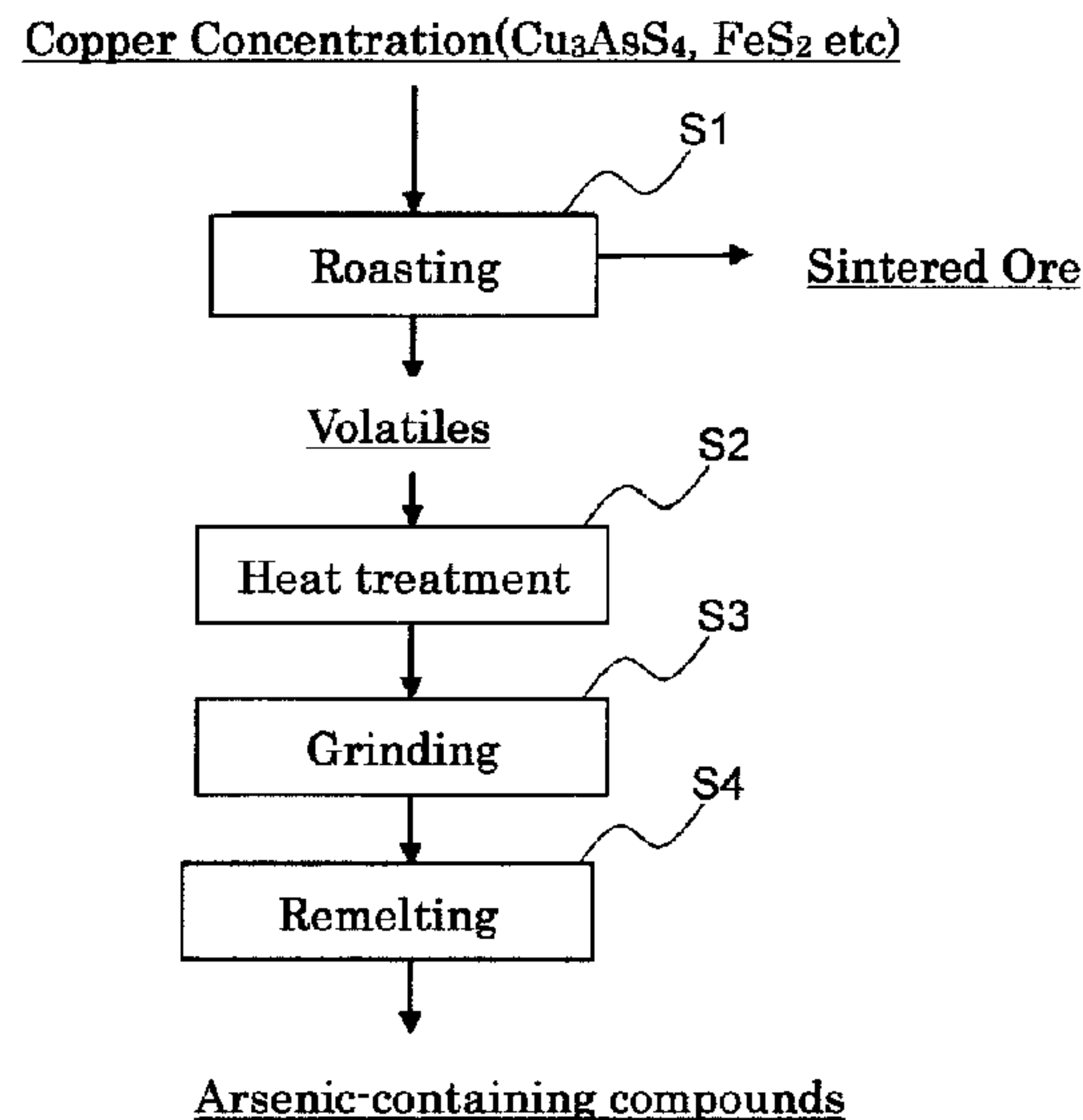




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(54) Titre : PROCEDE DE TRAITEMENT DE L'ARSENIC ET COMPOSE CONTENANT DE L'ARSENIC
(54) Title: METHOD FOR PROCESSING ARSENIC AND ARSENIC-CONTAINING COMPOUND



(57) Abrégé/Abstract:

Provided is a processing method for arsenic, with which it is possible for the arsenic that is contained in copper ore containing arsenic to be processed into a stable form suitable for long-term storage and preservation. This arsenic processing method is characterized by including: a roasting step for roasting copper ore containing arsenic in a non-oxidative atmosphere, and separating the copper pyrites from the volatiles that contain arsenic sulfides; a heat treatment step for heat treating the volatiles obtained in the roasting step, in a non-oxidative atmosphere, causing the arsenic sulfides in the volatiles to melt; a grinding step for grinding the volatiles subsequent to the heat treatment step; and a remelting step for heating and remelting the volatiles subsequent to the grinding step.

