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(71) **Demandeur/Applicant:**
JX NIPPON MINING & METALS CORPORATION, JP

(72) **Inventeurs/Inventors:**
TATSUMI, RYOSUKE, JP;
HATANO, KAZUHIRO, JP

(74) **Agent:** MARKS & CLERK

(54) **Titre : PROCÉDE DE TRAITEMENT DE L'ARSENIC**

(54) **Title: METHOD FOR PROCESSING ARSENIC**

(57) **Abrégé/Abstract:**

A method for processing arsenic which includes a roasting process in which an arsenic-containing copper ore is roasted in an inert gas atmosphere to separate chalcopyrite from a volatile matter containing sulfides of arsenic; and a heat treatment process in which sulfur and an antioxidant are added to the volatile matter obtained in the roasting process followed by heat-treating in the inert gas atmosphere for dissolving sulfides of arsenic in the volatile matter.



ABSTRACT OF THE DISCLOSURE

A method for processing arsenic which includes a roasting process in which an arsenic-containing copper ore is roasted in an inert gas atmosphere to separate chalcopyrite from a volatile matter containing sulfides of arsenic; and a heat treatment process in which sulfur and an antioxidant are added to the volatile matter obtained in the roasting process followed by heat-treating in the inert gas atmosphere for dissolving sulfides of arsenic in the volatile matter.

METHOD FOR PROCESSING ARSENIC

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 crystalline compound obtained with a resin.

[0007]

Arsenic in the copper ore containing a large amount of arsenic is generally removed in stages of the ore dressing process while spending money to yield a low-arsenic-grade copper concentrate. However, in recent years there is an attempt for processing a high-arsenic-grade copper concentrate as it is or an attempt for processing a high arsenic-bearing copper concentrate from which arsenic is removed in stages of the ore dressing process.

[0008]

For example, JP 2012-87400 A discloses a method for roasting in an inert atmosphere enargite containing relatively high concentration of arsenic or an enargite-containing copper concentrate to separate the sintered ore constituted with chalcopyrite as a major component from the volatile matter constituted with arsenic sulfide as a major component followed by wet processing of the sintered ore.

[0009]

However, the method described in JP 2009-39666 A may cause elution of an arsenic-containing compound from the area of which coat of the arsenic-containing compound coated with a resin is peeled off due to deterioration of the resin, external stress and the like when the arsenic-containing compound coated with the resin is stored and preserved over a long period of time.

[0010]

The invention described in JP 2012-87400 A discloses isolating a sintered ore from enargite or an enargite-containing copper concentrate followed by performing a wet process of the sintered ore, but neither describes nor investigates a specific method for processing an arsenic-containing volatile matter obtained from a copper ore.

SUMMARY OF THE INVENTION

[0011]

In view of the problem above, the present invention provides a method for processing arsenic in which arsenic contained in the arsenic-containing copper ore can be processed

to be converted to a stable form which can be stored and preserved for a long period of time.

[0012]

To solve the problem above, the present inventors extensively studied and found that arsenic can be converted to a stable form while preventing its elution over a long period of time by roasting the arsenic-containing copper ore to extract from the copper ore the arsenic-containing volatile matter, and performing a given process on the volatile matter.

[0013]

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 an inert gas atmosphere to separate chalcopyrite from a volatile matter containing sulfides of arsenic; and a heat treatment process in which sulfur and an antioxidant are added to the volatile matter obtained in the roasting process followed by heat-treating in the inert gas atmosphere for dissolving sulfides of arsenic in the volatile matter.

[0014]

An embodiment of a method for processing arsenic related to the present invention includes adding sulfur to the volatile matter obtained in the roasting process so as to adjust the mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 3 or more.

[0015]

Another embodiment of the method for processing arsenic related to the present invention includes adding 0.2 mol/m³ or more of an antioxidant.

[0016]

In still another embodiment of the method for processing arsenic related to the present invention the antioxidant is one or more types of antioxidants selected from the group consisting of monophenol type, bisphenol type, and polyphenol type antioxidants.

