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DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

(Name of
applicant)

(Title)

(Full name
and address
of signatory)(Full name and
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inventor(s))(State whether
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employment)(Delete
paragraphs 3
and 4 for
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application)(Place and
date of
signing)

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In support of an application made by:
INSTITUT TSENTRALNO-KAZAKHSTANSKOGO OTDELENIA AKADEMII NAUK
KAZAKHSTANSSKOY SSRfor a patent for an invention entitled: METHOD OF
CONCENTRATION OF REBELLIOUS OXIDIZED COPPER ORESI, .. Dzhantore Nurlanovich Abishev.....
of .. USSR, Karaganda, ulitsa Michurina, 21/3, kv. 4.....

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for
the patent to make this declaration on its behalf.2. The name and address of each actual inventor of the
invention is as follows: NURALY SULTANOVICH BEKTURGANOV,
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to make this application are as follows:... The applicants are the assignees of the actual
inventors3. The basic application(s) as defined by Section 141 of
the Act was(were) made as follows:
Country on
in the name(s)
and in on
in the name(s)
and in on
in the name(s)4. The basic application(s) referred to in the preceding
paragraph was(were) the first application(s) made in a
Convention country in respect of the invention the
subject of this application.

Declared at... Moscow this... 25 day of... July 1986

I. Directorsigned: Dzhantore Nurlanovich Abishev
II. Director II. Vladimir Ivanovich Revnyitsev
III. Director Position: Mikhail Grigorievich Sedlov

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METHOD OF CONCENTRATION OF REFRACTORY OXIDIZED COPPER ORES
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AU 575944 42713/85 C22B B03B
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(57) Claim

1. A method of concentration of complex oxidized copper ores, comprising:

- preparation of a pulp of said complex oxidized copper ores, wherein the said pulp is formed by mixing together crushed copper ores with water, said crushed complex oxidized copper ores containing 50-100% of particles having a screened size to 0.74mm, and the prepared pulp has a ratio of solid to liquid phases equal to

1:0.5-3.0;

- sulphidizing the pulp with elemental sulphur in the absence of leaching agents, acids, sulphites and hydroxysulphides, wherein the mass ratio of elementary sulfur to oxidized copper is 0.2-1.5:1; said sulphidizing being performed at a temperature of at least 115°C and for at least 20 minutes, and being characterized in that the pulp is sulphidized with molten sulphur; and
- subjecting the sulphidized pulp mixture to flotation to obtain a sulphide-copper concentrate.

3. A method as claimed in Claim 1 or 2, wherein pulp sulphidizing is carried out at pressure of a 1.5-10 atm.

4. A method as claimed in any one of Claims 1 to 3, wherein pulp sulphidizing is carried out in the presence of an additive, which is sodium sulphate or a natural mineral (mirabilite) or sodium chloride or calcium chloride.

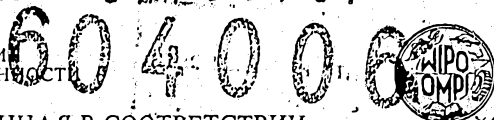
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ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ
Международное бюро

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МЕЖДУНАРОДНАЯ ЗАЯВКА, ОПУБЛИКОВАННАЯ В СООТВЕТСТВИИ
С ДОГОВОРом О ПАТЕНТНОЙ КООПЕРАЦИИ (PCT)

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С отчетом о международном поиске

(54) Title: METHOD OF CONCENTRATION OF ~~DIFFICULT TO CONCENTRATE~~ OXIDIZED COPPER ORES

(54) Название изобретения: СПОСОБ ОБОГАЩЕНИЯ МЕДНЫХ ОКИСЛЕННЫХ ТРУДНООБОГАТИМЫХ РУД

(57) Abstract

The method provides for preparation of a pulp, its sulphidizing and floatation. The sulphidizing of the pulp is effected with melted sulphur at a temperature of 115-180°C and at a pressure of 1.5-10 atm in the presence of sodium sulphate or sodium chloride at a mass ratio between the sulphur and the oxidized copper of (0.2-1.5):1.

