UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING ORES.

1,197,589. Specification of Letters Patent. Patented Sept. 12, 1916.

No Drawing. Application filed June 28, 1915. Serial No. 36,698.

To all whom it may concern:

Be it known that I, RAYMOND F. BACON, a citizen of the United States, residing in Pittsburgh, Allegheny county, State of Pennsylvania, have invented certain new and useful Improvements in Processes of Treating Ores; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the treatment of non-sulfid ores, and ores containing non-sulfid metal constituents, in order to make the same amenable to flotation methods of concentration, and to the subsequent concentration thereof by flotation.

It has heretofore been proposed to effect the flotation and separation of oxidized or other non-sulfid ores from the gangue with which they are associated by first converting the ores into sulfids by treatment with soluble sulfids, and then subjecting the sulfidized ore to flotation methods of concentration.

The process of the present invention is an improvement upon such prior processes and also an improvement upon the colloidal sulfur flotation process of my Patent No. 1,140,865, granted May 25, 1915, and it involves the conversion of such non-sulfid ores into sulfids, and the production of colloidal sulfur therein, by treatment of the ores, either simultaneously or successively, with sulfur dioxid and hydrogen sulfid; whereby the ores are subjected to the action of hydrogen sulfid in the presence of sulfur dioxid and the sulfidation of the ore and the formation of colloidal sulfur effected by a single operation.

The invention will be more particularly described in connection with the treatment of copper oxid ores, but it will be understood that such description is intended to be illustrative of one embodiment of the invention, and that other copper ores, such as carbonate ores, or ores containing mixed oxids, carbonates, silicates, sulfids, etc., as well as ores of other metals such as zinc, lead, etc., or mixed ores of two or more metals, can be treated in a more or less similar manner. Accordingly, while the description of the invention is of a more or less specific nature, the invention is of a more comprehensive nature, being applicable to many different ores, which are referred to, generically, as non-sulfid ores.

In practising the invention, various alternative methods of procedure may be followed, depending upon the nature of the ore treated, its physical condition, etc. As applied to copper oxid ores, the following equations illustrate the various reactions, which, under proper conditions, may take place:

(1) $CuO + SO_2 + 3H_2S \longrightarrow CuS + 3S + 3H_2O$
(2) $CuO + SO_2 \longrightarrow CuSO_3$
(3) $CuSO_3 + H_2S \longrightarrow CuS + SO_2 + H_2O$
(4) $CuSO_3 + 3H_2S \longrightarrow CuS + 3S + 3H_2O$
(5) $CuO + H_2S \longrightarrow CuS + H_2O$
(6) $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$

If the ore is first treated with sulfur dioxid in sufficient amount to convert all the copper to sulfite, the subsequent treatment with hydrogen sulfid in the presence of sulfur dioxid already present in a free or combined form will precipitate the copper as sulfid and will further set free colloidal sulfur within the pulp. The precipitate in such case will be physically separated from the gangue and the subsequent flotation will be correspondingly facilitated. It is not essential, however, that the metal values be completely dissolved before precipitation, although such procedure may be more advantageous with some ores. Where complete solution is not desired, a smaller amount of sulfur dioxid is used. The dissolved metal will still be precipitated as sulfid, and colloidal sulfur set free, although the sulfidizing reaction may be much less complete. With many ores, it is not essential that there should be complete sulfidizing, since a partial or superficial sulfidizing may be sufficient.

Where the sulfur dioxid and hydrogen sulfid are used simultaneously the resulting reaction may be that of the first equation above, or that of all of the equations in varying proportions. Thus there may be realized a direct sulfidizing without solution, or with only temporary or transitory solution. Again, there may be direct combination of the sulfur dioxid and hydrogen sulfid to give colloidal sulfur, particularly where these reagents are used in excess.