[0017]

Still another embodiment of the method for processing arsenic related to the present invention includes heat-treating of the volatile matter at 200°C to 600°C in the heat treatment process.

[0018]

Another aspect of the present invention is the method for processing arsenic including: roasting an arsenic-containing copper ore in an inert gas atmosphere to separate a roasted copper concentrate from a volatile matter containing sulfides of arsenic; adding sulfur as needed so as to adjust the mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 3 or more; adding further the antioxidant to the volatile matter; and heat-treating in an inert gas atmosphere the volatile matter to which the antioxidant is added to dissolve sulfides of arsenic in the volatile matter.

[0019]

The present invention can provide the method for processing arsenic in which arsenic contained in the arsenic-containing copper ore can be processed to be converted to a stable form which can be stored and preserved for a long period of time.

BRIEF DESCRIPTION OF DRAWINGS

[0020]

FIG. 1 is an example of photomicrographs illustrating features of a volatile matter obtained in a roasting process;

FIG. 2 is a graph representing effects of antioxidants added on the amount of As eluted from a heat-treated object which is heat-treated after addition of antioxidants A to C to volatile matters to which sulfur is added (samples 1 and 3) and to a volatile matter to which sulfur is not added (sample 2); and

FIG. 3 is a graph indicating the stability over time, as demonstrated as the amount of As eluted, of a conventional arsenic-containing heat-treated object (sample 4) and arsenic-containing heat-treated objects (samples 5 to 7) obtained using the method for processing arsenic related to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENT

[0021]

An embodiment for carrying out the present invention will be hereinafter described. 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.

[0022]

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.

[0023]

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.

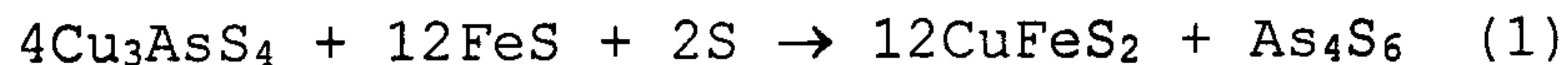
[0024]

The copper concentrate dried is roasted in an inert gas atmosphere at 550°C to 700°C for 10 to 60 minutes (roasting process). As an inert gas, for example, a nitrogen gas can be

used. 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.

[0025]

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



[0026]

The roasting process 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.

[0027]

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.

[0028]

Since the sulfides of arsenic and elemental sulfur volatilized in the roasting process are in a gaseous form, they can be cooled in an inert atmosphere as it is to solidify for recovery. FIG. 1 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.

[0029]

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 granular particle obtained in the roasting process 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.

[0030]

In the heat treatment process carried out after the roasting process, the particle in the volatile matter illustrated in Figure 1 is further heat-treated in an inert gas atmosphere to dissolve the sulfides of arsenic (arsenic sulfide) in the volatile matter to further reduce elution of arsenic from the volatile matter. Also, the heat-treated object can be stored in a stable form over a long period of time by further adding an antioxidant in the presence of sulfide.

[0031]

As an inert gas, for example, a nitrogen gas can be used. The process temperature in the heat treatment process 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 dissolved, 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.

[0032]

The process time in the heat treatment process 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.

[0033]

Sulfur and an antioxidant are added to a volatile matter in a heat treatment process. This is because the higher the process temperature in the heat treatment process becomes and the volume of sulfur volatilized is increased and the concentration of arsenic in volatile matter is increased accordingly, the more the effects of preventing arsenic from elution by the reaction of sulfur with arsenic become. 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.

[0034]

Elemental sulfur is preferred as a source of sulfur added from a point of view in material handling. Sulfur may be added before the heat treatment process or during the heat treatment process. In view of the process efficiency, it is preferred to adjust the sulfur concentration in advance before the heat treatment process. Sulfur may not be added when a large amount of sulfur is already contained in the copper ore as a process

object.