METHOD OF CONCENTRATION OF REBELLIOUS OXIDIZED COPPER ORES

Technical Field

The present invention relates to non-ferrous metallurgy, concerns a method of copper recovery and, more specifically, a method of concentration of rebellious oxidized copper ores.

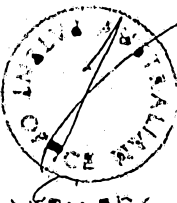
Background of the Invention

According to mineralogical composition copper ores are divided into the following types: sulphide, mixed (oxidesulphide) and oxide ores. Concentration of sulphide ores by conventional techniques of flotation is not accompanied with any difficulties. Oxide and mixed ores are, as a rule, complex for concentration.

By flotation of said ores a low-grade concentrate is produced. The degree of recovery of copper and other associated valuable ore constituents, for example, silver, is not high. This is due to the presence of badly-flotative minerals such as chrysocolla, cuprite, malachite, brochantite, etc. in oxide ores. However, as sulphide ore resources are being exhausted, concentration of oxidized ores becomes a matter of high practical importance.

Several methods of ^{concentration} ~~concentration~~ of oxidized copper ores are known in the art.

US Patent No. 4,200,455, IPC C22B 15/10 published on 29.04.80 teaches roasting of oxidized copper ores in a reducing medium at a temperature of 500-1000°C in the presence of additives of hydrochloric acid and hydrogen sulphide with subsequent leaching of copper from the roasted ore with an ammoniacarbonate solution. This method requires high energy consumption for heating the total amount of ore to said temperature. This technique involves emission of dust and toxic gases into the atmosphere during roasting, this requiring dust collection and purification of effluent gases. Besides, the use of such toxic materials as ammonia and hydrogen sulphide necessitates special safety means to be developed, this making the process more expensive.



According to another process, described in US Patent No. 2,989,394, published on 20.06.1961, oxidized copper ore is mixed with iron sulphides (pyrite and pyrrhotite) and chlorides of alkali- and alkali-earth metals. Then, the mixture is roasted at a temperature of 500-800°C in a neutral or reducing medium in the presence of water vapour. The object of such treatment is to convert oxidized copper constituents to sulphides which are readily recovered by foam flotation. As the previously mentioned technique, this method also involves high energy consumption and is accompanied with toxic gas and dust emission. The extraction of copper and silver in the concentrate produced by such a method is 82% and 72% respectively.

It is known that copper can be recovered from its oxidized ores through leaching by alkali and acid solutions. So, US Patent No 3,985,855, IPC C01G3/00, published on 12.11.1976, teaches to use a 25% solution of sodium hydroxide as a leaching agent. The process is carried out at a temperature of 60-100°C in the presence of an additive of a silicate material, taken in an amount of 50-100% by mass of the initial ore.

Then, a copper-containing solution is separated from the solid phase by filtration. However, this method is applicable only for copper extraction. Treatment of oxidized ores containing copper and silver is not efficient for silver extraction since silver compounds under such conditions are not leached out.

The use of sodium hydroxide is also undesirable as it is very expensive, toxic and difficult to handled.

Well known is a method of beneficiation of rebellious oxidized copper ores, which includes leaching of copper with hydrochloric acid, precipitation of copper from its solution, addition of iron chips or sponge iron into the pulp and flotation of the metal copper deposition thereby obtained.

There are known other methods of ^{concentration} ~~concentration~~ oxidized



ores with the use of acids for leaching. According to US Patent No. 4,008,072 IPC C22B 15/08, published on 15.02.1977, a pulp, obtained by leaching oxidized copper ore with sulphuric acid, is treated with ionized sulphides, preferably hydrogen sulphide. The copper sulphides thus obtained are then recovered by flotation.

US Patent No 3,728,430, IPC G01G, 3/12, published on 17.04.1973, discloses a method of concentration of oxidized and mixed oxide-sulphide ores, wherein leaching of copper and its precipitation in the form of sulphides occur simultaneously. According to this method crushed ore is mixed with water, elementary sulphur, an acid, and water soluble sulphites (bisulphites).