Where the ores require a preliminary crushing or grinding, as is the case with most ores, the sulfur dioxid can be added

at the time of wet crushing, as by using an aqueous solution, and the treatment with hydrogen sulfid, either with or without further treatment with sulfur dioxid, subsequently effected. Where the ores are in the form of slimes or tailings, and grinding or crushing is not necessary, they may be mixed with water to form a pulp of suitable consistency, and the reagents added to this pulp.

The ores treated may be treated cold with the cold reagents, either in gaseous form or in solution, or the ores may be heated, as by the use of hot smelter fumes containing the sulfur dioxid, and the reaction thereby facilitated.

The amount of sulfur dioxid and hydrogen sulfid required will necessarily vary with different ores, as well as with the particular method of use and the result desired. A partial or superficial conversion of the metal values may be sufficient, and a relatively small amount of added colloidal sulfur may sufficiently facilitate the subsequent flotation; while by prolonging the treatment, a more complete conversion into sulfids, and a larger production of colloidal sulfur, will take place. With ores already of a sulfid nature, but containing oxid or other non-sulfid metal constituents, a corresponding conversion of such non-sulfid constituents is all that is necessary. By avoiding an excess of sulfur dioxid, or by the use of hydrogen sulfid with it, the sulfids are protected from solution. It is also possible, by the use of a suitable excess of sulfur dioxid, to effect a selective sulfidation of certain metal constituents, without complete sulfidation of the metal values.

The sulfur dioxid may be used as a gas, and passed into the ore pulp, or it may be used in aqueous solution, as sulfurous acid. A convenient form is smelter fumes, containing it in variable amount, mixed with air and other gases. More or less sulfur trioxid may also be present and may form sulfuric acid when absorbed by water, but such acid in small amounts will assist in dissolving the ore as sulfate which will be subsequently converted into sulfid by the hydrogen sulfid.

By using hot smelter fumes, as already pointed out, the ore pulp can be heated and the reaction thereby facilitated.

The hydrogen sulfid can be produced by any suitable process, *e. g.*, by a reducing roast of sulfid ores, or by burning sulfur dioxid with an excess of a suitable reducing gas. It may be used either as a gas or in solution in suitable solvents, *e. g.*, as a soluble sulfid such as a sodium or potassium sulfid.

The production of the colloidal sulfur within the pulp, from the same reagents used in the sulfidizing process, results in a particularly intimate intermixture of the sulfur and sulfid which is made use of to advantage in the subsequent flotation procedure.

It will, of course, be understood that the pulp, during treatment, can be suitably agitated, and that various forms of apparatus can be employed.

The ore should, in general, be ground fine enough to separate the metal particles from the gangue, but where complete solution of the metal values is effected, this is not so important. In fact, with some ores, the metal and gangue is present in an exceedingly intimate state of intermixture, and it may be advantageous to effect complete solution of the metal values and thus separate them from the gangue and precipitate them from solution as physically separate particles.

If, during the later stages of the process, there is an excess of hydrogen sulfid or other soluble sulfid present, such as might prejudice the flotation process, this can be neutralized by further amounts of sulfur dioxid, and it is advantageous that it should be so neutralized and that the ore pulp should have an acid character, as described in my prior Patent No. 1,140,866.

After the ore has been sufficiently sulfidized, and the colloidal sulfur has been formed therein, it is subjected to flotation in order to separate the metal values from the gangue.

Where the ore is a simple copper oxid or carbonate ore, and the copper can be separated physically from the gangue by suitable crushing, it is possible to convert the copper oxid or carbonate either superficially or completely into sulfid. A superficial sulfidizing is sufficient in such case, and it is not necessary that the copper should first be dissolved. Where, however, the ore is so intimately blended with the gangue that physical separation by crushing is impossible or imperfect, it may be more advantageous to effect complete solution of the copper as sulfite by treatment first with the sulfur dioxid and subsequently with hydrogen sulfid.