[0035]

A rubber antioxidant can be used as an antioxidant. One or more types of antioxidants selected from the group consisting of monophenol type, bisphenol type, and polyphenol type antioxidants can be suitably used as the rubber antioxidant. The antioxidant is reacted with sulfur in a heat treatment process described below for preventing an arsenic-containing heat-treated object obtained after the heat treatment process from the deterioration by oxidation.

[0036]

As the amount of the antioxidant added, preferably 0.2 mol/m³ or more, and more preferably 0.4 mol/m³ or more are fed, and more specifically the amount is from 0.2 mol/m³ to 2.0 mol/m³. The amount of the antioxidant added is half or less than half of the amount added to rubber in general.

[0037]

For example, when a monophenol type antioxidant is used as the antioxidant, 0.4 mol/m³ or more of the antioxidant is more preferably added to the arsenic-containing volatile matter. When a bisphenol type antioxidant is used as the antioxidant, 0.9 mol/m³ or more of the antioxidant is more preferably added. When a polyphenol type antioxidant is used as the antioxidant, 1.6 mol/m³ or more of the antioxidant is more preferably added. Heat-treating of the arsenic-containing volatile matter to which the antioxidant is added can prevent the elution of As over a long period of time from the arsenic-containing

heat-treated object after the heat treatment.

[0038]

In the heat treatment process, the concentration of sulfur and arsenic in the volatile matter is preferably adjusted to the mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 3 or more, more preferably to be 4 or more by adding sulfur as needed. When the mass ratio of S/As is, for example, approximately 2, even if the process time for heat treatment is extended, effects of reducing arsenic to be eluted may not sufficiently be obtained over a long period of time.

[0039]

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.

[0040]

The arsenic grade in the arsenic-containing heat-treated object finally obtained in the method for processing arsenic related to an embodiment of the present invention is from 12

mol% to 15 mol%. The heat-treated object is constituted with granular substances with an irregular shape having angular forms, and uneven distribution of arsenic and sulfur is not observed as in the volatile matter obtained after the roasting process as illustrated in FIG. 1.

EXAMPLES

[0041]

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

[0042]

(Effects of the amount of As eluted by the addition of antioxidants)

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.

[0044]

	Grade (% by mass)			
	As	S	Cu	Fe
Crude copper ore	6.8	38	21	23
Roasted copper concentrate	0.3	31	29	31
Volatile matter	33	64	-	-

[0045]

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. A sample 1 is prepared as the volatile matter obtained as it is and samples 2 and 3 are prepared as the volatile matter to which elemental sulfur is added to adjust the mass ratio of S/As in the volatile matter to be 5.9. The antioxidant was added to the samples 1 and 3, whereas the antioxidant was not added to the sample 2.

[0046]

The amount of As eluted was evaluated for cases in which 0.5% by mass of 2,6-di-t-butyl-4-methylphenol as the monophenol type antioxidant (antioxidant A in FIG. 2), 2% by mass of 4-ethyl-6t-notylphenol (also called 2,2-methylenebis) as the bisphenol type antioxidant (antioxidant B in FIG. 2), and 1%

by mass of 2,5-di-t-butylhydroquinone as the polyphenol type antioxidant (antioxidant C in FIG. 2) were added, respectively, to the volatile matter of the sample 1. The amount of As eluted was evaluated for the sample 3, in which half of the amount of three types of the antioxidants above used in the sample 1 was added to the volatile matter

[0047]

The samples 1-3 were heat-treated in a nitrogen gas atmosphere at the heat treatment temperature of 280°C for the process time of 30 minutes to obtain the heat-treated object. The obtained heat-treated object was 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 of the heat-treated object, deionized water, acetic acid or acetate buffer solutions were used as a leachant for the heat-treated object with the particle size below 9.5 mm (0.5 mm to 5 mm) while keeping pH at 2.88, and the solid sample was 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 μ m to 0.8 μ m) for the leaching procedure. The results are illustrated in FIG. 2.