The pulp obtained by such technique is heated. Leaching copper with its simultaneous sulphidizing is carried out at a temperature of 25-100°C for 20 minutes. Then the pulp is cooled and delivered to flotation. Recovery of copper in flotation concentrate provided by this method is 75-85%.

The use of acid leaching for treatment of oxidized copper ores of high calcium content and ^{magnesium} ~~magnesium~~ carbonates is not expedient as it results in high consumption of the acid which reacts with said carbonates and thereby is ^{irretrievably} ~~irretrievably~~ lost. There are also other disadvantages in using acids: as they are highly corrosive the problem of protecting equipment against destructive action of acids raises and the environment is polluted with dump waste product, flotation tailings and acid-containing waste water.

All the hereinbefore-mentioned prior art methods of concentration of ores fail to provide for the most efficient recovery of copper and associated valuable components from them. Besides, some of these methods involve high energy consumption and environment pollution, other demand utilization of acids and alkalis which are harmful for the working personnel and bring about additional difficulties caused by separation of solid and liquid phases and neutralization of waste products.



Summary of the Invention

The object of the present invention is to provide such a method of concentration of rebellious oxidized copper ores, which would provide for the most efficient recovery of copper in concentrate with simultaneous recovery of silver from said ores, decrease environment pollution and simplify the process.

An aspect of the present invention provides a method of concentration of refractory

oxidized copper ores, which comprises preparation of a pulp, sulphidizing the pulp with elementary sulphur, flotation of the pulp and producing a sulphide-copper concentrate,

in that sulphidizing of the pulp is carried out with molten sulphur.

In accordance with one aspect of the invention there is provided a method of concentrating complex oxidized copper ores which comprises:

- preparation of a pulp of said complex oxidized copper ores, wherein the said pulp is formed by mixing together crushed copper ores with water, said crushed complex oxidized copper ores containing 50-100% of particles having a screened size to 0.74mm, and the prepared pulp has a ratio of solid to liquid phases equal to 1:0.5-3.0;

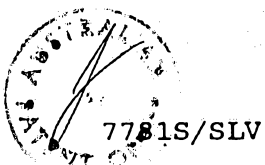


- sulphidizing the pulp with elemental sulphur in the absence of leaching agents, acids, sulphites and hydroxysulphides, wherein the mass ratio of elementary sulfur to oxidized copper is 0.2-1.5:1; said sulphidizing being performed at a temperature of at least 115°C and for at least 20 minutes, and being characterized in that the pulp is sulphidized with molten sulphur; and
- subjecting the sulphidized pulp mixture to flotation to obtain a sulphide-copper concentrate.

The method of the invention permits increasing copper recovery in the concentrate up to 92.6%. Besides, the method permits extracting silver in the same process with a high recovery of up to 90.2%. Furthermore, the method of the invention permits considerable reduction of harmful emissions into the environment. The method of the invention also permits simplification of the production process through obviation of the ore leaching stage and the stage of converting copper from the ore into a solution.

It is expedient for sulphidizing a pulp to use a mass ratio of elementary sulphur to oxidized copper equal to 0.2-1.5:1. Such a quantity is sufficient for an efficient sulphidisation reaction. It is preferable to carry out pulp sulphidizing at a temperature from 115 to 180°C and pressure from 1.5 to 10 atm. Under such conditions sulphur melts and efficiently reacts with oxidized copper in the ore as well as with other valuable associated components, for example, silver.

It is advisable to sulphidize pulp in the presence of sodium sulphate or a mineral containing sodium sulphate,



for example, mirabilite. This promotes an additional increase of copper recovery up to 98.6%. It is desirable to maintain a mass-ratio of sodium sulphate or mirabilite to elementary sulphur corresponding to 3-7 parts by mass of sodium sulphate being taken for one part by mass of elementary sulphur.

Besides said additions of sodium sulphate and mirabilite, pulp can be sulphidized in the presence of sodium chloride or a calcium chloride taken in a mass ratio to sulphur equal to 0.7-3:1. The additions of said materials can increase copper recovery by 2-5% and that of silver by 3-7%.

