

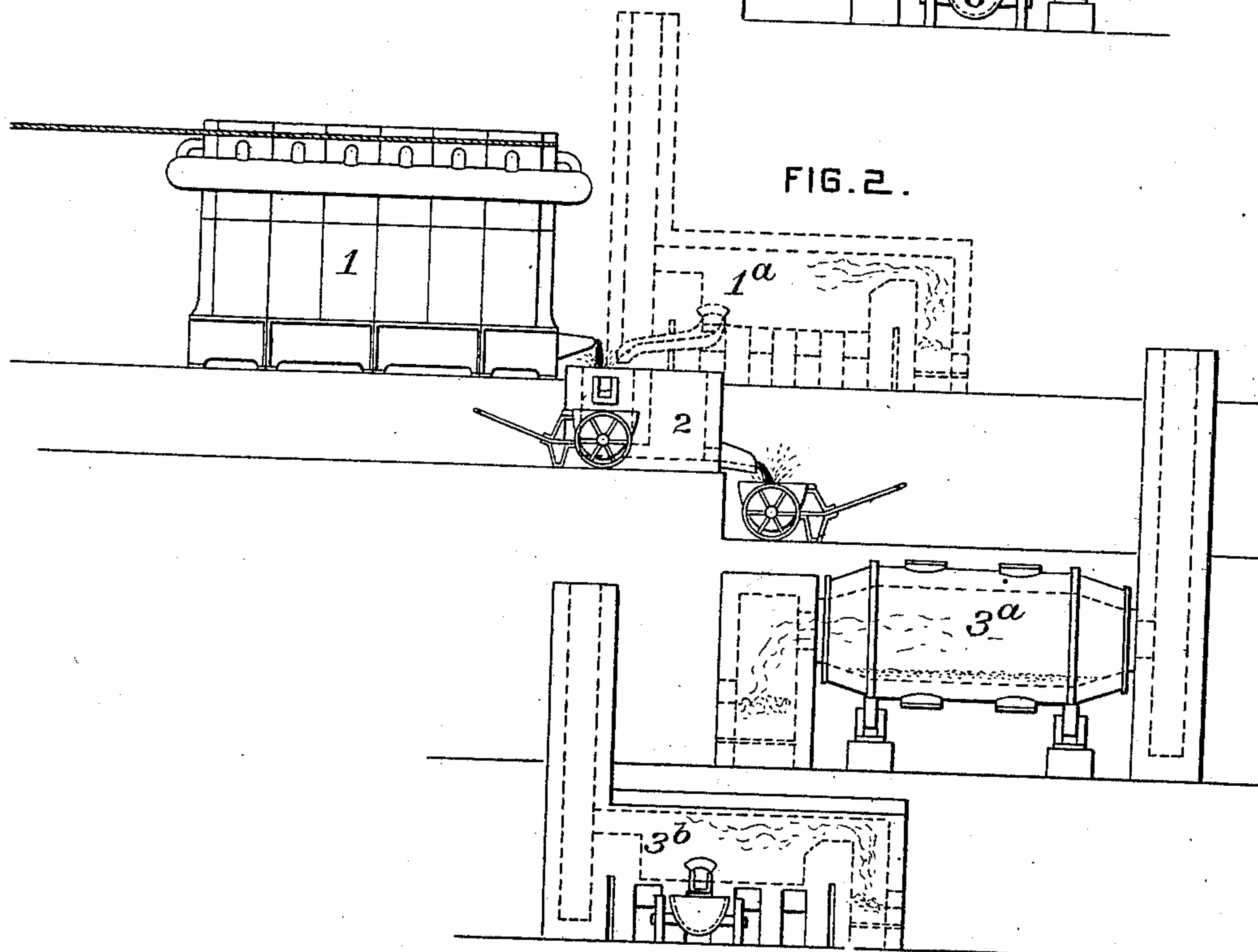