[0048]

In the sample 2 in which sulfur is not added to the volatile matter after the roasting process, the effects of the

antioxidant added on the amount of As eluted was not observed. On the other hand, in the samples 1 and 3 in which sulfur is added to the volatile matter after the roasting process, addition of the antioxidant reduces the amount of As eluted as compared to the case in which the antioxidant is not added. The sample 3 is an example in which the amount of the antioxidant added is reduced to half of the amount in the sample 1, enabling to reduce the amount of As eluted to the environmental standard value or less.

[0049]

(Stability over time in the amount of As eluted)

Elemental sulfur was added to the volatile matter obtained in the roasting process in Example 1 so as to adjust the mass ratio of S/As in the volatile matter to be 5.9. A sample 4 in which the antioxidant was not added to the volatile matter after adjustment, a sample 5 in which 0.5% by mass of the monophenol type antioxidant (2,6-di-t-butyl-4-methylphenol) was added to the volatile matter after adjustment, a sample 6 in which 2% by mass of the bisphenol type antioxidant (2,2-methylenebis) was added to the volatile matter after adjustment, and a sample 7 in which 1% by mass of the polyphenol type antioxidant (2,5-di-t-butylhydroquinone) was added to the volatile matter after adjustment were prepared, respectively.

[0050]

The samples 4 to 7 were heat-treated in a nitrogen gas atmosphere at the heat treatment temperature of 280°C for the process time of 30 minutes to obtain the heat-treated object.

The heat-treated object obtained immediately after heat treatment and the heat-treated object stored in an air for 1 month immediately after heat treatment were subjected to the leaching procedure under the similar condition to the above for evaluation of the amount of As eluted. The results are illustrated in FIG. 3.

[0051]

While in the sample 4 in which the antioxidant was not added, the amount of As eluted was kept low immediately after heat treatment, the amount of As eluted was increased to 40 mg/L after one month. In the samples 5 to 7 in which the antioxidant was added, the samples were not affected by the external environment impact such as oxidation either immediately or one month after heat treatment and the amount of As eluted was stably kept 5 mg/L or less.

What is claimed is:

1. A method for processing arsenic comprising:

a roasting process in which an arsenic-containing copper ore is roasted in an inert gas atmosphere to separate chalcopyrite from a volatile matter containing sulfides of arsenic; and

a heat treatment process in which sulfur and an antioxidant are added to the volatile matter obtained in the roasting process followed by heat-treating in the inert gas atmosphere for dissolving sulfides of arsenic in the volatile matter.

2. The method of claim 1, wherein the heat treatment process comprises adding the sulfur to the volatile matter obtained in the roasting process so as to adjust a mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 3 or more.

3. The method of claim 1 or 2, wherein the heat treatment process comprises adding 0.2 mol/m³ or more of the antioxidant.

4. The method of any one of claims 1-3, wherein the antioxidant is selected from the group consisting of monophenol type, bisphenol type, and polyphenol type, and a combination thereof.

5. The method of any one of claims 1-4, wherein the volatile

matter is heat treated at 200°C to 600°C in the heat treatment process.

6. A method for processing arsenic comprising:

roasting an arsenic-containing copper ore in an inert gas atmosphere to separate a roasted copper concentrate from a volatile matter containing sulfides of arsenic;

adding sulfur as needed so as to adjust the mass ratio of sulfur to arsenic (mass ratio of S/As) contained in the volatile matter to be 3 or more;

adding an antioxidant to the volatile matter; and

heat-treating in an inert gas atmosphere the volatile matter including the antioxidant to dissolve sulfides of arsenic in the volatile matter.