After sulphidizing the pulp is treated by flotation to obtain a sulphide concentrate from which copper, silver and other valuable components are extracted by metallurgical treatment.

It is advisable to return a part of sulphide concentrate in the amount of 1.5-3.0% by mass as related to the initial oxidized ore, back to the preparation stage. This promotes a decrease in the consumption of elementary sulphur used for sulphidizing by as much as 1.5-3 times.

These and other advantages of the invention will be more apparent from a detailed description of the method.

An oxidized complex copper ore is crushed to 0.74 mm size. Then a fraction containing said size in the amount of 50-100% is screened, mixed with water and a pulp is prepared with a ratio of solid and liquid phases (S:L) equal to 1:0.5-3.0.

Then elementary sulphur is added to the pulp thus obtained in the amount corresponding to the mass ratio of sulphur to oxidized copper equal to 0.2-1.5:1, that is for 1 part by mass of oxidized copper 0.2-1.5 part by mass of sulphur should be taken. Then, according to the invention, pulp is sulphidized with molten sulphur. One of simple and available ways of keeping sulphur in the molten state



is heating the pulp to a temperature within the range from 115 to 180°C in an air-tight vessel, for example in an autoclave. During heating the pulp to said temperature the pressure in the vessel increases to a value within
5 the range of from 1.5 to 10 atm. Under such conditions sulphidizing is carried out for 20-120 minutes. At said temperature the elementary sulphur melts and reacts with oxidized copper and silver compounds being in a solid phase. The process results in the highest yield of copper and
10 silver sulphides, so that their recovery in flotation is increased up to 90% and more.

It is desirable to perform sulphidizing at a temperature of 115-180°C because a temperature lower than 115°C would not be sufficient for melting the sulphur and the
15 reaction of the copper with the sulphur would not be efficient, whereas a temperature over 180°C does not increase the yield of copper and silver sulphides but results in extraenergy consumption.

Said quantity of sulphur used for sulphidizing is
20 so defined because a quantity of less than 0.2 part by mass is not enough to convert all copper from the ore into sulphides, whereas a quantity over said upper limit, i.e. 1.5 part by mass, does not increase sulphide yield, but results in unreasonably high sulphur consumption.

25 The duration of sulphidizing as stated above is 20-120 minutes. This duration is so defined because during a period shorter than 20 minutes sulphides are not obtained with a high yield whereas sulphidizing for
30 a period longer than 120 minutes does not increase the sulphide yield but prolongs the process, and this is not desirable.

Thus, according to the invention, sulphidizing of the pulp is carried out with elementary sulphur at a temperature of an ore pulp of 115-180°C, wherein sulphur
35 is in molten state and copper is in the solid phase but not in dissolved state as in the methods known in the art.



The prior art methods envisage obligatory leaching of ore with an acid or an alkali to convert copper to a solution and only after that copper in its dissolved state is subjected to sulphidizing.

5 In the present method sulphides are produced through the reaction of molten sulphur directly with copper present in the solid phase but not in solution. Such a way of pulp sulphidizing permits one to obtain an unexpected effect of a higher copper sulphide yield. This, in its turn, fa-
10 vourably tells on copper sulphide recovery in flotation concentrate, which has considerably increased to 90% and even more. Besides, there is also another unexpected effect, that is, high recovery of silver, while in the methods known in the prior art, silver recovery was rather
15 low or silver was not recovered at all.

The method of the invention of concentration of oxidized copper ores rules out the operation of leaching copper from ore and thereby simplifies the production process.

After sulphidizing, the pulp containing copper and
20 silver sulphides is cooled to an ambient temperature (10-30°C) and subjected to foam flotation, which is accomplished with the utilization of a conventional collector reagent (butyl xanthate) and a frothing reagent (a mixture of mono- and dihydric alcohols of the thioran and dioxane
25 alcohols). Recovery of copper in flotation concentrate amounts to 92.6%. We have found that by the present method a sufficiently full recovery of silver is obtained, amounting to 90.1%.

