Patented Nov. 24, 1931

1,833,682

UNITED STATES PATENT OFFICE

RALPH F. MEYER, OF FREEPORT, PENNSYLVANIA, ASSIGNOR TO MEYER MINERAL SEPARATION COMPANY, OF PITTSBURGH, PENNSYLVANIA, A CORPORATION OF DELAWARE

PROCESS OF TREATING ORES

No Drawing. Application filed December 28, 1928. Serial No. 329,078.

This invention relates to processes for recovering metal values from metalliferous materials by treatment with gaseous reagents.

An object of the invention is to provide a process of treating metalliferous materials for extraction of their metal values, in which gaseous reagents are used, which is generally applicable to materials extracted by chemical processes and to materials which could not previously be treated economically, which is simple and easily performed, and in which the gaseous reagents exert a rapid and powerful action.

Another object is to provide a process of treating ores in which the joint action of liquid and gaseous reagents is intensified, which simplifies and reduces the length of treatment, and generally improves the prior practice.

A further object is to provide a process of the type referred to which is applicable to sulfatizing, chloridizing, cyaniding and similar treatments using one or more gaseous reagents, in which the action of the gas is enhanced.

The invention is based upon my discovery that by subjecting ores and other metalliferous materials in a quasi-wet condition to gaseous reagents, there is obtained a rapid and powerful action by which the ores are rendered readily amenable to extraction of their metal values, extraction treatments may be accelerated or simplified, ores which are refractory or could not be treated economically by prior processes may be extracted simply and at low cost, and the treatment may be carried out at temperatures materially below those hitherto considered necessary.

The invention is applicable to either oxidized or sulfide ores of the types now treated commercially, containing zinc, manganese, cobalt, nickel, copper, or other metals. It is especially adapted for the treatment of refractory and low grade ores which have not heretofore been commercially extractable because of their nature and the high extraction costs, but whose treatment is desirable because of their metal values. For example, zinc ferrits and other insoluble and refractory compounds, such as manganese silicates, can be easily broken up and made readily amenable to economical extractive treatment. The invention is not limited to practice with ores, but is applicable generally to metalliferous materials, such as ore concentrates, mine dumps, tailings, and the like, all of which are included within the term "ores" as used herein and in the claims.

In the preferred practice of the invention the ore is prepared for treatment by mixing it with a liquid in an amount such that each particle is permeated by the liquid, or is provided with a surface film, or both, but insufficient to occupy any material portion of the voids between the particles. It is important also that the particles shall not be dampened sufficiently to cause their agglomeration, or stickiness of the ore mass. This dampening of the ore to provide each particle with an amount of liquid sufficient to cause reaction but insufficient to interfere with free gas passage between the particles, is an essential feature of the invention, and because the ore is neither actually wet, nor yet dry, it is herein referred to as quasi-wet. There is a maximum moisture content, varying with different ores, above which the ore volume diminishes rapidly and the particles agglomerate as the voids between them begin to be occupied materially with liquid. This volume change affords a ready practical test of the quasi-wet condition.

In this quasi-wet condition substantially the entire surface of every particle is exposed to the action of the gaseous reagents, and a very rapid and powerful action is obtained, which may be explained as follows. Owing to the dispersion of the dampening liquid in the pores of the particles, and the absence of free liquid (i. e. between the particles) the gas dissolves very rapidly in the liquid, to form a reagent solution in direct contact with the surfaces of each particle. This condition, as will be understood, is best suited for maximum action.

The reagents act upon constituents of the ore to form compounds, and as these compounds form in and on the individual particles they take up moisture contained in the particles and become hydrated. This causes

spalling of the compounds in and on the particles and thus provides fresh surfaces for further gas action. Since there is no excess of liquid in the ore mass in its quasi-wet condition, there is no liquid flow from the mass, and no appreciable asportation of the compounds referred to. Other actions than these may take place, but it appears probable that this much occurs in the majority of cases.

Because the damping liquid is continuously consumed during action of the gaseous reagent, as by forming a reactive solution or in hydration of the compounds formed, it is necessary to replace the liquid consumed, to continuously maintain the ore in its quasi-wet condition. In some instances, the ore may initially contain sufficient liquid to begin treatment directly, but in the majority of cases the ore must be preliminarily brought to the properly dampened condition. Maintenance of the quasi-wet condition may be accomplished by intermittently adding liquid to the ore mass during its treatment, or the liquid may be continuously supplied in regulated amount during the treatment. In both cases the additions must be regulated so as not to cause accumulation of excess liquid, or over-wetting, and so that the mass, or portions of it, do not become sticky.