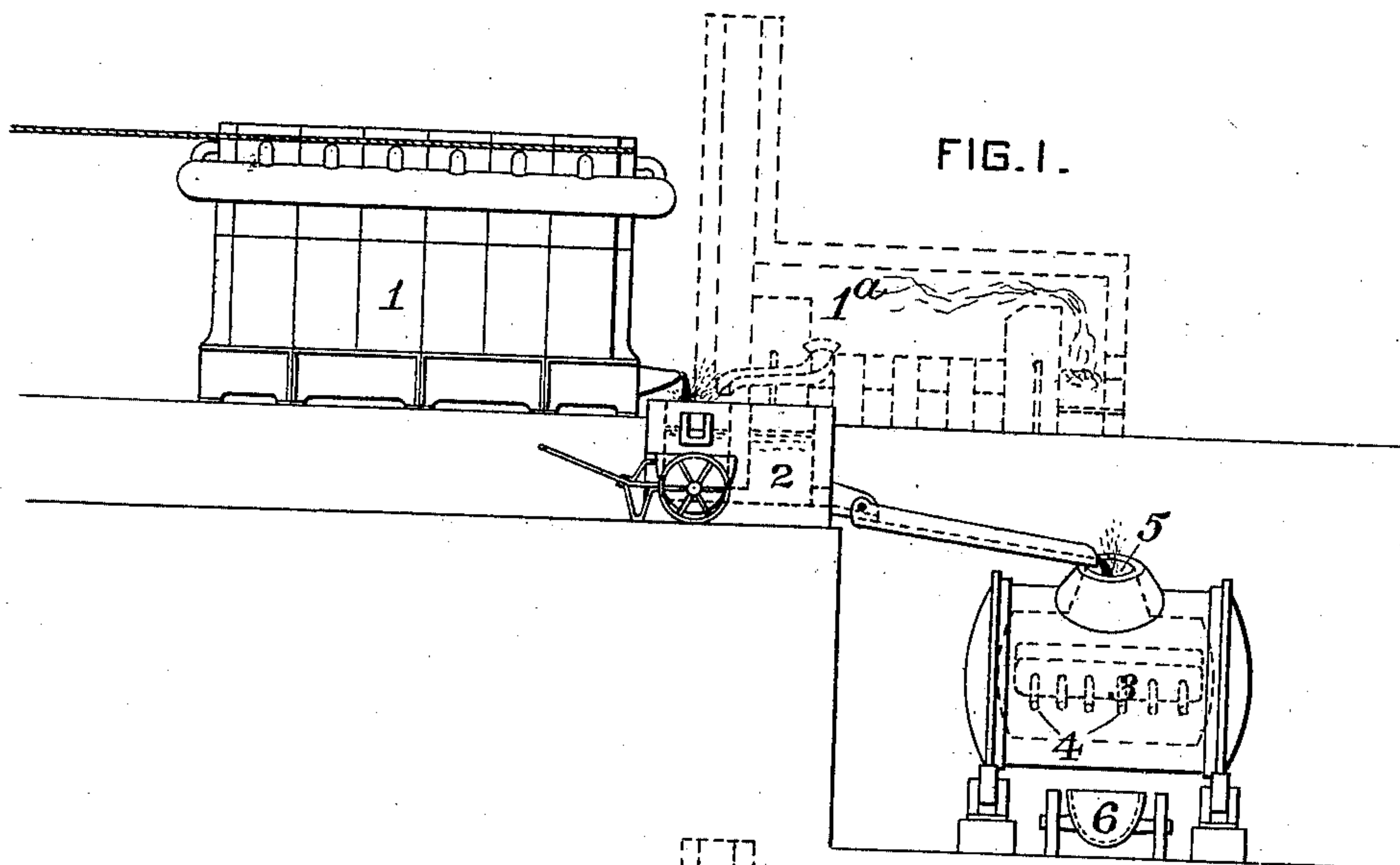
No. 692,310.