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Figures: 1

Pages: _____

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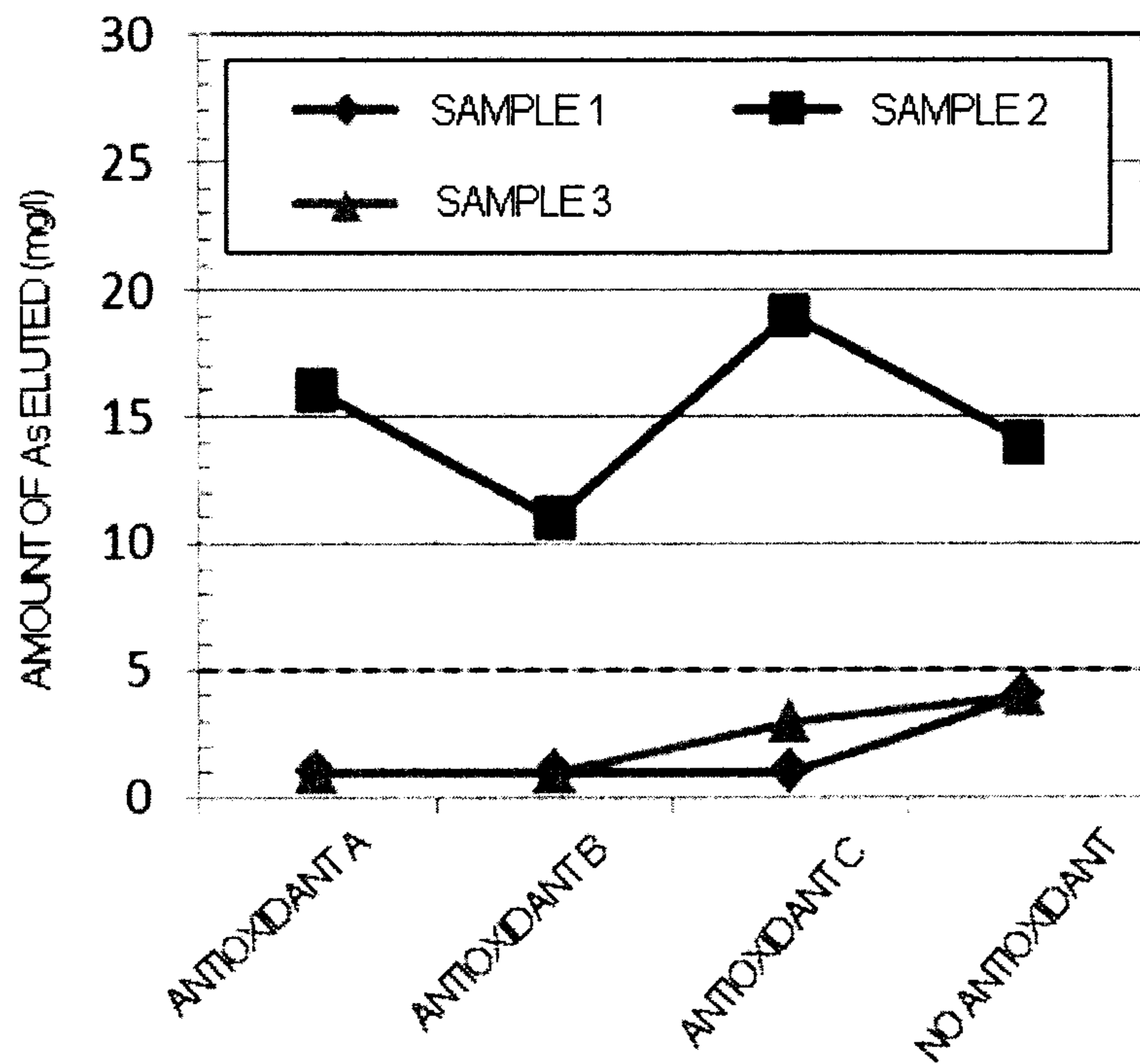
Drawings

Unscannable items received with this application
(Request original documents in File Prep. Section on the 10th floor)

Joan

Documents reçu avec cette demande ne pouvant être balayés
(Commander les documents originaux dans la section de la préparation
des dossiers au 10^{ième} étage)

[FIG. 2]



[FIG. 3]