During flotation there is no necessity to use reagents,
30 regulating pH-medium, what simplifies the flotation process. This is due to the fact that the pulp after sulphidizing has a pH=6-7 ^{which} ~~what~~ corresponds to the value required for efficient flotation and therefore the use of additional reagents-regulators of the medium is not necessary.

35 It is advisable to sulphidize the pulp in the presence



of sodium sulphate or a mineral containing sodium sulphate, for example, mirabilite, whose composition is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Said additive permits a further 4-6% increase in the recovery of copper and silver.

5 It is advisable to keep the mass of sodium sulphate or mirabilite to elementary sulphur such that for 1 part by mass of elementary sulphur 3-7 parts by mass of sodium sulphate would be taken. Said additive improves the efficiency of the reaction of copper and silver with elementary
10 sulphur and thereby promotes for increasing the copper- and silver sulphide yield. When sodium sulphate or mirabilite (on conversion to sodium sulphate) is added in an amount of less than 3 parts by mass additional yield of said sulphides does not occur, so that its addition in an
15 amount of more than 7 parts by mass does not further increase said sulphide yield.

Sulphidizing the pulp may be carried out in the presence of sodium or calcium chlorides. The addition of said chlorides also permits further increase in the recovery of
20 copper and silver sulphides. The advisable consumption of said materials is from 0.7 to 3 parts by mass per part by mass of elementary sulphur.

If sodium or calcium chlorides are added in an amount less than 0.7 part by mass an additional increase of sulphide recovery does not occur.
25

Addition of said chlorides in an amount of more than 3 parts by mass does not further increase sulphide recovery but only unreasonably enlarges the consumption of said agents. Introduction of sodium chloride into the pulp increases copper and silver recovery by 5-7% each and introduction of calcium chloride increases same by 2-3%.
30 It is preferable to use sodium chloride from said materials due to its availability, low cost and efficient action on the process.



It is advisable to return a portion of the sulphide concentrate thus produced to the initial pulp in an amount of 1.5-3.0% to the total mass of the ore treated. Such an approach permits one to reduce sulphur consumption without
5 deteriorating sulphidization and flotation results. This is provided by the fact that unreacted sulphur remaining in the concentrate in the form of fine particles can participate in the sulphidization reaction along with sulphur introduced into the initial pulp. Said amount of sulphide
10 concentrate returned to the stage of pulp preparation is determined by the presence of unreacted sulphur therein. An amount of reused concentrate less than 1.5% by mass does not provide for significant decrease of sulphur consumption, whereas its amount of more than 3% by mass while
15 providing for its additional saving increases the volume of materials, which is not desirable.

Thus, return of the sulphide concentrate in said amounts to the stage of ore pulp preparation permits 1.5-3 times reduction of elementary sulphur consumption resulting
20 in its saving.

The preferred embodiment of the present invention is described below.

A rebellious oxidized copper ore is crushed to the particle size than 0.74 mm in an amount of 70%. The crushed ore
25 is mixed with water in a mass ratio of solid and liquid phases S:L-1:0.5, then elementary sulphur is introduced into the obtained pulp in a mass ratio to the oxidized copper equal to 0.5:1 and then sodium sulphate is added therein in a ratio of 7 parts by mass to 1 part by mass
30 of elementary sulphur. Then the pulp is charged into an air-tight tank, for example, an autoclave, and heated.

The process is carried out at temperature of 160°C and pressure of 6 atm. Under such conditions the sulphur melts and efficiently reacts with the oxidized copper ore and
35 associated valuable components. The products of the sulphi-



dization reaction, viz., copper and silver, are recovered by foam flotation. To this end, after sulphidizing the pulp having pH=6.4 is cooled to 25°C, then a collector (butyl xanthate), a frothing reagent (a mixture of mono- and ^{dihydric} ~~dihydric~~ thioran and dioxane alcohols) are introduced therein and the pulp is subjected to flotation. A part of the concentrate produced in the amount of 1.5% by mass related to the ore quantity is returned back to the stage of the initial pulp preparation and sulphidizing of new portions of the ore is carried out in the presence of this concentrate.

Copper recovery from the ore is 98.6%, that of silver is 97.5%.