Any suitable liquid may be used to dampen the ore, depending upon the ore and the type of treatment. For example, in the use of sulfur dioxide, water may be used. Liquid solutions are also applicable in some instances, such as cyanide solutions in the extraction of precious metals. The liquid may be, and preferably is, added in the form of a mist, because in this form it is best suited to produce the proper dampening. In some cases steam may be used to maintain the quasi-wet condition. The amount of liquid used will be governed by the ore, only the quantity necessary to the quasi-wet condition described above being used.

The action is, of course, dependent in part upon the magnitude of surface presented by the ore particles. Although some ores may not require preliminary sub-division, it will in general be desirable to crush them. Where tailings and the like are treated further sub-division will usually be unnecessary.

It is usually desirable to turn the ore over frequently, or continuously, since agitation not only assists in permeation of the dampening liquid and penetration of the gas, but also in spalling of newly-formed compounds from the particle surfaces and the opening of new crevices therein while the particles are maintained in quasi-wet condition.

The gaseous reagent may be one which exerts a preliminary action by reacting with constituents of the ore, or it may be a gas which supplements the action of a reagent solution. A single gas may be used, or mixtures of reagent gases, and alternate treatment with two or more gaseous reagents is likewise within the scope of the invention. For example, to produce soluble sulfates sulfur dioxide may be used admixed with air, or the ore may be treated alternately with sulfur dioxide and with air. For this purpose roaster or smelter gases may be used, and the reagent gases may in general be supplied from any desired source.

Any material evaporation of the liquid is, of course, undesirable, and in general the treatments are carried out at normal temperature. Because steam under pressure may be used in some cases, temperatures from atmospheric to those not substantially in excess of 300° F. and generally below 250° F. are herein contemplated as being "normal". These temperatures are materially below those commonly used in gas treatments, sulfatizing, for example, but nevertheless, the action is powerful and rapid, and in some instances so much heat may be evolved that cooling must be resorted to in order to prevent volatilization of the liquid.

Because of this operation at normal temperature the process possesses added advantages. For example the refractory compounds produced in some ores when treated at elevated temperatures cannot form, temperature control is easier or entirely eliminated, and simpler apparatus may be used.

The following examples are illustrative of the practice of the invention, and the benefits thereby obtained.

A sulfide ore containing about one-half ounce of gold and about thirty-four ounces of silver per ton, about 6 per cent of lead, 44 per cent of zinc, 20 per cent of sulfur, together with iron and silica and small amounts of other customary impurities, was ground, roasted to eliminate sulfur, and then digested with 5 per cent sulfuric acid. This treatment removed 60 per cent of the zinc from the ore. The residue after drying was then mixed with water sufficient to dampen the particles without causing them to stick together, and was treated for six hours with an atmosphere of air and sulfur dioxide with periodical addition of water, after which it was extracted with 5 per cent sulfuric acid. After this treatment the residue contained 2 per cent of zinc, thus giving a total extraction from the material of 95 per cent of its zinc content. By continuing the gas treatment for twenty-four to forty hours, the zinc in such ores can be substantially entirely converted to soluble sulfate, so that the ore may be leached with water, thus eliminating the use of sulfuric acid with the attendant costs and difficulties in treatment of the solutions obtained. After the treatment described the tailings were in excellent condition for cyanide treatment to extract the gold and silver. The roasted ore may also be treated directly

with air, sulphur dioxide and water without first digesting with sulfuric acid.

In another test, a sulfide-oxide tailing containing 0.65 per cent of copper, 0.78 per cent of cobalt and some arsenic, sulfur, iron and silica was given a four-hour quick roast, and then treated in accordance with the invention by treating with sulfur dioxide, air and water for six hours, after being properly dampened with water. At the end of this period the material was leached with water, and an anaylsis of the washed residue showed that it contained 0.18 per cent of copper, 0.08 per cent of cobalt. Stated in another way, there was recovered 72 per cent of the copper and 90 per cent of the cobalt. By treatment of this same material for two hours with an atmosphere of air and chlorine, 85 per cent of the copper and 99 per cent of the cobalt was rendered soluble in water.

The invention is particularly applicable to ores of a refractory nature such as the manganese silicate ores, nickel and cobalt ores, and those which tend to form refractory compounds when treated by prior processes. For example, an ore containing 30 per cent of manganese, together with iron, alumina and silica, was roasted five hours at 500 to 700° C., and after cooling and rendering quasi-wet with water, was treated twenty-four hours with sulfur dioxide, air and water. The reaction between the gases and the ore is so rapid as to exert a powerful heating effect, and during the first part of treatment the ore must be cooled to prevent undue loss of water. After leaching with water, the tailings showed 82 per cent of the manganese to have been extracted. The tailings were roasted two hours, and the gas treatment repeated for ten hours, after which they contained 1.5 per cent of manganese, showing 95% of the total manganese to have been extracted.

