials allows low cost operation and improved efficiencies.

This invention resulted from work done by the Bureau of Mines of the Department of the Interior, and the domestic title to the invention is in the Government.

BACKGROUND OF THE INVENTION

Field of Invention

This invention relates to the smelting of copper ores. More particularly, the invention is concerned with an improved process for smelting copper ores of low sulfur content such as chalcocite.

DESCRIPTION OF THE PRIOR ART

Copper metal is usually recovered from copper sulfide ores or concentrates by a pyrometallurgical process of smelting, converting, and refining. In the initial step, iron and copper sulfides plus fluxing materials are smelted in a reverberatory furnace which is a long shallow vessel consisting of a hearth, side and end walls, and a roof. The furnace is heated by means of burners placed in one end wall and the products of combustion escape at the other end. Gas, fuel oil, or pulverized coal is used to produce a long flame which heats the material on the hearth by radiation. Consequently, the reverberatory is essentially a melting furnace and there are no extensive reaction between the furnace gases and the charge. Chemical reactions which occur in the furnace are mostly between various constituents in the charge.

The principal function of the reverberatory furnace is to melt the charge and permit the formation of matte and slag. The charge consists of impure copper or ore concentrate, plus a fluxing material to flux the impurities (silica and alumina). The matte consists of a solution of two sulfides, Cu_2S and FeS and may range in grade from 20 to 80 percent Cu; the combined percentages of Cu, Fe and S will usually exceed 95 percent. The matte has a greater density than the slag; consequently, the liquid matte and slag segregate into two layers which serve as the basis for their separation from the furnace.

The matte is withdrawn from the reverberatory furnace and transferred to a converter where it is blown with air. This oxidizes the FeS , and by adding a siliceous flux, the FeO is slagged and removed. Further blowing oxidizes the sulfur preferentially from the Cu_2S , leaving metallic copper. This product, called blister copper, is porous, brittle, and contains small amounts of impurities. The blister copper is refined to improve its physical properties by electrolytic or pyrometallurgical methods.

The smelting process is most adaptable to iron-bearing copper sulfide materials containing an excess of sulfur, such as chalcopyrite (CuFeS_2). When the non-iron bearing copper minerals containing a deficiency of sulfur,

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such as chalcocite (Cu_2S), are treated by this process, iron and sulfur must be added to the furnace charge to produce the copper-iron-sulfur matte. Usually, iron and sulfur are added to the smelting furnace in the form of pyrite (FeS_2) or chalcopyrite (CuFeS_2). These additives are expensive and often must be transported great distances to the smelter site. Consequently, there exists in the art a need for effective and less expensive copper smelting additives.

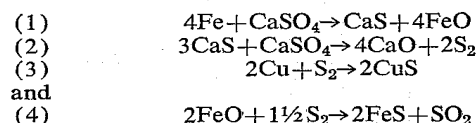
SUMMARY OF INVENTION

Briefly, the present invention consists of smelting copper ores of low sulfur content with calcium sulfate and metallic iron.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the present invention, the conventional procedure for smelting copper ores is retained with the exception that calcium sulfate and metallic iron are substituted for the use of pyrite as an additive to the smelter charge. The calcium sulfate used may be in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4). The metallic iron is supplied in the form of low-value ferrous scrap. For this purpose machine shop turnings, cast iron borings, mixed borings and turnings, short shoveling turnings and auto body scrap can be used.

Though the exact relationship between the various materials present in the charge during the smelting process is not known, it is believed that the calcium sulfate and metallic iron participate in the following reactions to make sulfur available for matte formation.



Further, the CaO formed in reaction (2) above lowers the requirements for limestone as a fluxing agent.

The amount of ingredients used is a function of the mineralogical and chemical composition of the copper ore or concentrate to be processed, the quantity and grade of secondary materials such as converter slags, dusts and scrap fed to the smelter, the grade of matte desired and the analysis of the scrap iron and calcium sulfate added to the charge. Consequently, it is impossible before hand to specify preferred or optimum ranges for the additives. However, taking the products of reactions 1-4 above into consideration, the concentrate, and additives should be combined in proportions so as to maintain a smelting charge having a composition within the range set forth in Table 1 below.