ABSTRACT OF THE DISCLOSURE

Provided is a processing method for arsenic, with which it is possible for the arsenic that is contained in copper ore containing arsenic to be processed into a stable form suitable for long-term storage and preservation. This arsenic processing method is characterized by including: a roasting step for roasting copper ore containing arsenic in a non-oxidative atmosphere, and separating the copper pyrites from the volatiles that contain arsenic sulfides; a heat treatment step for heat treating the volatiles obtained in the roasting step, in a non-oxidative atmosphere, causing the arsenic sulfides in the volatiles to melt; a grinding step for grinding the volatiles subsequent to the heat treatment step; and a remelting step for heating and remelting the volatiles subsequent to the grinding step.

METHOD FOR PROCESSING ARSENIC AND ARSENIC-CONTAINING COMPOUND

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001]

The present invention relates to a method for processing arsenic, in particular, to a method for processing arsenic applicable to a processing of an arsenic-containing copper ore.

2. Description of the Related Art

[0002]

In recent years, copper ores excavated in a copper mine operated in the world is constituted mainly with primary copper sulfide ores in which iron, sulfur, and other impurities are increased and the copper ore quality tends to decrease. This causes an increase of production cost of a copper concentrate for pyrometallurgy of copper.

[0003]

Arsenic is regarded as the most troublesome impurity among impurities in the copper ore. Arsenic is extremely harmful depending on its existing form and its use in industrial sectors is very small so that most of arsenic has to be discarded or stored in a stable form.

[0004]

A custom smelter for pyrometallurgy of copper therefore sets a certain limit for arsenic (generally in a range of <0.3% by mass) in the copper concentrate purchased. A miner generally

pays the custom smelter a penalty corresponding to an excess amount of arsenic when exceeding the limit.

[0005]

Hence an effective method for processing a copper sulfide ore containing a large amount of arsenic is matter of concern for the miner in order to reduce cost and to extend the mine life. On the other hand, the custom smelter for pyrometallurgy of copper will be potentially required in future to respond to the copper concentrate containing a large amount of arsenic by depletion of good quality copper ore and tight supply of the copper concentrate.

[0006]

JP 2009-39666 A discloses a method for processing arsenic in which an arsenic-containing compound is converted to a form of a compact crystalline particle of the compound with a low water content followed by coating the resultant crystalline compound with a resin.

[0007]

However, the method described in JP 2009-39666 A includes a step of adjusting an arsenic-containing compound that is coated with resin into a certain form. The drawback of the method is that a preliminary adjustment for this step is complicated and cost for this process is expensive. Considering long-term storage of an arsenic-containing compound for years or decades, resin for coating may be deteriorated and gradually eluted.

SUMMARY OF THE INVENTION

[0008]

In view of the problems above, the present invention provides an easier method for processing arsenic in which arsenic contained in the arsenic-containing copper ore can be processed to convert to a stable form suitable for long-term storage and preservation.

[0009]

To solve the problem above, the present inventors extensively studied and found that arsenic can be converted to a stable form that is more stable than conventional form while preventing its elution for longer time by: roasting the arsenic-containing copper ore to extract the arsenic-containing volatile matter from the copper ore; subjecting the volatile matter to a given process; and further subjecting the volatile matter to other given processes to increase the density of the volatile matter.

[0010]

One aspect of the present invention which is completed based on the findings above is a method for processing arsenic including:

a roasting process in which an arsenic-containing copper ore is roasted in a non-oxidative atmosphere to separate chalcopryrite from a volatile matter containing sulfides of arsenic; and

a heat treatment process in which the volatile matter

obtained in the roasting process is heat treated in a non-oxidative atmosphere to melt the sulfides of arsenic in the volatile matter.

a grinding process in which the volatile matter is ground after the heat treatment process,

a remelting process in which the volatile matter is heat treated to be remelted in a non-oxidative atmosphere after the grinding process

[0011]

An embodiment of a method for processing arsenic related to the present invention includes heat-treating the volatile matter at from 200°C to 250°C in the remelting process.

[0012]

Another embodiment of the method for processing arsenic related to the present invention includes heat-treating the volatile matter such that a density of the volatile matter after the remelting process is from 1.5g/cm³ to 3.0 g/cm³

[0013]

Another embodiment of the method for processing arsenic related to the present invention further includes adding sulfur in the heat treatment process.

[0014]

Yet another embodiment of the method for processing arsenic related to the present invention further includes adjusting a mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 1.2 or more in the heat

treatment process.

[0015]

Yet another embodiment of the method for processing arsenic related to the present invention further includes adding a rubber antioxidant in the heat treatment process.

[0016]

Yet another aspect of the present invention is a solid arsenic-containing compound consisting of Arsenic and Sulphur, wherein the concentration of Arsenic is from 1 % by mass to 40 % by mass and the density is from 1.5g/cm³ to 3.0g/cm³ .