With ores containing different metals such as copper, lead and zinc, it may be advantageous to effect complete solution of the copper and zinc, without effecting solution of the lead. To the extent that sulfuric acid is present, due to oxidation of the sulfur dioxid or the presence of sulfur trioxid mixed with the sulfur dioxid, the lead will be in part converted into the insoluble sulfite and in part into the insoluble sulfate. Subsequently, upon treatment with hydrogen sulfid, the copper will be precipitated as sulfid and the lead will be to a greater or less extent also converted into sulfid, while the zinc will remain in solution so long as

the solution is acid. By then subjecting the ore to flotation it is possible to separate the copper sulfid, together with lead sulfid, from the zinc. By a subsequent precipitation of the zinc with an alkaline sulfid which will neutralize the excess acid, the zinc can be converted into sulfid and then separated by a subsequent flotation treatment. As such alkaline sulfids, may be mentioned sodium sulfid, calcium sulfid, etc.

With ores containing copper and nickel, the nickel will remain in solution in the presence of an excess of acid while the copper will be precipitated by the hydrogen sulfid. The present invention accordingly enables the separation of copper from nickel by the combined fractional precipitation and flotation treatment.

In all of these various procedures, the flotation treatment is materially promoted and improved by the colloidal sulfur present, as more fully pointed out in my prior Patent No. 1,140,865. The process of the present invention is an improvement upon such colloidal sulfur flotation process of my said prior patent in that it involves the treatment of non-sulfid ores and constituents with sulfur dioxid and hydrogen sulfid, simultaneously or successively, whereby the conversion of the ores into sulfids and the formation of colloidal sulfur is effected in a particularly advantageous manner, and the sulfur and sulfids formed in a most intimate state of intermixture.

In separating the sulfur and sulfids from the gangue by flotation, the pulp may be subjected to aeration, with agitation, and the flotation thereby effected; or a small amount of oil can be beaten into the pulp together with air, and a froth thus obtained. In either case, the flotation is materially improved by the presence of the colloidal sulfur and by the nature and composition of the pulp which is subjected to the flotation treatment. Where oil is used, a smaller amount is required to give a froth of proper consistency than where colloidal sulfur is not present. Some ores are too poor in metal values to form a coherent froth with oil in the oil flotation process. With such ores, the flotation is improved by the presence of the colloidal sulfur. The flotation is also improved by the intimate nature of the intermixture of sulfur with the sulfids.

From the above description, it will be seen that the invention is of more or less general application, both to the treatment of completely oxidized ores, and to the treatment of ores only partially oxidized. It will also be seen that other non-sulfid ores can be treated in a similar manner, and that in some cases the procedure may be one of complete solution and precipitation, while in others it may be one of sulfidization without such complete solution. It will also be seen that the reagents employed are simple and readily produced in amounts necessary for commercial operations, from the various roasting operations of the sulfid ores themselves. It will also be seen that the process is capable of many different applications in the art, and accordingly that many variations and modifications can be made in the invention as described, without departing from its spirit and scope, as set forth in the accompanying claims.

What I claim is:

1. The method of effecting the separation of non-sulfid ores from associated gangue, which comprises subjecting the mixture, in a finely divided condition, to the action of hydrogen sulfid in the presence of sulfur dioxid and thereby converting the metal values into sulfids and forming colloidal sulfur within the mixture, and subjecting the resulting mixture to a flotation treatment; substantially as described.

2. The method of effecting the separation of non-sulfid ores from associated gangue, which comprises subjecting the mixture, in a finely divided condition, to the action of hydrogen sulfid in the presence of and thereby converting the metal values into sulfids and forming colloidal sulfur within the mixture, and subjecting the resulting mixture to a flotation treatment; substantially as described.

3. The method of effecting the separation of non-sulfid ores from associated gangue, which comprises subjecting the mixture, in a finely divided condition, first to the action of sulfur dioxid and thereby effecting solution of metal values as sulfites, then subjecting the mixture to the action of hydrogen sulfid and thereby precipitating dissolved metal values as sulfids and forming colloidal sulfur within the mixture, and finally subjecting the resulting mixture to a flotation treatment; substantially as described.