Patented Feb. 4, 1902.

W. J. KNOX.  
METHOD OF TREATING COPPER ORES.

(Application filed Feb. 4, 1901.)

(No Model.)



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# UNITED STATES PATENT OFFICE.

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## METHOD OF TREATING COPPER ORES.

SPECIFICATION forming part of Letters Patent No. 692,310, dated February 4, 1902.

Application filed February 4, 1901. Serial No. 45,969. (No specimens.)

*To all whom it may concern:*

Be it known that I, WILLIAM JOHN KNOX, a citizen of the United States, and a resident of Edgewood Park, in the county of Allegheny and State of Pennsylvania, have invented certain new and useful Improvements in Methods of Treating Copper Ores, of which the following is a specification.

My invention relates to the treatment of copper ores.

The object of the invention is to provide an economical, convenient, and simple method of deriving copper sulfid or metallic copper, as desired, from copper matte or from copper-sulfid ores.

The general plan of the invention is to first obtain from the ore a suitable matte by any of the well-known smelting processes and to then separate therefrom the iron in the form of an oxysulfid of iron and by the same operation throw off the excess of sulfur as sulfurous acid. This is accomplished by oxidizing the matte in a basic-lined vessel, care being taken to exclude any considerable amount of silica, the presence of which would result in the formation of a silicate-of-iron slag, and thus prevent the formation of the oxysulfid.

In the oxidation of an iron-bearing copper matte in a molten state in a basic-lined vessel, little or no silica being present, I have found that there is formed a highly-fusible compound of iron and sulfur, which may be properly designated as "oxysulfid of iron." The oxysulfid of iron is of less specific gravity than the enriched copper matte which is left by the separation of the iron, and it readily separates therefrom by gravity while in a molten state. The enrichment of the copper matte may be interrupted at any desired stage, obtaining a copper matte of any desired concentration, or the process may be carried on until the copper sulfids are reduced to metallic copper. The resulting iron oxysulfid corresponding to the lower grades of matte carries more sulfur than the iron oxysulfid resulting from the complete conversion of the matte to metallic copper; but even in the latter case sufficient sulfur remains to render the iron compound readily fusible.

While, as stated above, the presence of any

considerable amount of silica would prevent the formation of the iron oxysulfids by converting the iron into silicates, yet it is possible to have silica present in small quantities, in which case a small amount of iron silicates will be formed, which, being of less specific gravity than the iron oxysulfids and not soluble therein, will rise to the surface as a difficultly-fusible slag, which can be removed. It is desirable, however, that there shall be practically no silica present, for not only does it form a difficultly-fusible crust upon the bath, which must be removed, but also its presence is detrimental to the basic lining of the converting vessel.

The oxysulfid of iron, which in practice may carry with it more or less entrained copper and copper sulfid, is useful as a basic flux in the smelting-furnace for the slagging of silica from the gangue of the ore. I therefore usually transfer the iron oxysulfids to the smelting-furnace, and thus all of the iron of the ore becomes available as a basic flux in the smelting-furnace. In the processes heretofore employed it has been customary to roast the ore for the purpose of converting a large portion of the sulfid of iron to the oxid of iron, so as to render it in a measure available as a basic flux for the silica. As much of the silica and iron as possible are thus removed as a slag from the smelting-furnace; but necessarily a large amount of iron remains in the matte, and it is necessary to remove this in the separation of the copper from the matte. This removal has been accomplished by oxidizing the iron of the matte in the presence of silica, and this silica is usually obtained from an external source, such as the lining of the converting vessel. The former processes therefore involve the positive addition of silica, even where the ore itself contains a large excess of silica. By my process the preliminary oxidizing of the iron by roasting is rendered unnecessary, it being found more economical to smelt directly to a lower-grade matte having a high percent. of iron and then to oxidize and separate this iron in the basic converter and use the iron compound thus obtained in the smelting-furnace.