[0017]

The present invention can provide the easier method for processing arsenic in which arsenic in the arsenic-containing copper ore can be processed to be converted to a stable form of arsenic suitable for long-term storage and preservation.

BRIEF DESCRIPTION OF DRAWINGS

[0018]

FIG. 1 is a flowchart showing a method for processing arsenic according an embodiment of the present invention;

FIG. 2 is an example of photomicrographs illustrating features of a heat-treated object obtained in a heat treatment process;

FIG. 3a is a photograph illustrating an appearance of a volatile matter (a heat-treated object) obtained in a heat treatment process;

FIG. 3b is a photograph illustrating an appearance of a volatile matter (a heat-treated object) obtained in a heat

treatment process; and

FIG. 4 is a graph representing an amount of elution for Arsenic in an arsenic-containing compound obtained via volatilization, heat treatment, and remelting.

DETAILED DESCRIPTION OF THE EMBODIMENT

[0019]

As shown in Fig. 1, a method for processing arsenic according to an embodiment of the present invention includes: a roasting process(S1) in which an arsenic-containing copper ore is roasted in a non-oxidative atmosphere to separate chalcopryrite from a volatile matter containing sulfides of arsenic; a heat treatment process(S2) in which the volatile matter obtained in the roasting process (S1) is heat treated in a non-oxidative atmosphere to melt the sulfides of arsenic in the volatile matter; a grinding process(S3) in which the volatile matter is ground after the heat treatment process (S2), a remelting process(S4) in which the volatile matter is heat treated to be remelted in a non-oxidative atmosphere after the griding process (S3).

[0020]

A processing object in the method for processing arsenic related to an embodiment of the present invention is an arsenic-containing copper ore. Specifically, for example, enargite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), the copper concentrate in which such arsenic-containing copper ores are mixed, or the like can be used. Incidentally, needless to say,

the copper ore is not limited to such copper ores as long as the ore is the arsenic-containing copper ore and can be processed in a two stage process described below.

[0021]

For example, the grade of the copper concentrate constituted with enargite as a major component applicable for the present invention may be varied depending on the grade of coexisting pyrite (FeS_2) and the gangue element, but the copper concentrate typically contains 15% to 35% copper by mass and 3% to 15% arsenic by mass.

[0022]

In the present embodiment, the copper concentrate is preferably predried at a temperature that does not have the effect on the mineral species and content. Generally, when the copper concentrate is dried with high-temperature air, the temperature of the copper concentrate at a dryer outlet is kept around 90°C to adjust the moisture content in the copper concentrate to be 0.5% by mass or less.

[0023]

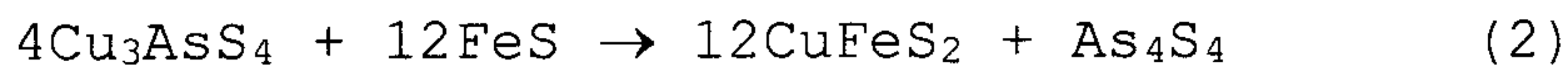
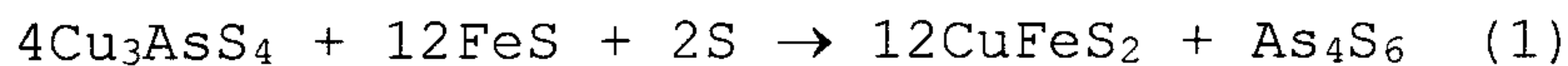
A roasting process (S1)

The copper concentrate dried is roasted in a non-oxidative atmosphere at 550°C to 700°C for 10 to 60 minutes. As a gas to render apparatus a non-oxidative atmosphere, for example, a nitrogen gas can be used. Incidentally, control of the processing temperature and the atmosphere in the roasting process is a condition required for converting the copper concentrate constituted with enargite as a major component to

arsenic sulfide, chalcopyrite and the like and the reaction time is a time required for not leaving enargite unreacted.

[0024]

A reaction to form sulfides of arsenic in a copper concentrate in the roasting process (S1) follows Formulas (1) or (2) as follows. When a large amount of pyrite and the like is contained in an initial copper concentrate, addition of S in Formula (1) becomes unnecessary since pyrite is decomposed in a temperature zone for processing according to Formula (3) to form S which compensates for the lost sulfur.



[0025]

The roasting process (S1) is carried out, for example, using a rotary kiln. As illustrated in Formulas (1) to (3) above, roasting of the copper concentrate generates the arsenic-containing sulfide compound which is vaporized at the vapor pressure corresponding to the temperature and removed from the copper concentrate of a raw material.