TABLE 1

	Wt. percent
Cu	13-16
Fe	4-10
S	4-12
CaO	14-16
Al_2O_3	9-12
SiO_2	29-34

In practice, the ingredients are mixed before being fed to the smelting furnace. The smelting operation can be carried out continuously or by batch and the temperatures used should be within the range of from about 1200-1500° C. and preferably from about 1300-1400° C. Following the smelting operation, the matte is transferred to a converter where the FeS content of the matte is oxidized, slagged with a siliceous flux and removed. The remaining copper is then refined by conventional electrolytic or pyrometallurgical techniques.

In the following examples the smelting procedure of the present invention is compared with a conventional treatment using pyrite and lime as additives and also with a treatment using gypsum and coal as described in U.S. Pat. 3,155,492 to Udy.

TABLE 3.—COMPARISON OF 3-HOUR SMELTING TESTS WITH NORMAL AMOUNTS OF SULFUR-BEARING ADDITIVES

Test No.	Additives ¹	Smelting conditions		Charge composition, percent			Product composition, percent Cu		Cu distribution, percent		Sulfur loss, percent
		Time, hrs.	Temp., ° C.	Cu	S	Fe	Matte	Slag	Matte	Slag	
5	Pyrite, lime	3.0	1,300	15.5	6.1	8.0	61.7	0.34	98.3	1.7	13.5
6	Gypsum, coal	3.0	1,300	14.7	6.4	7.0	60.8	10.3	54.0	46.0	49.0
7	Gypsum, metallic iron	3.0	1,300	16.7	5.4	7.3	71.0	0.25	98.9	1.1	8.5
8	Gypsum, lime, metallic iron	3.0	1,300	16.3	5.3	6.6	72.0	0.20	98.8	1.2	10.0

¹ Materials added to the base charge of copper concentrate and reverberatory slag.

The general test procedure used in the following examples consisted of combining selected proportions of chalcocite concentrate, smelter slag, and the desired flux and matte forming constituents to maintain a smelting charge of the following composition by weight: 4-10 per-

Example 2.—A series of four tests using additives corresponding to the tests of Example 1 were run at 1300° C. but for 3 hours.

The results of these tests are listed in Table 3 below.

Example 3.—Another series of four tests were run at 1300° C. as in the previous examples with the exception that an excess of sulfur-containing ingredients was employed and the smelting time was 2 hours.

The results of these tests are listed in Table 4 below.

TABLE 4.—COMPARISON OF 2-HOUR SMELTING TESTS WITH EXCESS AMOUNTS OF SULFUR-BEARING ADDITIVES

Test No.	Additives ¹	Smelting conditions		Charge composition, percent			Product composition, percent Cu		Cu distribution, percent		Sulfur loss, percent
		Time, hrs.	Temp., ° C.	Cu	S	Fe	Matte	Slag	Matte	Slag	
9	Pyrite, lime	2.0	1,300	14.3	7.4	9.0	49.2	0.49	97.5	2.5	7.7
10	Gypsum, coal	2.0	1,300	13.2	8.7	3.9	51.4	5.0	79.5	20.5	33.0
11	Gypsum, metallic iron	2.0	1,300	14.1	8.7	7.6	71.7	0.46	97.9	2.1	52.0

¹ Materials added to the base charge of copper concentrate and reverberatory slag.