The treatment of the matte in the basic-



lined converter produces the oxysulfid, which is a basic flux suitable to be returned to the smelting-furnace and there utilized as a flux.

The treatment of the matte in a basic-lined vessel by my process results in the formation of a magnetic oxid of iron, which, combining with such sulfids as are formed or exist therein, produces the compound which is herein termed "iron oxysulfid," and this process has also the advantage of removing from the copper any metalloids which may be present in the ore—such, for instance, as arsenic, antimony, and phosphorus—because these metalloids are acid with reference to the oxid of iron, and therefore form a salt of iron which separate from the copper and enters into solution with the oxysulfid leaving the copper practically free therefrom.

The treatment of the matte in the basic-lined vessel requires some means of introducing oxygen in the required quantities for effecting the oxidation of the iron and the major portion of the sulfur. This may be conveniently accomplished by oxidizing the molten matte in the basic-lined vessel by means of a current of air. The oxidation of the sulfids in the molten bath is sufficiently exothermic to maintain the bath in a molten state without the application of external heat. In some cases, however, instead of supplying the necessary oxygen to the molten mass by means of air the matte may be oxidized to the required degree in a roasting-furnace, and the formation and separation of the oxysulfids of iron are then accomplished by melting the matte thus roasted in a basic-lined vessel. In this latter case, the fuel value of the sulfids having been destroyed in the roasting-furnace external heat is required to bring the matte into a state of fusion, so as to permit the formation and separation of the iron oxysulfids from the copper or the copper sulfids.

In the accompanying drawings, Figure 1 is a diagram representing in a graphic manner the various steps of the process, in connection with a general organization of apparatus for carrying out the invention; and Fig. 2 illustrates, graphically, the various steps of the process when the partial oxidation is performed by roasting.

Referring to the drawings, the ore, consisting of iron and copper sulfids, together with such other metallic compounds and gangue as may be present, is taken to the smelting-furnace 1 in such quantities as may be required. This furnace may be of any suitable well-known construction, either in the form of a cupola or open-hearth furnace, adapted to the smelting of the ore. From the smelting-furnace 1 the matte is passed to the basic converter 3, either directly or through a forehearth 2. This forehearth may be of such character as to retain the heat of the molten matte, or, if desired, external heat may be applied, the purpose being to permit the slag to separate from the matte and to be drawn off, while the matte itself is passed to the

basic-lined converter 3. This converter may be of any convenient construction. In practice I have obtained excellent results by the use of a trough-converter adapted to be turned about its longitudinal axis for the purpose of depressing the tways 4 below the surface of the molten matte and also for permitting the pouring of the resulting products of the operation from the spout 5. The iron oxysulfids from the converter may be poured into ladles, as represented at 6, and returned to the smelting-furnace 1. If this smelting-furnace is a cupola-furnace, it is desirable that the iron oxysulfid should be allowed to cool and solidify before being returned thereto, it being reduced to proper size either by breaking up or by pouring into suitable sized molds. In case, however, an acid-lined open-hearth furnace is used, such as indicated in dotted lines at 1<sup>a</sup>, then the iron oxysulfids may be returned thereto while still in a molten state. The slag is drawn off from the forehearth, and the only products of the process are therefore this slag and the copper or the copper sulfid which is obtained in the basic converter.

In Fig. 2 a modification is illustrated in which 1 and 1<sup>a</sup> represent the smelting-furnaces, as before, and 2 represents the forehearth. The matte from the forehearth after being cooled and broken to suitable size is passed to the roasting-furnace 3<sup>a</sup>, where the matte is given an oxidizing roasting. Thence it is passed to the basic-lined open-hearth furnace 3<sup>b</sup>, which is heated by external heat in any usual well-known manner, the resulting products being copper or copper sulfids and the iron oxysulfids, which latter are returned, as before, to the smelting-furnace 1 or 1<sup>a</sup>, as the case may be.