[0026]

As a result of the roasting process, a sintered ore constituted with chalcopyrite and cubanite as a major component and a volatile matter containing an arsenic compound (arsenic sulfide) which is volatilized and recovered and elemental

sulfur are obtained from the copper concentrate of a raw material. A ratio of chalcopyrite to cubanite in the sintered ore is varied in a temperature range between 550°C and 700°C depending on the amount of the copper sulfide ore such as chalcopyrite and chalcocite contained before reaction, the amount of pyrite contained before reaction, and the amount of pyrite to be added.

[0027]

Since the sulfides of arsenic and elemental sulfur volatilized in the roasting process (S1) are in a gaseous form, they can be cooled in a non-oxidative atmosphere as it is to solidify for recovery. FIG. 2 illustrates an example of photomicrographs of the volatile matter recovered. The volatile matter recovered contains granular particles with a diameter of approximately 10 μm to 15 μm and is provided with a two-layered structure of an inner layer 1 and an outer layer 2 with a different grade in arsenic.

[0028]

The inner layer 1 of the particle in the volatile matter is constituted with a layer containing approximately 30 mol% of arsenic and approximately 70 mol% of sulfur. The outer layer 2 of the particle in the volatile matter is constituted with the layer containing approximately 5 mol% of arsenic and approximately 95 mol% of sulfur. That is, the volatile matter consisting of the granular particles obtained in the roasting process (S1) has the two-layered structure in which the inner layer 1 containing a large amount of arsenic in the inside of

the particle is covered with the outer layer 2 containing a large amount of sulfur.

[0029]

A heat treatment process (S2)

In the heat treatment process (S2), the particle in the volatile matter illustrated in Figure 2 is further heat-treated in a non-oxidative atmosphere to melt the sulfides of arsenic (arsenic sulfide) in the volatile matter to further reduce elution of arsenic from the volatile matter.

[0030]

As a gas rendering a non-oxidative atmosphere in a heat-treatment system, for example, a nitrogen gas can be used. The process temperature in the heat treatment process (S2) is preferably from 200°C to 600°C, and more preferably from 250°C to 400°C. When the process temperature is below 200°C, the sulfides of arsenic in the volatile matter may not be fully melted, and effects of reducing the amount of arsenic eluted may not sufficiently be obtained. When the process temperature is above 600°C, hydrogen sulfide contained as the sulfides of arsenic in the volatile matter is gasified to volatilize, and therefore, the heat-treated object may not be recovered.

[0031]

The process time in the heat treatment process (S2) is varied depending on the process temperature, but is preferably at least 30 minutes or more, and more preferably 50 minutes or more in order to proceed with the reaction to completion from a point of view of the effects for reducing the amount of As

eluted from the heat-treated object.

[0032]

Sulfur is preferably added to the volatile matter in the heat treatment process (S2). This is because the higher process temperature in the heat treatment process (S2) increases the volume of sulfur volatilized from volatile matter and the concentration of arsenic in volatile matter accordingly, resulting the less effects of preventing arsenic from elution (this prevention may be achieved by the reaction of sulfur with arsenic). For example, when the volatile matter with the mass ratio of S/As to be 3.0 is processed at 400°C, an S component in the volatile matter is volatilized to reduce the mass ratio of S/As to be approximately 2.4, whereas when processed at 500°C, the S component may be volatilized to reduce the mass ratio of S/As to be approximately 1.2. Elemental sulfur is preferred as a source of sulfur to be added from a point of view in material handling. Sulfur may be added before the heat treatment process or during the heat treatment process.

[0033]

In the heat treatment process (S2) sulfur and arsenic concentrations in the volatile matter are preferably adjusted by addition of sulfur as needed so as to keep the mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 1.2 or more, more preferably 2.3 or more, further preferably 3 or more. When the mass ratio of S/As is reduced to below 1.2, even if the process time for heat treatment is extended, effects of reducing arsenic to be eluted may not

sufficiently be obtained.

[0034]

Incidentally, an upper limit of the mass ratio of S/As is not particularly limited, but the higher the mass ratio of S/As, the stronger effects of preventing As from elution can be achieved in a shorter heat treatment time. On the other hand, when too much amount of sulfur is added in order to increase the mass ratio of S/As, there is little change in the effects of preventing As from elution. Rather, the amount of sulfur is in excess relative to levels of arsenic and aftertreatment of excess sulfur is required, which results in cost increase. Therefore, the upper limit of the mass ratio of S/As can be set to be approximately 6.

[0035]

In the heat treatment process (S2), a rubber antioxidant can be added in addition to elemental sulfur. This can prevent the elution of arsenic from the arsenic-containing volatile matter over a longer period of time. As a rubber antioxidant any one or more types of antioxidants selected from, for example, monophenol type, bisphenol type, and polyphenol type antioxidants can be used. An additive amount for a rubber antioxidant is 0.2 mol/m^3 or more, more preferably 0.4 mol/m^3 or more, more specifically from 0.2 to 2.0 mol/m^3 .