In all of the foregoing examples the ores were first mixed with water to dampen the particles, the amount of water being insufficient to cause noticeable stickiness of the mass. Likewise, water was added during treatment to maintain them in the quasi-wet condition. As mentioned previously, the total amount of water used varies with the material, it being readily determinable for any ore. In the case of the copper-cobalt tailing there was required a total amount of water equivalent to about twenty per cent of the weight of ore, while the manganese ore required an amount of water equivalent to its weight. The zinc ore requires a variable amount of water depending upon the length of treatment.

The invention is not limited to practice in the foregoing manner, and the gas treatments may be varied, as will be understood. For example, the ore may be saturated with a gas, such as sulfur dioxide, and then treated with another gas, air for example, until all of the first gas has been used up, and the cycle then repeated. The invention is also well suited for the chlorination of refractory gold ores by treating such ores with chlorine, air and water as explained above.

The invention is also applicable to treatments in which a gas is used to supplement the action of a liquid reagent, in order to accelerate the reactions. Thus in some cyanide processes the ore is covered with the solution and air used to complete the reaction. By employing the cyanide solution in amounts in accordance with the invention, to render the ores quasi-wet, the air need saturate only a very small amount of liquid at any time and in consequence the cyaniding action is greatly hastened. That is, air being but slightly soluble in water, its action in prior processes was slow because of the large amount of solution, and the diminished contact of air. In my process, the air-solution-ore contact is infinitely greater, and substantial benefits are realized.

Other variations are, of course, possible and within the scope of the invention. For example, with some low grade ores the treatment may be carried out under low steam pressure, the ores not being over-wetted and the full benefits of the invention being secured. Also, reagents may be introduced by solution in the liquid. That is, to chloridize ores, a solution of salt may be used as the dampening liquid, and sulfur dioxide and air as gaseous reagents. It is also possible to use steam admixed with the gases, either as a reagent itself or to replace the water used in reaction, and other variations will be understood by those skilled in the art.

It is a characteristic of the process provided by the invention, that the reactions are powerful and rapid, as compared with prior processes. In some cases, the time of treatment may be materially reduced, for instance by application of the process of cyaniding, as discussed hereinabove. I have further found that the reactions produced in accordance with the invention may be accelerated considerably by light activation during treatment. For example, the time of treatment may be materially reduced by exposing the ore during treatment to sunlight or other source of actinic radiation. This is an important feature, as it is possible by thus varying the procedure to appreciably cut down the period of time required for treatment.

From what has been said hereinabove it will be understood that the term "quasi-wet" as used herein and in the claims is used to concisely indicate that while undergoing gas treatment the material contains a liquid in an amount such as to provide the particles with the liquid necessary for reaction, but insufficient to occupy any considerable portion of the interstitial spaces between the individual particles or to seep or percolate

through the ore mass. The quasi-wet particles do not agglomerate, and at no time during the gas treatment, and prior to final extraction, is there passage of liquid through the ore mass. Therefore, the gas always has free access to and readily reacts with the ore, and solubilized products of reaction are not leached out during gas treatment.

I claim:

1. A process of recovering metals from their ores, comprising bringing finely divided ore to quasi-wet condition and then treating it with acidic reagent gas, and during the gas treatment agitating the ore and continuously maintaining it in quasi-wet condition by regulated addition of moisture.

2. A process of recovering metals from their ores, comprising bringing finely divided ore to quasi-wet condition by admixture with liquid, then agitating the quasi-wet ore and treating it with acidic reagent gas, while applying an atmosphere of steam to the quasi-wet ore to minimize loss of water by evaporation and maintaining the ore in quasi-wet condition by regulated addition of moisture.

3. A process of recovering metals from their ores, comprising bringing finely divided ore to quasi-wet condition and then treating it with a plurality of fluid reagents in repeated alternation, and during said treatment agitating the ore and maintaining it in quasi-wet condition by regulated addition of moisture.

4. A process of recovering metals from their ores, comprising bringing finely divided ore to quasi-wet condition and then treating it in repeated alternation with air and with sulfur dioxide, and during said treatment agitating the ore and maintaining it in quasi-wet condition by regulated addition of moisture.

In testimony whereof, I sign my name.

RALPH F. MEYER.