In practice it may be found advantageous in many cases, especially in the treatment of low-grade mattes, to pour off more or less of the iron oxysulfids before the conversion is carried to metallic copper and to then add successive charges of the matte, repeating the operation until a sufficiently large amount of enriched matte has accumulated in the converter. This enriched matte may be then converted directly into metallic copper, with the separation therefrom, as oxysulfid, of the relatively small amount of iron remaining in it.

In the treatment of ores containing an excessive amount of iron there may be an excess of the oxysulfids beyond that required for fluxing purposes, in which case such excess becomes a useful product, and in some cases it may be desirable to use all of the oxysulfids produced by this process for other purposes than as a flux in the smelting-furnace, other basic fluxes being used therein. More or less of the iron oxysulfid may, for instance, be used in treating other ores deficient in iron.

It should be noted particularly that the process must be carried on in basic-lined vessels—that is to say, whereas heretofore the presence of silica has been required for ef-



fecting the removal of the iron my process practically prohibits the use of silica in considerable quantities, the presence of which would serve to prevent or interfere with the formation of the oxysulfids.

It is understood that any convenient means of adding the oxygen to the sulfid matte may be employed. For instance, suitable oxid of iron, wherever obtained, may be used, and I therefore wish it to be understood that I do not limit myself, except as otherwise expressly stated in the claims, to the specific apparatus described, nor to the specific manners of bringing oxygen into the presence of the sulfids of the copper and the iron, for in addition to the various other features involved in the process I believe that I am the first to appreciate and utilize the facts that the oxysulfids of iron may be formed in the presence of copper sulfids and are readily fusible and have such specific gravities and characteristics as to permit them to separate by gravity, and I also believe that I am the first to effect the concentration of copper matte in the above-described manner in a basic-lined vessel.

By the term "oxysulfid of iron" as used in this specification is to be understood any fusible combination or mixture of iron oxids and sulfids which may result from the treatment of the matte in the manner described—such, for instance, as the mixture or combination of iron oxids with copper sulfids. It is difficult to give any definite chemical formula for this mixture or combination, as it seems to vary within fairly-wide limits; but it is formed only when the matte is very low in silica or other acid components and treated in a basic-lined vessel.

It will be understood that certain features of this process are also applicable to mattes containing iron accompanied by metals other than copper, provided the sulfids of such other metals are of the character which will form a fusible compound under the conditions named, which compound has such specific gravity with reference to the resulting enriched matte, so as to permit of the separation of said matte therefrom.

The degree to which the copper is freed from other elements of the matte is dependent somewhat upon the duration of the process, it being possible to obtain practically pure copper; but in ordinary practice it is more convenient to carry the process only to a point where reasonably pure copper or copper compounds are obtained, and it will be understood that where the word "copper" is used in the claims it is intended to refer not necessarily to pure copper, but to include such compounds of copper as may result from carrying out the process to such an extent only as will yield reasonably pure copper compounds.

In some ores there are present such materials as arsenic and other materials commonly called "metalloids," the presence of which associated with the copper is objectionable. I

am enabled to cause these to be separated from the copper by this process.

The operation of the apparatus and the carrying out of the process thereby will be evident from the previous description, and it will be understood that the organization of apparatus shown in the drawings is merely illustrative and that it may be variously modified to suit the requirements of the process.

I claim as my invention—

1. The method of separating copper from copper matte in which the iron and other metals exist largely as sulfids, which consists in melting the matte, oxidizing iron and sulfur of the matte by forcing air into contact therewith while in a molten state, thereby generating heat sufficient to maintain the mass in a molten state and thereby causing the formation of iron oxysulfids under such conditions that substantially no silicate of iron is formed, and in separating the copper therefrom by causing it to remain quiescent a sufficient time to separate by gravity.