[0037]

Fig 3(a) is a photograph illustrating an appearance of a volatile matter (a heat-treated object) obtained in a heat treatment process (S2). This heat-treated object is recovered

in a form of a bulky and pillar-shaped material. The amount of Arsenic contained in the heat-treated object is from 12 to 15 mol% and the density of the heat-treated object is approximately from 0.6 to 1.5g/cm³. Because the heat-treatment process (S2) expands a sample, the density of the heat-treated object is approximately half of that of a pure arsenic sulfide. This heat-treated object can be stored as it is (i.e., can be stored without any further processing). However, since lower density leads to larger specific surface area, resulting in a larger area that contacts with an atmosphere (such as air or liquid) external to a heat-treated object. Thus, Arsenic is likely to elute in some cases.

[0038]

A grinding process (S3) and a remelting process (S4)

In an embodiment of the present invention, the heat-treated object thus is ground after the heat treatment process S2, and then the heat-treated and ground object is re-heat treated and remelted, thereby increasing the density of the heat-treated object. Fig 3 (b) shows an example of the remelted object. Means for grinding in a grinding process (S3) is not limited to any specific one and any conventional method may be performed. For example, an operator may manually grind with use of certain instrument. Alternatively, grinding machine may be used.

[0039]

In remelting process (S4), the ground and heat-treated object (the volatile matter) may be heat-treated under a

non-oxidative atmosphere (such as nitrogen) to melt arsenic sulfide in the heat-treated object. The heat-treated object is preferably heat-treated such that the density of the remelted and heat-treated object is from 1.5 to 3.0g/cm³. The temperature for a remelting process (S4) is preferably 200 ~250 °C and more preferably about 220~250 °C. If the temperature is less than 200 °C, the heat treated object may be not sufficiently remelted in some cases. If the temperature is more than 250 °C, a portion of sulfur contained in a raw material may volatile to expand a sample, resulting in that the density is not increased.

[0040]

The remelted object (sulfur-containing compound) that is obtained in a remelting process (S4) is a solid and arsenic-containing compound consisting of arsenic and sulfur, which includes arsenic with an amount of from 1 to 40 % by mass, and the density of which is from 1.5 to 3.0 g/cm³. This remelted object is preferably stored in water, thereby, allowing arsenic included in copper ore to be stored and preserved in a stable form for long time.

EXAMPLES

[0041]

Hereinafter, the present invention is described in further details by way of examples, but is in no way limited thereto.

[0042]

Example 1

A high-arsenic-grade copper concentrate with the grade of 21% Cu by mass, 23% Fe by mass, 38% S by mass, and 6.8% As by mass was used as a copper concentrate of a raw material. The high-arsenic-grade copper concentrate was analyzed by using an X-ray diffractometer (XRD) and an electron probe microanalyzer (EPMA) to characterize a major mineral composition of 11% chalcopyrite (CuFeS_2) by mass, 42% pyrite (FeS_2) by mass, 36% enargite (Cu_3AsS_4) by mass, and 11% gangue element (SiO_2 and the like) by mass.

[0043]

After 100 g of the arsenic-containing copper concentrate were predried, the predried material was roasted in a nitrogen gas atmosphere at the process temperature of 650°C to separate the copper concentrate (roasted copper concentrate) containing chalcopyrite with little arsenic from the volatile matter containing 33% arsenic by mass and 64% sulfur by mass as illustrated in Table 1.

[0039]

	Grade (% by mass)			
	As	S	Cu	Fe
Crude copper ore	6.8	38	21	23
Roasted	0.3	31	29	31

copper concentrate				
Volatile matter	33	64	-	-

[0044]

When the volatile matter obtained in the roasting process was cooled to solidify for recovery, the mass ratio of S/As in the volatile matter was 2.3. The volatile matter was heat-treated for 30 minutes at the temperature of 280 °C under a non-oxidative atmosphere to obtain the heat-treated object. The obtained heat-treated object was ground and then the grounded object was heated for 10 minutes at the temperature of 240 °C under a non-oxidative atmosphere to obtain the remelted object.

[0045]

Example 2

The volatile matter obtained via the roasting process of Example 1 (the mass ratio of S/As being 2.3) was added with elemental sulfur such that the mass ratio of S/As in the volatile matter was adjusted to 4.1. Further the volatile matter was added with 0.5mol/m³ of monophenol-based rubber antioxidant (2,6-di-t-butyl-4-methylphenol). Then, the volatile matter was heat-treated for 30 minutes at the temperature of 280 °C under a nitrogen gas atmosphere. The obtained and heat-treated object was ground and then the grounded object was heated for 10 minutes at the temperature of 240 °C to obtain the remelted object.