cent iron, 13-16 percent copper, 14-16 percent calcium oxide, 4-12 percent sulfur, 9-12 percent alumina and 29-34 percent silica. The test mixture was thoroughly blended and 300 grams were charged into a fire clay crucible which was then placed into an induction furnace. The laboratory apparatus used has been pictured and described in Bureau of Mines Report of Investigations No. 5955 entitled, "A Study of Copper Reverberatory Slags From White Pine, Mich." by L. M. Irwin, R. E. Lubker and R. A. Marsyla. The furnace was a 35-kva. induction unit and the procedure simulated that of a commercial reverberatory furnace. The laboratory furnace was fitted with a graphite cylinder insulated from the copper induction coil by a sheet of mica and lamp black. The graphite cylinder was lined with stabilized zirconia to prevent excessive oxidation. Standard fire clay crucibles (250 ml. capacity) were used to contain the furnace charge, and the slag temperatures were measured optically. The temperature of the tests was 1300° C. After remaining at that temperature for the allotted time, the crucible was removed from the induction furnace, cooled to room temperature, and the products were separated, weighed and chemically analyzed.

Example 1.—A series of four tests were run at 1300° C. for 2 hours. In each the sulfur level was maintained at a normal 5.2-6.4 percent.

Test 1 includes pyrite as the matte-forming ingredient and limestone was added as flux.

Test 2 was performed using a combination of gypsum and bituminous coal to stimulate the practice of U.S. Pat. 3,155,492.

Test 3 was run using gypsum and powdered metallic iron as the additives.

Test 4 was run similar to Test 3 but slightly less iron was used and limestone flux was added to improve the fluidity of the bath.

The results of these tests are listed in Table 2 below.

TABLE 2.—COMPARISON OF 2-HOUR SMELTING TESTS WITH NORMAL AMOUNTS OF SULFUR-TESTING ADDITIVES

Test No.	Additives ¹	Smelting conditions		Charge composition, percent			Product composition, percent Cu		Cu distribution, percent		Sulfur loss, percent
		Time, hrs.	Temp., ° C.	Cu	S	Fe	Matte	Slag	Matte	Slag	
1	Pyrite, lime	2.0	1,300	14.5	6.2	7.6	59.0	0.73	96.1	3.9	15.8
2	Gypsum, coal	2.0	1,300	14.5	6.6	4.8	59.4	5.7	72.6	27.4	31.9
3	Gypsum, metallic iron	2.0	1,300	14.3	5.6	8.6	67.3	0.42	98.0	2.0	12.8
4	Gypsum, lime, metallic iron	2.0	1,300	16.0	5.6	6.2	70.9	0.48	97.8	2.2	9.4

¹ Materials added to the base charge of copper concentrate and reverberatory slag.

From Tables 2-4 it can be seen that smelting chalcocite using the additives disclosed in the present invention is not only equivalent but in most respects superior to prior smelting techniques.

Though the invention has now been described with reference to preferred embodiments and specific examples, it will readily be appreciated by those of ordinary skill in the art that many modifications and adaptations of the invention are possible without departure from the spirit and scope of the invention as claimed hereinbelow. For example, while the invention has been described primarily in connection with copper ores of low sulfur content such as chalcocite, the principles of the invention may also be applied to other copper sulfide and oxide ores.

What is claimed is:

1. A method for smelting low sulfur containing copper ores comprising mixing a material consisting essentially of calcium sulfate and metallic iron with said ore, which said iron reduces said sulfate to provide additional sulfur and lime for smelting said ore, and treating said ore at a temperature of from 1200 to 1500° C.

2. The method of claim 1 wherein said ore is a sulfide ore.

3. The method of claim 2 wherein said sulfide ore is chalcocite.

4. The method of claim 3 wherein CaO or limestone is added as a flux.

5. The method of claim 3 wherein said calcium sulfate and metallic iron are added in such proportions to produce a smelting charge having a composition by weight of

from 13 to 16 percent Cu,
from 4 to 10 percent Fe,
from 4 to 12 percent S,
from 14 to 16 percent CaO,
from 9 to 12 percent Al₂O₃,

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and from 29 to 34 percent SiO_2 , and wherein CaO or limestone is added if necessary to meet said composition requirements.

6. The method of claim 5 wherein said smelting is accomplished in a temperature range of from 1300-1400° C.

7. The method of claim 6 wherein said charge is smelted from about 2 to 3 hours.

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