4. The method of effecting the separation of non-sulfid ores from associated gangue, which comprises subjecting the mixture, in a finely divided condition, first to the action of sulfur dioxid and thereby effecting substantially complete solution of the metal values as sulfites, then subjecting the mixture to the action of hydrogen sulfid and thereby precipitating the dissolved metal values as sulfids and forming colloidal sulfur within the mixture, and finally subjecting the resulting mixture to a flotation treatment; substantially as described.

5. The method of effecting a selective separation of the constituents of non-sulfid ores from associated gangue and from each other, which comprises subjecting the mixture, in a finely divided condition, to the action of hydrogen sulfid in the presence of sulfur dioxid, and maintaining an excess of sulfur dioxid and an acid reaction within

the mixture, and thereby forming colloidal sulfur within the mixture and converting into sulfids metal constituents forming sulfids insoluble in the acid, and finally subjecting the resulting mixture to a flotation treatment; substantially as described.

6. The method of effecting a selective separation of the constituents of non-sulfid ores from associated gangue and from each other, which comprises subjecting the mixture, in a finely divided condition, to the action of sulfur dioxid and thereby effecting substantially complete solution of the metal values as sulfites, then subjecting the mixture to the action of hydrogen sulfid and maintaining an acid reaction within the mixture, and thereby forming colloidal sulfur within the mixture and precipitating as sulfids metal constituents forming sulfids insoluble in the acid, and finally subjecting the resulting mixture to a flotation treatment; substantially as described.

7. The method of effecting the separation of copper oxid, carbonate, and other non-sulfid ores from associated gangue, which comprises subjecting the mixture, in a finely divided condition, to the action of hydrogen sulfid in the presence of sulfur dioxid and thereby converting the copper, into sulfid, and forming colloidal sulfur within the mixture, and subjecting the resulting mixture to a flotation treatment; substantially as described.

8. The method of effecting the separation of copper oxid, carbonate, and other non-sulfid ores from associated gangue, which comprises subjecting the mixture, in a finely divided condition, to the action of hydrogen sulfid in the presence of sulfur dioxid and thereby converting the copper, superficially or completely, into sulfid, and forming colloidal sulfur within the mixture, the sulfur dioxid being used in excess to make the mixture acid at the end of the reaction, and subjecting the resulting mixture to a flotation treatment; substantially as described.

9. The mehod of effecting the separation of constituents of non-sulfid ores from associated gangue, and of effecting a selective separation of zinc from lead, copper, and other metal constituents forming acid-insoluble sulfids, which comprises subjecting the mixture, in a finely divided condition, to the action of hydrogen sulfid in the presence of sulfur dioxid, and maintaining an excess of sulfur dioxid and an acid reaction within the mixture, and thereby forming colloidal sulfur within the mixture and converting the lead, copper, and other metals forming acid-insuloble sulfids, into sulfids, without converting the zinc into sulfid, and finally subjecting the resulting mixture to a flotation treatment; substantially as described.

10. The method of effecting the separation of constituents of non-sulfid ores from associated gangue, and of effecting a selective separation of zinc from lead, copper, and other metal constituents forming acid-insoluble sulfids, which comprises subjecting the mixture, in a finely divided condition, to the action of sulfur dioxid and thereby effecting substantially complete solution of the metal values as sulfites, then subjecting the mixture to the action of hydrogen sulfid and maintaining an acid reaction within the mixture, and thereby forming colloidal sulfur within the mixture and precipitating the copper, lead, and other metals forming acid-insoluble sulfids, as sulfids without precipitating zinc sulfid, and finally subjecting the resulting mixture to a flotation treatment; substantially as described.

In testimony whereof I affix my signature.

RAYMOND F. BACON.