[0046]

The volatile matter, the heat-treated object, and the remelted object that were obtained via each step of Examples 1 and 2 were subjected to the Toxicity Characteristics Leaching Procedure (TCLP) by the US Environment Protection Agency (EPA) for the characterization of a soil pollution substance. That is, in the leaching procedure, the volatile matter, the heat-treated object, and the remelted object were ground to obtain samples with the particle size below 9.5 mm (0.5 mm to 5 mm). Then, for leaching the samples, deionized water, acetic acid or acetate buffer solutions were used as a leachant while keeping pH at 2.88, and the sample were shaken at the liquid-solid ratio of 20 in a rotary shaker at 30 rpm and temperature of 22.3°C for 18 hours to separate the liquid extract from the solid phase through the pressure filtration (using glass fiber filter (GFF) with the pore size of 0.6 μm to 0.8 μm) for the leaching procedure. The results are illustrated in FIG. 4.

[0047]

As the process proceeds to roasting, heat-treating, and remelting as shown in Fig 4, the amount of elution for As decreased. The ultimate amounts of elution for As in the remelted object for both of Examples 1 and 2 were 1mg/L or less.

[0048]

The density for the heat-treated object and the remelted object in Example 1 was measured respectively. As a result, the density for the heat-treated object was 1.0g/cm³ while the density for the remelted object was 2.5g/cm³. Also, the density

for the heat-treated object and the remelted object in Example 2, in which the additives were added, was measured respectively. As a result, the density for the heat-treated object was 1.0g/cm^3 while the density for the remelted object was 2.4g/cm^3 . These results indicate that the remelting process produces a density-increased bulk (block state) that is more stable in view of low amount of elution for As.

[0049]

Explanation of references

1 Inner layer

2 Outer layer

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for processing arsenic comprising:

a roasting process in which an arsenic-containing copper ore is roasted in a non-oxidative atmosphere to separate chalcopyrite from a volatile matter containing sulfides of arsenic, the ore containing Fe and S; and

a heat treatment process in which the volatile matter obtained in the roasting process is heat treated in a non-oxidative atmosphere to melt the sulfides of arsenic in the volatile matter.

a grinding process in which the volatile matter is ground after the heat treatment process,

a remelting process in which the volatile matter is heat treated to remelt in a non-oxidative atmosphere after the grinding process.

2. The method of claim 1, wherein the remelting process comprises heating the volatile matter at 200°C to 250°C.

3. The method of claims 1 or 2, wherein the remelting process comprises heating the volatile matter such that a density of the volatile matter after the remelting process is from 1.5g/cm³ to 3.0 g/cm³.

4. The method of any one of claims 1 to 3, wherein the heat treatment process comprises adding sulfur.

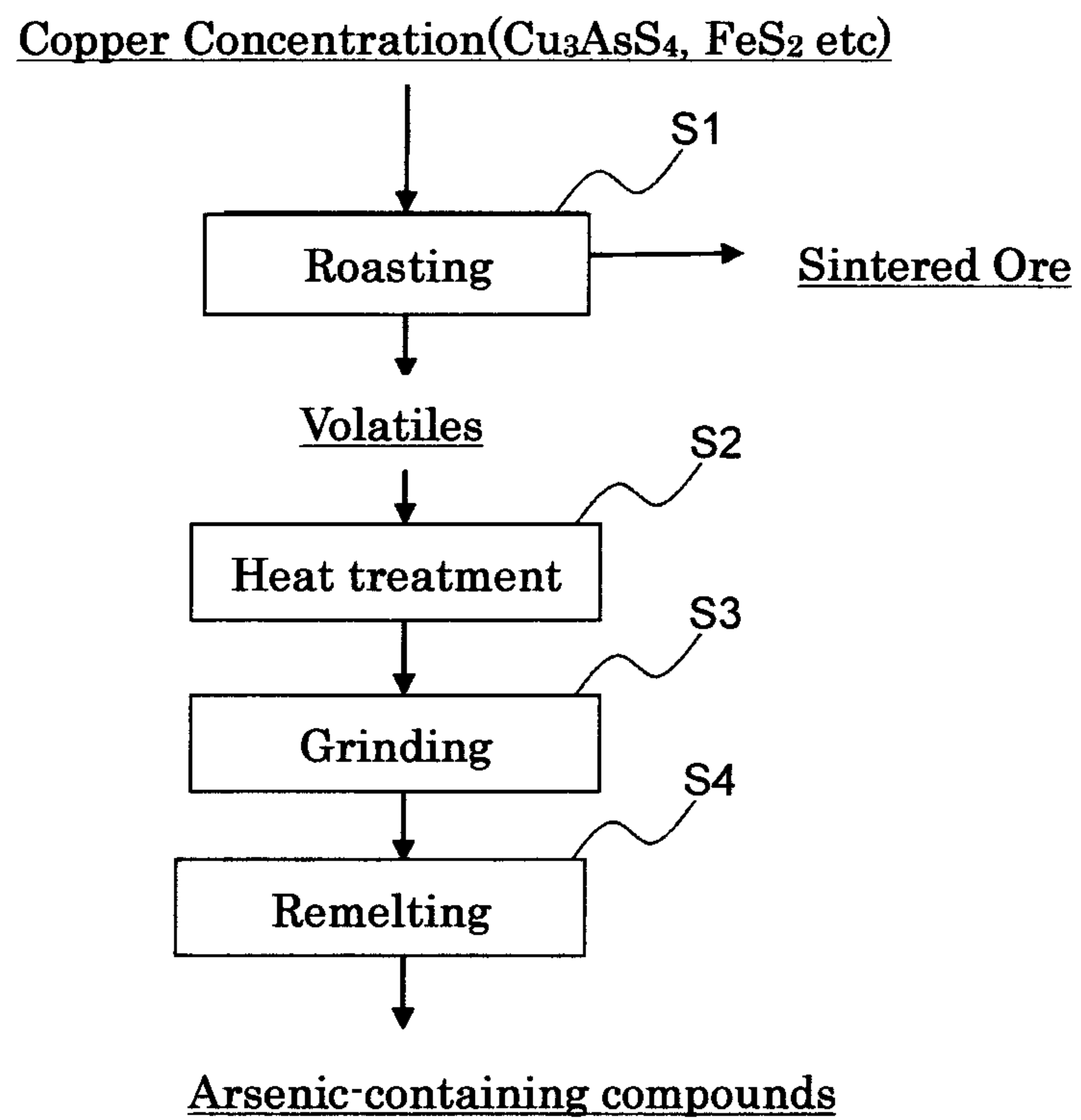
5. The method of any one of claims 1 to 4, wherein the heat treatment process comprises adjusting the content of sulfur to adjust a mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 1.2 or more.