The method of the invention has commercial advantages over the methods known in the art.

1. It permits to efficiently solve the problem of processing rebellious oxidized copper ores and surpasses in its technical and economic characteristics all the known methods intended for the same purpose.

2. The important advantage of the present invention is an increased copper recovery. If ores contain silver, gold and platinum, these metals can be adequately recovered as well.

3. The present invention simplifies the concentration process due to obviation of leaching, which usually involves additional problems associated with separation of solid and liquid phases, protection of the equipment against corrosive action of acids, subsequent recovery or neutralizing of the leaching agent, etc.

4. The present invention promotes environment pollution control. The implementation of the method is not accompanied with gas emission, and waste products (flotation tailings, waste water) do not contain acids and alkalis, and, therefore, do not create additional ecological problems.



5. The present invention can be readily used in commercial production as it does not require any special equipment. The method may be successfully used in any heated air-tight vessel, for example in an autoclave.

5 6. The copper-sulphide concentrate produced by this method can be efficiently processed in the copper-smelting production by the same method which is usually used for the concentrate recovered from the sulphide ores. If a concentration plant is located close to a copper-smelting plant,
10 the possibility of obtaining high economic profits is apparent.

7. The subject invention may be efficiently used for processing of copper plant intermediate and ~~waste~~^{waste} products, containing oxidized copper compounds: dust, cinder, slimes,
15 etc.

To make the present invention more apparent, illustrative examples of the embodiment of the method for concentration of oxidized copper ores are given below.

Example 1

20 The initial oxidized rebellious copper ore contained 1.2% copper and 10.4 g per ton of silver, including 0.93% copper present in the composition of oxidized minerals (chrysocollas; malachites, brochantites) and 0.39% copper in the form of sulphides. Said ore was crushed to particle
25 size of less than 0.74 mm (70% of particles). The ground ore was mixed with water in a mass ratio S:L equal to 1:1.5.

Elementary sulphur was added to the pulp thus produced in the mass ratio to the oxidized copper of 0.2-
-1.5:1.

30 The pulp was charged into an autoclave of 1 litre capacity, equipped with a mixer, and heated to 160°C. As the temperature increased the pressure in the autoclave also increased and amounted to 6 atm. The pulp sulphidizing lasted 60 minutes. Under said conditions the sulphur
35 melted and reacted with the oxidized copper from the ore.



Thereby copper sulphides, mainly covellite, as well as silver sulphides were produced.

Then the pulp, which by the end of the sulphidizing process had pH=6-7, was cooled to 25°C and directed to flotation. In flotation butyl xanthate was used as a collector and a mixture of mono- and ^{dihydric} ~~dihydric~~ thioran and dioxane alcohols was used as a frothing reagent. The characteristics of copper and silver recovery in concentrate depending on the quantity of sulphur used are shown in Table 1.

Table 1

Amount of elementary sulphur, kg	0.2	0.5	0.75	1.0	1.5
Copper recovery in concentrate, %	74.9	84.3	91.5	91.7	91.8
Silver recovery in concentrate, %	72.3	82.7	90.0	90.1	90.2

Example 2

The same ore as in Example 1 was used. The process was carried out as described in Example 1, except that pulp sulphidizing was accomplished with temperature varying within the interval of 115-180°C and pressure within the range of 1.5-10 atm. Sulphur was added in the amount of 0.75 kg per kg of the oxidized copper ore. The ^{characteristics} ~~characteristics~~ of copper and silver recovery in concentrate are shown in Table 2.

Table 2

Temperature of sulphidizing, °C	115	140	160	180
Pressure in autoclave, atm.	1.5	4	6	10
Copper recovery in concentrate, %	81.5	87.2	91.5	92.6
Silver recovery in concentrate, %	80.8	86.0	90.0	90.1



Example 3

The ore and conditions of concentration were the same as in Example 1, except that sodium sulphate was introduced in the pulp in a mass ratio to elementary sulphur equal to 3-7:1, or natural mineral (mirabilite) of the composition $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was added therein in the amount as converted to sodium sulphate and related to sulphur, according to the same ratio 3-7:1. Elementary sulphur in this case was added in the amount according to the ratio 1.2:1.