2. The method of utilizing iron of an iron-bearing copper ore as a flux for removing the acid components of the ore, which consists in smelting the ore, thereby forming a matte producing iron oxysulfids by oxidizing in a basic-lined vessel the matte while in a molten state, and returning to the smelting-furnace the oxysulfids thus obtained.

3. The method of separating copper from iron-bearing copper ores, which consists in smelting the ore with the addition of iron oxysulfids, oxidizing the resulting matte in a basic-lined vessel by forcing air therethrough, thus producing iron oxysulfids, separating the copper from the iron oxysulfids by gravity, and utilizing the latter as a basic flux in the smelting-furnace.

4. The method of treating iron-bearing copper ore, which consists in smelting the ore, withdrawing the slag therefrom, oxidizing the resulting matte in a basic-lined vessel substantially free from silica, thereby forming iron oxysulfids and copper, and performing the act of separating the copper from such iron compounds by subjecting the mass to the action of gravity while in a molten state, thereby leaving basic-iron compounds substantially free from copper and silica and utilizing practically all of the iron thus obtained for fluxing the ore.

5. The method of separating metals capable of reaction and separation, as described, existing in the form of sulfids, which consists in melting the matte, creating oxysulfids of certain of the metals under such conditions that substantially no silicates are formed, and performing the act of separating the oxysulfids from the remaining constituents by permitting the same to remain in a state of quiescence while in a molten condition a sufficient time to permit stratification.

6. The hereinbefore-described method of eliminating iron from a copper matte composed largely of copper and iron sulfids prac-



5 tically free from silica, which consists in melting the matte, oxidizing the iron into non-silicious compounds of iron and performing the act of separation of the same from the enriched matte while in a fluid state by utilizing the difference in their specific gravities.

10 7. The method of separating the copper from a matte composed largely of copper and iron sulfids practically free from silica, which consists in melting the matte, oxidizing the sulfids of iron, thereby forming oxysulfids under such conditions that substantially no silicate of iron is formed, and then occasioning the separation of the copper from the oxysulfids through the instrumentality of their different specific gravities, while in a molten state.

20 8. The method of treating iron-bearing copper ore in which the iron or other metals exist as sulfids, which consists in first smelting the ore thereby producing a matte composed largely of iron and copper sulfids, oxidizing the major portion of the iron of the matte into magnetic oxid of iron while in a molten state, thereby producing a bath composed essentially of oxysulfid of iron and sulfid of copper, and precipitating the latter from the former by reason of the difference in their specific gravities.

30 9. The method of producing from iron-bearing copper matte, copper free from metalloids, which consists in melting the matte, transforming the copper matte into metallic copper and a basic compound of iron by oxidizing the iron sulfids, and causing the metalloids to unite with the iron compounds thus formed.

10. The process of treating copper matte containing iron existing in the form of sulfids, which consists in melting the matte, oxidizing the iron into magnetic oxid of iron, and transforming this into a fusible compound of iron by heating it in the presence of metallic sulfids capable of uniting therewith under such conditions that substantially no silicate of iron is formed.

11. The method of extracting copper from copper matte containing iron and practically free from acid components, which consists in melting and oxidizing the matte in a vessel neutral to the compounds formed in the vessel, thereby creating a fusible basic compound of iron of less specific gravity, then causing the mass to remain quiescent, and separating copper from such molten mass by the action of gravity.

12. The process of treating copper matte containing iron in the form of sulfid, which consists in melting the matte, oxidizing a portion of the iron contained therein to magnetic oxid of iron in the presence of the remaining sulfids contained in the matte under such conditions that substantially no silicate of iron is formed, maintaining the mass in a molten state, and thereby transforming the magnetic oxid of iron into a fusible compound of iron.

Signed at Pittsburg, in the county of Allegheny and State of Pennsylvania, this 31st day of January, A. D. 1901.

WILLIAM JOHN KNOX.

Witnesses:

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BIRNEY HINES.