6. The method of any one of claims 1 to 5, wherein the heat treatment process comprises further adding a rubber antioxidant.

7. A solid arsenic-containing compound consisting of arsenic and sulfur, wherein the concentration of arsenic is from 1 % by mass to 40 mass % by mass and the density is from 1.5g/cm³ to 3.0g/cm³.

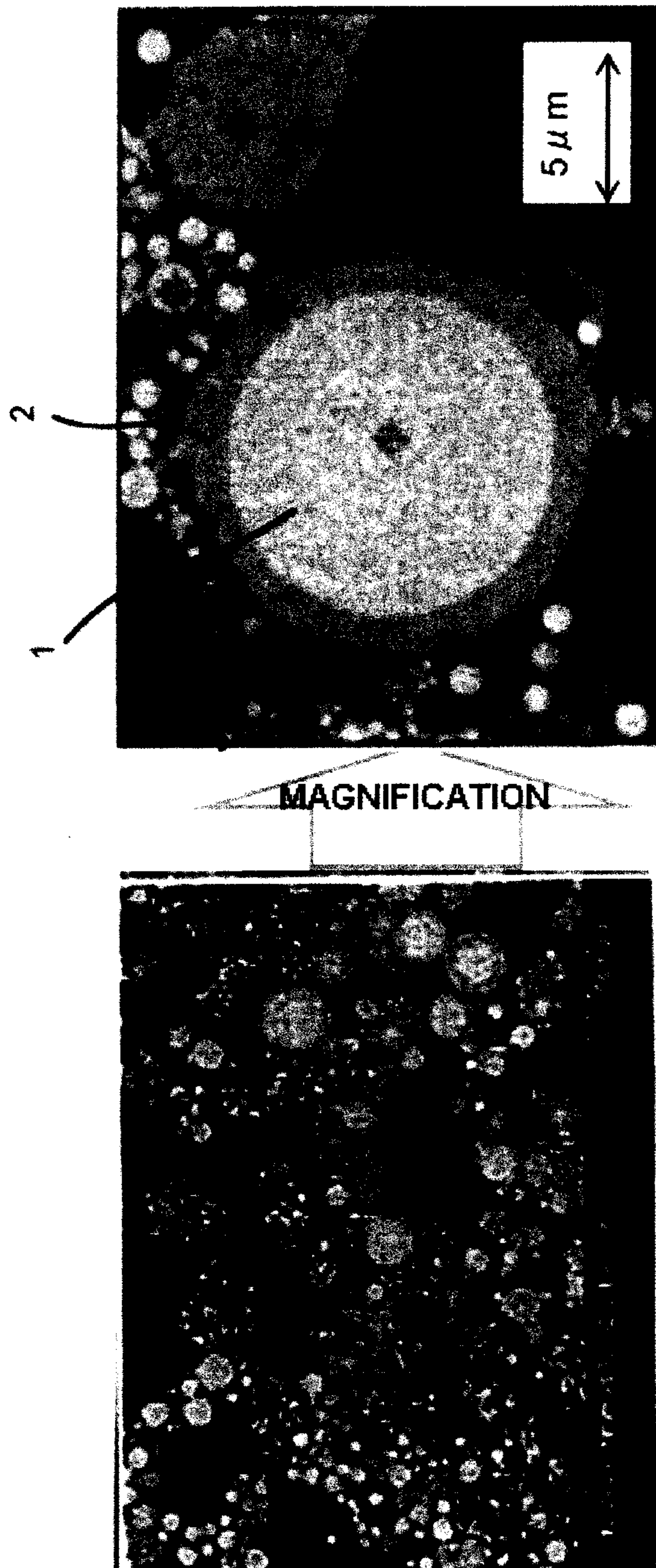
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[FIG. 1]