The data characterizing recovery of copper in flotation concentrate within said alteration range of sodium sulphate or mirabilite consumption are shown in Table 3.

Table 3

Sodium sulphate consumption			
in sulphidizing, kg	3:1	5:1	7:1
Copper recovery in concentrate, when sodium sulphate was used, %	92.1	97.5	98.6
Copper recovery in concentrate, when natural mineral (mirabilite) was used, %	91.3	96.3	7.5

Example 4

The method of ore concentration was the same as in Example 1, except that sodium chloride was added to the pulp in the amount of 0.7:3.0 kg per kg of the sulphur charged.

Sulphur consumption in this case was 0.75 kg/kg. The data obtained are shown in Table 4.

Table 4

Sodium chloride consumption in sulphidizing, kg	0.7	1.5	3.0
Copper recovery in concentrate, %	95.6	97.1	97.8
Silver recovery in concentrate, %	94.1	96.6	96.8



Example 5

The ore used and the conditions of concentration were the same as described in Example 4 with the only difference that instead of sodium chloride before sulphidizing calcium chloride was added to the pulp in an amount of 0.7-3.0 kg per kg of the sulphur charged.

The data obtained are shown in Table 5.

Table 5

Calcium chloride consumption in sulphidizing, kg	0.7	1.5	3.0
Copper recovery in concentrate, %	92.7	94.5	94.7
Silver recovery in concentrate, %	92.1	92.8	93.0

10 Example 6

The initial ore contained 1.22% copper including copper in the form of oxidized minerals (chrysocollas, malachites, azurites) in the amount of 1.10%. The ore was concentrated under the conditions described in Example 1 with S:L=1:0.5 and the quantity of sulphur added was equal to 0.75:1. Copper recovery in the concentrate was 95.0%. A portion of copper-sulphide concentrate in the amount of 1.5-3.5% to the mass of the initial ore was returned back for the preparation of a new portion of the pulp. In this case the amount of sulphur used for sulphidizing was decreased, as this reduction was balanced with sulphur present in the concentrate. The data characterizing the ore concentration with sulphur consumption of 0.2:1 depending on the quantity of recovered concentrate used in sulphidizing are shown in Table 6.

Table 6

Amount of recovered concentrate, % by mass	1.5	2.5	3
Copper recovery in concentrate, %	74.7	86.5	89.8



Industrial Applicability

The present invention may be used for concentration of rebellions oxidized copper ores and for processing of copper plant intermediate and waste products containing
5 oxidized copper compounds: dust, cinder, slimes and for recovery of copper thereof.

Sulphide concentrates produced by this method are recovered concurrently with copper and noble metal impurities such as silver, gold and other valuable metals.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of concentration of complex oxidized copper ores, comprising:

- preparation of a pulp of said complex oxidized copper ores, wherein the said pulp is formed by mixing together crushed copper ores with water, said crushed complex oxidized copper ores containing 50-100% of particles having a screened size to 0.74mm, and the prepared pulp has a ratio of solid to liquid phases equal to 1:0.5-3.0;
- sulphidizing the pulp with elemental sulphur in the absence of leaching agents, acids, sulphites and hydroxysulphides, wherein the mass ratio of elementary sulfur to oxidized copper is 0.2-1.5:1; said sulphidizing being performed at a temperature of at least 115°C and for at least 20 minutes, and being characterized in that the pulp is sulphidized with molten sulphur; and
- subjecting the sulphidized pulp mixture to flotation to obtain a sulphide-copper concentrate.

2. A method as claimed in Claim 1, wherein pulp sulphidizing is carried out at a temperature of 115-180°C.

3. A method as claimed in Claim 1 or 2, wherein pulp sulphidizing is carried out at pressure of a 1.5-10 atm.



4. A method as claimed in any one of Claims 1 to 3, wherein pulp sulphidizing is carried out in the presence of an additive, which is sodium sulphate or a natural mineral (mirabilite) or sodium chloride or calcium chloride.

5

5. A method as claimed in Claim 4, characterized in that the mass ratio of sodium sulphate to sulphur is 3-7:1.

10

6. A method as claimed in Claim 4, characterized in that the mass ratio of sodium or calcium chlorides to sulphur is 0.7-3:1.

15

7. A method as claimed in any one of Claims 1 to 6, wherein pulp sulphidizing is carried out in an aqueous medium of pH=6-7.

20

8. A method as claimed in any one of Claims 1 to 7, characterized in that the obtained sulphide concentrate in an amount of 1.5-3% by mass to the initial oxidized ore is returned back for preparation of the initial pulp.

25

9. A method of concentration of complex oxidized copper ores substantially as herein described with reference to any one of the Examples.

DATED this 30th day of August 1990

30

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7781S/SLV

METHOD OF CONCENTRATION OF REBELLIOUS OXIDIZED
COPPER ORES

ABSTRACT

5 A method comprises preparation of a pulp, its sulphidizing and flotation. Sulphidizing of the pulp is carried out with molten sulphur at a temperature of 115-180°C and pressure 1.5-10 atm. in the presence of sodium sulphate or sodium chloride additives.



INTERNATIONAL SEARCH REPORT

International Application No PCT/SU 86/00097

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 22 B 15/00, B 03 D 1/00, B 03 B 1/02, 1/06		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 22 B 15/00, 3/00, 23/04, C 01 G 3/12, B 03 D 1/00, B 03 B 1/02 + 1/06	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	SU, Al, 709707, (Norilsky ordena Lenina i ordena Trudovogo Krasnogo Znameni gornometallurgicheskoy kombinat im A.P. Zavenyagina), 20 January 1980 (20.01.80), see the claims	1
A	SU, Al, 108670, (S.I. Sobol), 19 October 1958 (19.10.58), see the claims, columns 2,3	1
A	A.A. Abramov "Tekhnologia obogaschenia okislennykh i smeshannykh rud tsvetnykh metallov", 1986, Nedra (Moscow), see pages 70-71	1
A	Referativny zhurnal "Khimia", 19E, Prirodnye i organicheskie soedineniya i ikh sinteticheskie analogi, N5, 1986 (VINITI, Moscow, USSR), Shivrin G.N. et al. "Vliyanie sernistogo gaza na sulfidirovanie rastvorenykh tsvetnykh metallov	1
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the International filing date but later than the priority date claimed "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
03 June 1987 (03.06.87)	15 June 1987 (15.06.87)	
International Searching Authority	Signature of Authorized Officer	
ISA/SU		

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	elementnoi seroi", referat N 5 L 94 Dep. Krasnoyar. in-t tsv. met. Krasno- yarsk, 1985, Rus. --	
A	Referativny zhurnal "Khimia", 19E, Prirodnye i organicheskie soedineniya i ikh sinteticheskie analogi, N 6, 1986 (VINITI, Moscow, USSR), Shivrín G.N. et al. "Termodinamicheskaya otsenka vozmozhnosti sulfidirovaniya rastvo- rennykh metallov sulfidami metallov", referat N 6 L 185, Dep. Krasnoyar. in-t tsv. met. Krasnoyarsk, 1985, Rus	1
A	D.S. Sobolev et al. "Praktika obogasche- nia rud tsvetnykh i redkikh metallov", vol. II, 1960, Gosudarstvennoe nauchno- tekhnicheskoe izdatelstvo literatury po gornomu delu (Moscow), see page 45 --	1
A	SU, A1, 59343, (I.N. Shorsher), 31 March 1941 (31.03.41) --	1-3
A	SU, A1, 333208, (Gosudarstvenny nauchno- issledovatel'skiy institut tsvetnykh metallov), 27 April 1972 (27.04.72) --	1
A	US, A, 2989394, (Newmont Exploration Limited), 20 June 1961 (20.06.61), see column 3, lines 20-30 --	1-3
A	US, A, 3728430, (Jay B. Clitheroe et al.) 17 April 1973 (17.04.73), see column 2, lines 5-10 -----	1-3