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[FIG. 2]



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[FIG. 3a]



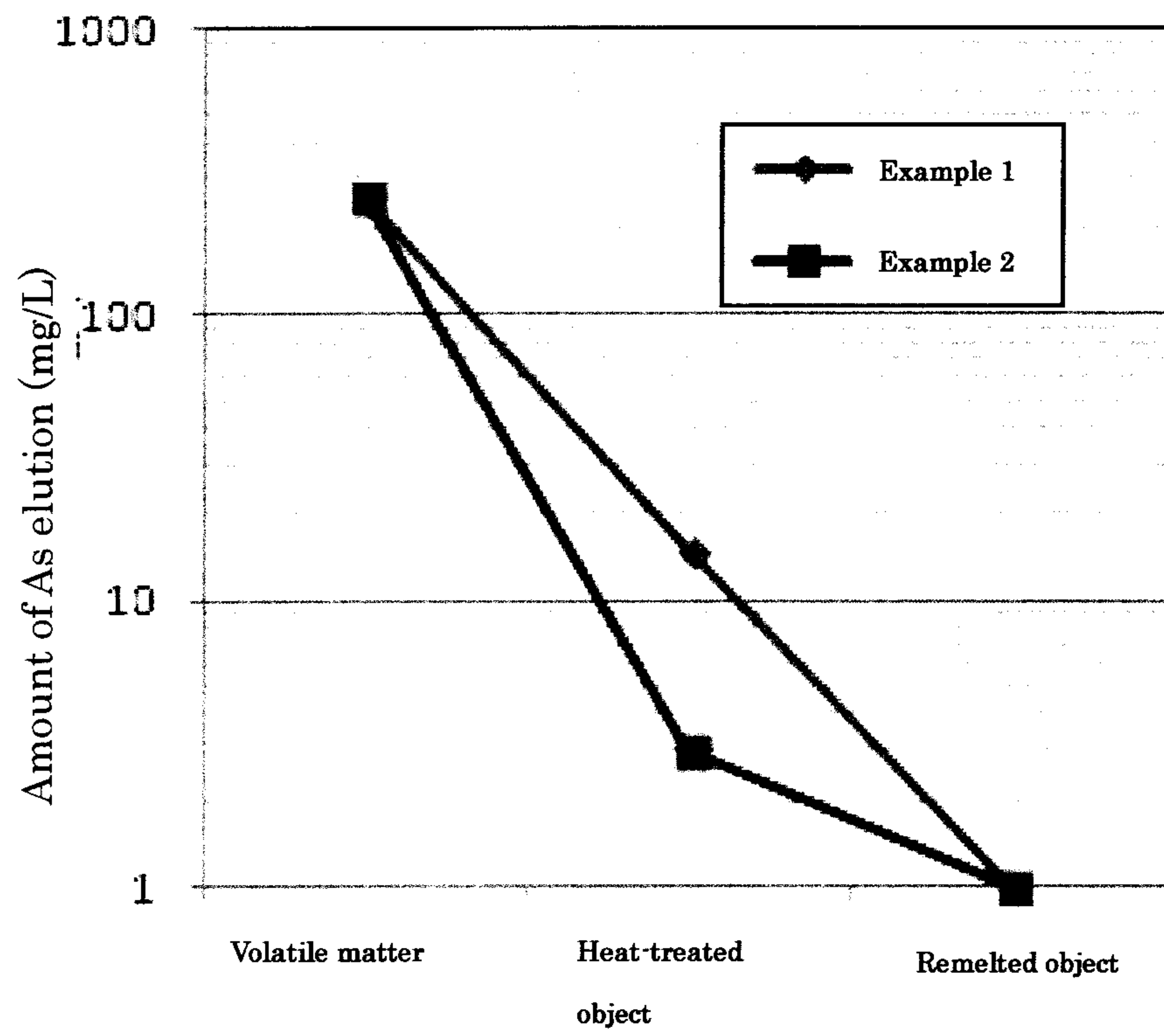
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[FIG. 3b]



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[FIG. 4]



Copper Concentration(Cu_3AsS_4 , FeS_2 etc)

